Environmental Chemistry for a Sustainable World 54

Inamuddin
Mohd Imran Ahamed
Eric Lichtfouse *Editors*

Water Pollution and Remediation: Organic Pollutants

Springer

Environmental Chemistry for a Sustainable World

Volume 54

Series Editors

Other Publications by the Editors

Books
Environmental Chemistry
http://www.springer.com/978-3-540-22860-8

Organic Contaminants in Riverine and Groundwater Systems
http://www.springer.com/978-3-540-31169-0

Sustainable Agriculture
Volume 1: http://www.springer.com/978-90-481-2665-1
Volume 2: http://www.springer.com/978-94-007-0393-3

Book series
Environmental Chemistry for a Sustainable World
http://www.springer.com/series/11480

Sustainable Agriculture Reviews
http://www.springer.com/series/8380

Journals
Environmental Chemistry Letters
http://www.springer.com/10311

More information about this series at http://www.springer.com/series/11480

Inamuddin • Mohd Imran Ahamed
Eric Lichtfouse
Editors

Water Pollution and Remediation: Organic Pollutants

Springer

Editors
Inamuddin
Department of Applied Chemistry
Zakir Husain College of Engineering
and Technology
Faculty of Engineering and Technology
Aligarh Muslim University
Aligarh, India

Mohd Imran Ahamed
Department of Chemistry
Faculty of Science
Aligarh Muslim University
Aligarh, India

Eric Lichtfouse
CNRS, IRD, INRAE, Coll France,
CEREGE
Aix-Marseille University
Aix-en-Provence, France

ISSN 2213-7114 ISSN 2213-7122 (electronic)
Environmental Chemistry for a Sustainable World
ISBN 978-3-030-52394-7 ISBN 978-3-030-52395-4 (eBook)
https://doi.org/10.1007/978-3-030-52395-4

© The Editor(s) (if applicable) and The Author(s), under exclusive license to Springer Nature Switzerland AG 2021
This work is subject to copyright. All rights are solely and exclusively licensed by the Publisher, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilms or in any other physical way, and transmission or information storage and retrieval, electronic adaptation, computer software, or by similar or dissimilar methodology now known or hereafter developed.
The use of general descriptive names, registered names, trademarks, service marks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.
The publisher, the authors, and the editors are safe to assume that the advice and information in this book are believed to be true and accurate at the date of publication. Neither the publisher nor the authors or the editors give a warranty, expressed or implied, with respect to the material contained herein or for any errors or omissions that may have been made. The publisher remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

This Springer imprint is published by the registered company Springer Nature Switzerland AG
The registered company address is: Gewerbestrasse 11, 6330 Cham, Switzerland

Preface

> *Water and air, the two essential fluids on which all life depends, have become global garbage cans*
>
> Jacques-Yves Cousteau

Earth's surface and ground waters are severely affected by the discharge of contaminants. Organic pollutants originate from industrial effluents, domestic sewage, water treatment plants, urban turn-off, agriculture, aquaculture, pulp and paper making, food processing, tannery, and various industries. Massive point-source pollution such as industrial pollution during fabrication, storage, processing, and transportation is of particular concern because the amount of discharged pollutants is usually high, thus inducing immediately severe health impact on ecosystems. Whereas, diffuse pollution such as low pesticide and drug levels in waters induce diseases in the long run. As a countermeasure, there is a need for efficient methods and techniques to remove organic pollutants from wastewater. This book reviews the occurrence, analysis, toxicity, and remediation technologies of water organic pollutants. Chapters discuss the treatment of pollutants such as hydrocarbons, microplastics and plastics, phthalates, polycyclic aromatic hydrocarbons, pharmaceutical drugs and metabolites, oil spill, petroleum hydrocarbons, personal care products, tannery waste, and dyes and pigments.

Chapter 1 by Godoy et al. includes a summary of techniques for sampling, extraction, purification, and identification of microplastics, a review of publications on the abundance of microplastics in different aquatic ecosystems around the world, and a brief synthesis of researches about sorption of chemicals on microplastics. Chapter 2 by Tahir et al. provides highlights on the nature of plastics, types, sources, consumption, effects, and pollution caused by excessive use of plastics. Techniques used for the identification of plastics present in water and the different remediation techniques such as primary, mechanical, chemical treatment, and recycling are elaborated. Finally, the chapter focuses on the health impact and utilization of degradable plastics. Chapter 3 by Muneer et al. discusses water pollution caused by plastics. Three strategies to tackle water pollution caused by nanoplastics, microplastics, and macroplastics are discussed: scientific methods, community involvement, and government policies. Chapter 4 by Jain et al. narrates how plastics and e-wastes contaminate our water system and their hazardous effect on living beings. All aspects of plastic and e-waste, such as types of plastics and e-waste, effects on marine and freshwater life, solution for prevention, and prospects are discussed.

Chapter 5 by Rachna et al. reviews concentrations, impact, and remediation of polycyclic aromatic hydrocarbons (PAH) in rivers and sediments, with focus on functionalized nanomaterials to degrade PAHs. Chapter 6 by Ghosh and Chakraborty presents aerobic granulation as a rapid, eco-friendly, and cost-effective technology for treatment of recalcitrant, hydrocarbon-rich wastewater. The chapter gives mechanisms, factors, characteristics, and techniques of aerobic granulation and applications to the oil remediation. Chapter 7 by Denaro et al. reviews the use and synergy of bacteria and algae to degrade petroleum hydrocarbons. Chapter 8 by Samanta and Mitra presents the types of petroleum hydrocarbons polluting waters and their abatement by physical, chemical, and biological methods. Chapter 9 by Mustapha examines aspects of pharmaceuticals such as active metabolites, influxes, distribution, analysis, fate, and transport routes. Chapter 10 by Saggioro reviews advanced oxidation processes (AOP) such as heterogeneous processes using TiO_2; homogeneous processes using ozone, ultraviolet, hydrogen peroxide, and the Fenton reagents; and coupling AOP and other treatment processes for the removal of personal care products, for example, triclosan and triclocarban, and pharmaceuticals compounds: carbamazepine, diclofenac, and ibuprofen. Chapter 11 by Othman et al. reports advanced technologies for the treatment of oily industrial wastewater, such as flotation, coagulation, biological treatment, membrane filtration, and electrochemical treatment.

Chapter 12 by Fatehi et al. details the source of oil contaminants and two types of oil removal technologies: remediation by physical, thermal, and chemical methods and bioremediation. Chapter 13 by Dheenadayalan and Thiruvengadathan reviews sources, health effects, and remediation of organic pollutants in waters. Remediation includes physical, chemical, and biological methods. Chapter 14 by Karim et al. proposes the application of soil as a heterogeneous Fenton catalyst for the abatement of organic pollutants. Performance of clay, laterite, and volcanic soils to decompose hydrogen peroxide in water medium is explained. Chapter 15 by Sun et al. discusses properties, toxicity, contamination levels, analysis, and treatment of waters contaminated by phthalates.

Chapter 16 by Patel et al. discusses adverse effects, treatment technologies, and management processes of tannery waste. Chapter 17 by Ashraf et al. compares methods for the treatments of dyes and pigments, such as physical, chemical, and biological techniques. Chapter 18 by Akram presents the methodologies used for the treatment of textile waste, with focus on nanomaterials such as silica and iron-based magnetic materials such as sorbents and photocatalysts. Synthetic and biomaterials-based composites are also discussed as next-generation materials for wastewater treatment.

Aligarh, India Inamuddin
Aligarh, India Mohd Imran Ahamed
Aix-en-Provence, France Eric Lichtfouse

Contents

About the Editors

Dr. Inamuddin is an assistant professor at the Department of Applied Chemistry, Aligarh Muslim University, Aligarh, India. He has extensive research experience in multidisciplinary fields of analytical chemistry, materials chemistry, electrochemistry, renewable energy and environmental science. He has published about 177 research articles in various international scientific journals, 18 book chapters, and 115 edited books with multiple well-known publishers. His current research interests include ion exchange materials, a sensor for heavy metal ions, biofuel cells, supercapacitors and bending actuators.

Dr. Mohd Imran Ahamed received his Ph.D. degree on the topic "Synthesis and characterization of inorganic-organic composite heavy metals selective cation-exchangers and their analytical applications" from Aligarh Muslim University, Aligarh, India, in 2019. He has published several research and review articles in the journals of international recognition. He has completed his B.Sc. (Hons) in chemistry from Aligarh Muslim University, Aligarh, India, and M.Sc. (organic chemistry) from Dr. Bhimrao Ambedkar University, Agra, India. His research works include ion-exchange chromatography, wastewater treatment and analysis, bending actuator, and electrospinning.

Dr. Eric Lichtfouse is a biogeochemist at Aix Marseille University who has invented carbon-13 dating, a molecular-level method to study the dynamics of organic compounds in temporal pools of complex environmental media. He is Chief Editor of the journal *Environmental Chemistry Letters* and the book series Sustainable Agriculture Reviews and Environmental Chemistry for a Sustainable World. He is the author of the book Scientific Writing for Impact Factor Journals, which includes an innovative writing tool: the Micro-Article.

Contributors

Mohd Azmuddin Abdullah Institute of Marine Biotechnology, Universiti Malaysia Terengganu, Kuala Terengganu, Terengganu, Malaysia

Zeeshan Abid Department of Chemistry, Government College University Lahore, Lahore, Pakistan

Md. Abu Bin Hasan Susan Department of Chemistry, Dhaka University, Dhaka, Bangladesh

Muhammad Afzal Department of Bioinformatics and Biotechnology, Government College University Faisalabad, Faisalabad, Pakistan

Amna Ahmad Department of Bioinformatics and Biotechnology, Government College University Faisalabad, Faisalabad, Pakistan

Javeed Akhtar Materials Laboratory, Department of Chemistry, Mirpur University of Science and Technology (MUST), Mirpur, AJK, Pakistan

Bilal Akram Department of Chemistry, Tsinghua University, Beijing, China

Zulfiqar Ali Department of Chemical Engineering, COMSATS University Islamabad, Islamabad, Pakistan

A. I. Almendros Chemical Engineering Department, Faculty of Sciences, Granada, Spain

Muhammad Altaf Department of Chemistry, Government College University Lahore, Lahore, Pakistan

Raja Shahid Ashraf Department of Chemistry, Government College University Lahore, Lahore, Pakistan

Muhammad Hussnain Azam Department of Bioinformatics and Biotechnology, Government College University Faisalabad, Faisalabad, Pakistan

Biswanath Bhunia Department of Bio Engineering, National Institute of Technology Agartala, Agartala, Tripura, India

M. Calero Chemical Engineering Department, Faculty of Sciences, Granada, Spain

Saswati Chakraborty Centre for the Environment, Indian Institute of Technology Guwahati, Guwahati, Assam, India
Department of Civil Engineering, Indian Institute of Technology Guwahati, Guwahati, Assam, India

Vinod Kumar Chaudhary Department of Environmental Sciences, Dr Ram Manohar Lohia Avadh University, Ayodhya, Uttar Pradesh, India

Deepak Chauhan Department of Civil Engineering, BIET, Jhansi, Uttar Pradesh, India

F. Crisafi Institute for Biological Resources and Marine Biotechnology, National Research Council of Italy (IRBIM - CNR), Messina, Italy

R. Denaro Water Research Institute, National Research Council of Italy (IRSA - CNR), Rome, Italy

Gangadharan Dheenadayalan Department of Sciences, Amrita School of Engineering, Amrita Vishwa Vidyapeetham, Coimbatore, India

F. Di Pippo Water Research Institute, National Research Council of Italy (IRSA - CNR), Rome, Italy

Tahir Farooq Department of Applied Chemistry, Government College University Faisalabad, Faisalabad, Pakistan

Marzie Fatehi Department of Chemical Engineering, Faculty of Engineering, Shahid Bahonar University of Kerman, Kerman, Iran

Masoom Fatima Department of Chemistry, COMSATS University Islamabad, Islamabad, Pakistan

Sayanti Ghosh Centre for the Environment, Indian Institute of Technology Guwahati, Guwahati, Assam, India

V. Godoy Chemical Engineering Department, Faculty of Sciences, Granada, Spain

Habib-ur-Rehman Materials Laboratory, Department of Chemistry, Mirpur University of Science and Technology (MUST), Mirpur, AJK, Pakistan

Muhammad Ibrahim Department of Applied Chemistry, Government College University Faisalabad, Faisalabad, Pakistan

Nurul Jannah Ismail Advanced Membrane Technology Research Centre (AMTEC), School of Chemical and Energy Engineering, Faculty of Engineering, Universiti Teknologi Malaysia, Johor Bahru, Johor, Malaysia

Juhana Jaafar Advanced Membrane Technology Research Centre (AMTEC), School of Chemical and Energy Engineering, Faculty of Engineering, Universiti Teknologi Malaysia, Johor Bahru, Johor, Malaysia

Bhawana Jain Department of Chemistry, Government V. Y. T. PG. Autonomous, College, Durg, Chhattisgarh, India

Ansaf V. Karim Environmental Science and Engineering Department, Indian Institute of Technology, Mumbai, Maharashtra, India

Md. Zafar Ali Khan Department of Civil Engineering, Government Polytechnic College, Gonda, Uttar Pradesh, India

M. Suresh Kumar CSIR-National Environmental Engineering Research Institute, Nagpur, Maharashtra, India

Yongxin Li West China School of Public Health and West China Fourth Hospital, Sichuan University, Chengdu, China
Provincial Key Lab for Food Safety Monitoring and Risk Assessment of Sichuan, Chengdu, China

Maryam Mansoori Kermani Department of Chemical Engineering, Faculty of Engineering, Shahid Bahonar University of Kerman, Kerman, Iran

M. A. Martín-Lara Chemical Engineering Department, Faculty of Sciences, Granada, Spain

Debarati Mitra Department of Chemical Technology, University of Calcutta, Kolkata, India

Ali Mohebbi Department of Chemical Engineering, Faculty of Engineering, Shahid Bahonar University of Kerman, Kerman, Iran

Gulzar Muhammad Department of Chemistry, Government College University Lahore, Lahore, Pakistan

Faizan Muneer Department of Bioinformatics and Biotechnology, Government College University Faisalabad, Faisalabad, Pakistan

Aliru Olajide Mustapha Department of Chemical, Geological and Physical Sciences, Faculty of Pure and Applied Sciences, Kwara State University Malete, Ilorin, Kwara State, Nigeria

Habibullah Nadeem Department of Bioinformatics and Biotechnology, Government College University Faisalabad, Faisalabad, Pakistan

Muhammad Shahid Nazir Department of Chemistry, COMSATS University Islamabad, Islamabad, Pakistan

P. V. Nidheesh CSIR-National Environmental Engineering Research Institute, Nagpur, Maharashtra, India

Mohd Hafiz Dzarfan Othman Advanced Membrane Technology Research Centre (AMTEC), School of Chemical and Energy Engineering, Faculty of Engineering, Universiti Teknologi Malaysia, Johor Bahru, Johor, Malaysia

Naveen Patel Department of Civil Engineering, NIT, Agartala, Tripura, India

L. Quesada Chemical Engineering Department, Faculty of Sciences, Granada, Spain

Rachna Department of Chemistry, Dr B R Ambedkar National Institute of Technology, Jalandhar, Punjab, India

Mukhlis A. Rahman Advanced Membrane Technology Research Centre (AMTEC), School of Chemical and Energy Engineering, Faculty of Engineering, Universiti Teknologi Malaysia, Johor Bahru, Johor, Malaysia

Dhananjai Rai Department of Civil Engineering, BIET, Jhansi, Uttar Pradesh, India

Manviri Rani Department of Chemistry, Malaviya National Institute of Technology, Jaipur, Rajasthan, India

Ijaz Rasul Department of Bioinformatics and Biotechnology, Government College University Faisalabad, Faisalabad, Pakistan

Muhammad Arshad Raza Department of Chemistry, Government College University Lahore, Lahore, Pakistan

Zia Ur Rehman Department of Chemistry, Government College University Lahore, Lahore, Pakistan

S. Rossetti Water Research Institute, National Research Council of Italy (IRSA - CNR), Rome, Italy

Enrico Mendes Saggioro Department of Sanitation and Environmental Health, National School of Public Health, Oswaldo Cruz Foundation, Rio de Janeiro, Brazil

Monalisha Samanta Department of Chemical Technology, University of Calcutta, Kolkata, India

Shraddha Shahane Department of Civil Engineering, NIT, Agartala, Tripura, India

Munazza Shahid Department of Chemistry (SSC), University of Management and Technology, Lahore, Pakistan

Uma Shanker Department of Chemistry, Dr B R Ambedkar National Institute of Technology, Jalandhar, Punjab, India

Ajaya K. Singh Department of Chemistry, Government V. Y. T. PG. Autonomous, College, Durg, Chhattisgarh, India

Chengjun Sun West China School of Public Health and West China Fourth Hospital, Sichuan University, Chengdu, China
Provincial Key Lab for Food Safety Monitoring and Risk Assessment of Sichuan, Chengdu, China

Rui Sun West China School of Public Health and West China Fourth Hospital, Sichuan University, Chengdu, China

Zaman Tahir Department of Chemical Engineering, COMSATS University Islamabad, Islamabad, Pakistan

Zhong Sheng Tai Advanced Membrane Technology Research Centre (AMTEC), School of Chemical and Energy Engineering, Faculty of Engineering, Universiti Teknologi Malaysia, Johor Bahru, Johor, Malaysia

Rajagopalan Thiruvengadathan Department of Electronics and Communication Engineering, Amrita School of Engineering, Amrita Vishwa Vidyapeetham, Coimbatore, India

Sadaf ul Hassan Department of Chemistry, COMSATS University Islamabad, Islamabad, Pakistan

Jamilu Usman Advanced Membrane Technology Research Centre (AMTEC), School of Chemical and Energy Engineering, Faculty of Engineering, Universiti Teknologi Malaysia, Johor Bahru, Johor, Malaysia
Department of Chemistry, Faculty of Science, Sokoto State University, Sokoto, Sokoto State, Nigeria

Xin Wu Jiangxi Institute for Food Control, Nanchang, China

Danni Yang West China School of Public Health and West China Fourth Hospital, Sichuan University, Chengdu, China

Shuo Yin West China School of Public Health and West China Fourth Hospital, Sichuan University, Chengdu, China

Muhammad Zubair Department of Bioinformatics and Biotechnology, Government College University Faisalabad, Faisalabad, Pakistan

Chapter 1
Microplastic Pollution in Water

V. Godoy, M. A. Martín-Lara, A. I. Almendros, L. Quesada, and M. Calero

Contents

Abstract Microplastics are ubiquitous in almost all environments, including freshwater, seawater, and coastal environments. Recently, researches about microplastics have increased due to their serious ecological and health impacts. In this chapter, firstly, the sources of microplastics are summarized. Then, the most important techniques for sampling, extraction, purification, and identification of microplastics are discussed. Next, abundance of microplastics in different aquatic ecosystems around the world is synthesized. According to reviewed publications, the rivers

---

V. Godoy · M. A. Martín-Lara (✉) · A. I. Almendros · L. Quesada · M. Calero
Chemical Engineering Department, Faculty of Sciences, Granada, Spain
e-mail: vgcalero@ugr.es; marianml@ugr.es; lucia9s@ugr.es; mcaleroh@ugr.es

Inamuddin et al. (eds.), *Water Pollution and Remediation: Organic Pollutants*, Environmental Chemistry for a Sustainable World 54,
https://doi.org/10.1007/978-3-030-52395-4_1

and coasts of East Asia, the Mediterranean Sea, the Portuguese coasts, the rivers of England, and parts of the eastern United States were the most polluted areas. The vast majority of microplastics were composed of polyethylene (PE), polypropylene (PP), or polystyrene (PS), and the forms that predominated were fibers, fragments, and pellets. Finally, a brief revision of publications based on sorption of chemicals on microplastics and their effect on freshwater organisms is also reported.

Keywords Microplastics · Marine debris · Freshwater · Emerging contaminants · Sorption · Polymer identification · Risk assessment

1.1 Introduction

In the last years, contamination produced by microplastics has become a concern problem due to the environmental damage they cause and their harmful effects on organisms. These particles can be primary, which are manufactured by humans with some proposal, or secondary, which result from the physical and chemical degradation of macroplastics in the environment (Cole et al. 2011). Primary microplastics can be found in some personal care products, drilling fluids for extracting oil or natural gas, sandblasting for cleaning, some boat paints, or the loss of pellets from a plastic manufacturing industry (Duis and Coors 2016; Sundt et al. 2014). On the other hand, secondary microplastics can be produced by the tire wear, the washing of synthetic clothes, or the physical-chemical degradation of larger macroplastics (De Falco et al. 2018; Karlsson et al. 2018; Sommer et al. 2018).

Microplastics are found in almost every marine and freshwater environment on the Earth and also on beaches, sediments, bottled water, or food (Hamid et al. 2018; Novotna et al. 2019; Vandenberg et al. 2007). Figure 1.1 shows sampling of sediment on a Spanish beach in order to determine the presence of microplastics. The amount of microplastics in aqueous media is still increasing due to the growth in worldwide plastic production, which was 348 Mt in 2017 (Plastics Europe 2018). Research on these particles and their concentration in the marine and freshwaterenvironments has not ceased to grow. There are citations of the presence of microplastics in all types of environments, including those considered to be the most virgin or distant from the sources of production of these particles, such as the depths of the oceans or Arctic ice (Obbard et al. 2014; Woodall et al. 2014). Not only their widespread distribution is important, but they are accessible to consumption by an extensive diversity of organisms.

One of the most important environmental problems caused by microplastics is ingestion by aquatic organisms when confused with plankton (Egbeocha et al. 2018; Fossi et al. 2012; Taylor et al. 2016). The presence of microplastics in the digestive tract of marine species has been demonstrated in numerous studies. There are a lot of species that are affected by this problem, such as molluscs, cetaceans, bivalves, pinnipeds, and zooplankton (Botterell et al. 2019; De Sá et al. 2018; Gallo et al. 2018; Lusher 2015; Nelms et al. 2019). These studies showed that almost all

Fig. 1.1 Sampling of microplastics on a Spanish beach

commonly used polymers can be ingested by organisms, especially polyethylene and polystyrene.

Microplastics also have the capacity to adsorb contaminating substances that are present in the watercourses, i.e., pharmaceuticals, heavy metals, or pesticides (Bakir et al. 2014; Brennecke et al. 2016; Li et al. 2018). This implies a high risk for marine fauna and for human health, although the effects are still poorly defined. Some studies have reported negative effects of these pollutants on feeding behavior, reproduction, and growth of marine organisms (Anderson et al. 2016; Botterell et al. 2019; Bouwmeester et al. 2015; De Sá et al. 2018; Schirinzi et al. 2017; Wright and Kelly 2017; Wright et al. 2013).

The main problems when studying and analyzing microplastics are their small size, which makes it difficult to choose the right technique to identify them. This means the absence of a standard method for extracting microplastics from samples and their quantification. The analysis of microplastics goes through different phases, in which a different technique must be applied. Collection is the first phase, which can take place in water or in sediments. Sediment can be dry or wet when microplastics are going to be removed, whereas in water samples it is common to use nets, pumps, or sieves (Prata et al. 2019). Microplastics must then be extracted from water and sediment samples with the objective of being quantified and characterized. This separation usually is based on density, as each polymer has a different value. Density methods usually used NaCl, NaI, or $CaCl_2$ solutions in water, in order to increase the density (Masura et al. 2015; Quinn et al. 2017; Sánchez-Nieva et al. 2017).

Finally, when microplastics have been extracted, numerous techniques can be employed for their identification. Most studies usually make a first visual

Fig. 1.2 Analysis of microplastics in Fourier transform infrared spectroscopy equipment, in order to find out their chemical composition

classification, followed by the application of more complex techniques such as Fourier transform infrared spectroscopy (Fig. 1.2), micro Raman, scanning electron microscopy, the application of pigments such as Nile red, or gas chromatography-mass spectrometry (Eriksen et al. 2014; Godoy et al. 2019; Maes et al. 2017; Rocha-Santos and Duarte 2017). The objectives are to identify the composition of the microplastics, the presence of additives, and the morphology and determine the size. The use of one or other technique depends to a great extent on the size of the microplastic, the type of extraction previously done, the nature of the original sample, or simply on the techniques available in each laboratory.

In the present chapter, research has dedicated to the distribution of microplastics in marine and freshwaterenvironments around the world, providing data on concentrations and characterization of these particles. Prior to this research, the main sources of current microplastic emissions have also been described, as well as the most frequent techniques used in the characterization of these microparticles.

1.2 Sources of Microplastics

To study microplastic sources, it can be distinguished between two kinds of microplastics, primary and secondary. According to Cole et al. (2011), primarymicroplastics are defined as microscopic particles manufactured by humans with some proposal. Most primary microplastics in the environment are dumped from products routinely used in households, such as facial or body cleansers, airblasting media, or drug vectors used in medicine (Li et al. 2016). On the other hand, secondary microplastics are generated by the disintegration or fragmentation of macroplastics into particles of smaller size (Ryan et al. 2009). Figure 1.3 shows the difference between the appearance of primary and secondary microplastics.

Primary microplastics, such as polyethylene beads (with sizes between 10 and 106 μm) pictured (Fig. 1.3a), are typically uniform in shape and composition. Secondary microplastics are typically much more diverse in size, shape, color, and composition than primary microplastics, as can be seen in a sample trawled from a Spanish beach (Fig. 1.3b).

Syberg et al. (2015) reported a complete summary of sources of primary and secondary microplastic. In personal care products, primary microplastics are usually composed of thermoplastic polymers such as polyethylene, polypropylene, styrene copolymers, or polymethyl methacrylate. They are added to provide the personal care products some interesting characteristics such as ability to form a film, abrasion, shine, and viscosity (Napper et al. 2015; UNEP 2015). On the other hand, drilling fluids often contain reinforced Teflon particles, and in recent decades, they have become more commercially available. The main sources of emissions to the environment are sludge wastes, which are not always collected and treated in the appropriate way to eliminate these microparticles (Sundt et al. 2014).

Microplastics are also present in pressure sandblasting for cleaning, in the form of acrylic polymers, melamine, or polyester to remove rust and paint on machines, engines, and boat hulls. The problem arises when these products are not used in

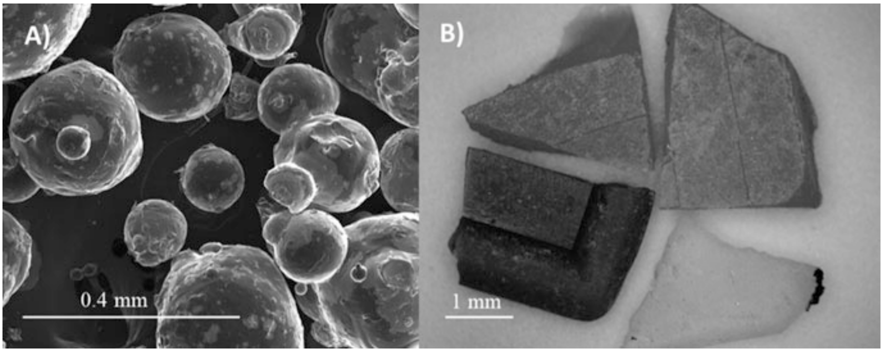


Fig. 1.3 (**a**) Primary microplastics from a cosmetic product; (**b**) secondary microplastics from a beach (Source: Original production)

closed systems with subsequent fluid recovery, making it very easy for them to end up in the environment through wastewater (Duis and Coors 2016). Microplastics can also be part of paints used for ships, increasing the emission of microparticles into the environment as the paint degrades and chip (Sundt et al. 2014). Pellets of virgin polymers can also be a source of primary microplastics. These pellets can be lost unintentionally during transport. Also, a loss of these pellets can be performed in the polymer processing facilities (Van Cauwenberghe et al. 2013). In fact, large ports and local plastic industries near the coast are the main sources of pellet contamination of the ocean and seawaters.

The main sources of secondary microplastics are tire wear and the washing of synthetic textile apparel. Tire wear accounts for approximately 5–10% of the world's total amount of microplastics ending up in the oceans (Kole et al. 2017). On the other hand, the washing of synthetic garments results in the release from two sources. Detergents may contain microplastics, and if there are no adequate filters for wastewater or water vapor, release to the environment occurs. In addition, a standard garment with some polymer can release up to 100 fibers per wash into the environment, and some garments have been shown to release up to 1900 fibers per wash (Browne et al. 2011).

Another source of secondary microplastics is the generation through the fragmentation of larger plastics. This happens when larger plastic waste is deposited on beaches or floating in water, exposed to solar radiation and weathering agents. Gradually, these wastes lose their mechanical and structural properties; their surfaces break down and decompose into smaller pieces until they reach the size of a microplastic (Auta et al. 2017).

It is hard to identify specifically how all these microplastics reach the water, but plastic debris can easily enter the different watercourses and oceans in different ways that include dumping or littering, effluents of water treatment plants, ineffective waste management, and even stormwater drainage systems. In Fig. 1.4, a schematic diagram shows the key sources and drive pathways.

1.3 Overview of Methods Used for the Sampling, Extraction, Purification, and Identification of Microplastics in the Environment

1.3.1 Sampling

Water Samples

Nets of different mesh sizes are the preferred technique used for sampling microplastics in waters. Particularly, bongo nets, plankton nets, and near-bottom trawls are extensively used for water column sampling, while manta trawls and neuston nets are used for surface water sampling (Wang and Wang 2018). Other

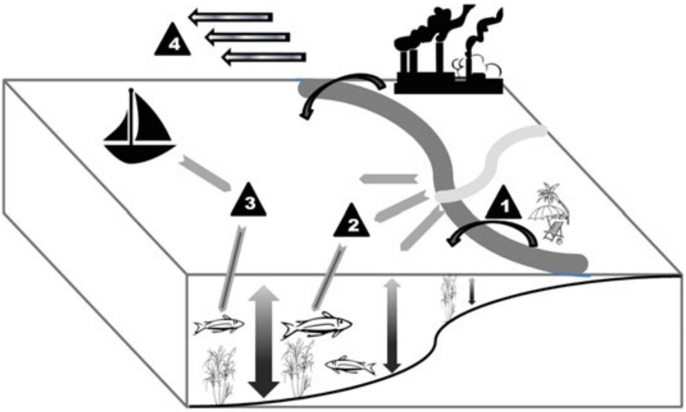


Fig. 1.4 Diagram of the main sources of microplastic emissions and their distribution flow through the marine environment; (1) microplastics from beaches; (2) and (3) microplastics from river estuaries and from maritime human activities, respectively, and their possible ingestion by organisms; (4) microplastics emitted to the air (Source: Original production)

tools used in water sampling are vessels or plankton traps (Crawford and Quinn 2017; Silva et al. 2018).

Some of the main factors that influence the sampling with nets and, therefore, the results of each study are the mesh size used and the network area that acts as a filter. According to the data collected in the literature, the nets usually have a length of 3–4.5 m, and most of the meshes are 300 μm size. It implies that not all microplastics are collected in commonly used sampling techniques. In addition, other techniques are occasionally used to evaluate microplastics in water. Particularly, the use of a cascade of filters is a very promising technique developed by -4H-JENA engineering GmbH, yet under development.

Sediment Samples

In the case of sediments, sampling is relatively easy. However, currently there is no official procedure for the sampling in terms of sampling depth, amount of collected sample, or location. Therefore, the comparison between data produced by different authors is restricted. At present, sediments of beaches are more often studied. Sampling work is performed on the whole beach. With respect to the location of the sample on the beach, the applied sampling strategies include random sampling in several sites, following perpendicular (vertically from the water edge) and parallel (horizontally to the water) lines. Transects are a common approach when conducting a beach sampling using quadrats of various sizes (Hanvey et al. 2017).

With regard to sampling depth, taking samples in the first 5 centimeters is the most common technique, although sampling at a greater depth has also been found in published works (Claessens et al. 2011). Authors as Hanvey et al. (2017) think that this procedure underestimates the levels of plastics, as sampling is only centering on the surface layer. Another point of interest is the quantity of sample, because some works collected less than 500 g of sediments, whereas others can reach about 10 kilograms (Hidalgo-Ruz et al. 2012).

As a general rule, the sampling is performed with the following instruments: (1) a sampling tool of a nonplastic material (usually a small spoon or shovel), (2) a frame that specifies the sampling area, and (3) a container also of a nonplastic material in which the collected sample is stored are required.

Biological Samples

The schemes for the biological sampling are diverse and strongly determined by the organism that will be analyzed. Normally, zooplankton, fish species, or crustaceans are getting by nets or traps. Also, smaller invertebrate organisms can be collected directly by hand. Generally, the interest is in the digestive system, tract, or excretions of the organism. Then, a dissection to release the intestinal content or the entire digestive system is performed (Lusher et al. 2013).

1.3.2 Extraction and Purification of Microplastics

Density Separation

The flotation technique is the most used for the extraction of microplastics from sediment samples. The objective is to take advantage of the difference in density between the most common plastic polymers, which range from 0.28 to 1.47 $g{\cdot}cm^{-3}$, and the sedimentary matrix, which has a density of approximately 2.55 $g{\cdot}cm^{-3}$. Particularly, a concentrated salt solution is prepared and put into contact with the sediment sample. The solid-liquid mixture is agitated during a certain time and then is left to decant. The plastic particles remain in suspension while grains of sand decant. Afterward, the microplastics are recovered from the supernatant by filtration.

Despite being a cheap and environmentally friendly procedure, not all common polymers are extracted using a concentrated salt solution. For example, high-density polymers as polyvinyl chloride or polyethylene terephthalate (PET), among others, end up settling with the sediment because the salt solution has a low density of approximately 1.2 $g{\cdot}cm^{-3}$. Therefore, high-density solutions are used to overcome this drawback, for example, sodium iodine solution (1.8 $g{\cdot}cm^{-3}$), zinc chloride solution (1.5–1.7 $g{\cdot}cm^{-3}$), or sodium polytungstate solution (1.4 $g{\cdot}cm^{-3}$) (Nuelle et al. 2014; Imhof et al. 2012; Liebezeit and Dubaish 2012; Corcoran et al. 2009).

The flotation technique is adequate to extract high-size microplastics reaching recoveries of 80–100% (Fries et al. 2013); however, microplastics with a particle size lower than 500 μm are more difficult to extract. In this sense, consecutive extraction stages are suggested to get better recoveries.

Matrix Removal and Purification of Microplastic Samples

For a correct identification of the microplastics, it is necessary to eliminate all the organic and inorganic compounds adhered to the surface thereof. In addition, particularly matrix removal, it is necessary to remove microplastic from biological samples. The softest method to clean samples is washing with fresh water (McDermid and McMullen 2004). Other purification techniques have also been used in the literature, for example, ultrasonic cleaning, treatments with hydrogen peroxide, and treatments with mineral acids (Andrady 2011; Cooper and Corcoran 2010; Liebezeit and Dubaish 2012).

Other authors have used mainly 37% of hydrochloric acid (HCl), various concentrations of sodium hydroxide (NaOH), and 30% of hydrogen peroxide (H_2O_2) or a specific mixture of them, for the tissue digestion of biotic samples (Claessens et al. 2013; Davidson and Dudas 2016; Dehaut et al. 2016; Löder and Gunnar 2015; Lusher 2015; Zhao et al. 2017). However, special care must be taken in the use of these techniques because some plastics can react especially to strong acid or alkaline solutions (Liebezeit and Dubaish 2012; Claessens et al. 2013). It notably restricts the applicability of these reagents. In this sense, the most promising technique is the use of enzymatic digestion which has shown good preliminary results (Cole et al. 2014; Catarino et al. 2017).

1.3.3 Quantification and Identification of Microplastics

Manual Counting by Visual Identification

The use of microscopes is widely extended to identify microplastics (Hanvey et al. 2017). The main drawbacks of this technique are the limitation in the identification of particles below a certain size and an excessive slowness. Another major drawback is that the quality of the data produced depends to a large extent on the microscope used, the characteristics of the person performing the study, and the sample matrix (i.e., sediment or intestinal content). Finally, mistakes by counting nonplastic particles as plastic can be made. According to all the limitations mentioned, the error rate of the visual classification increases with decreasing particle size and can fluctuate from 20% to 70% (Eriksen et al. 2013; Hidalgo-Ruz et al. 2012). This is the reason why it is important to analyze then the particles by other methods for a correct identification of plastics (Dekiff et al. 2014; Hidalgo-Ruz et al. 2012).

Norén (2007) suggests the following criteria for the visual identification of larger microplastics: (1) in the plastic particle, no structure of biological origin should be distinguished, (2) the plastic fibers must have a folded three-dimensional shape and a similar thickness to assure that there is no biological origin, (3) the particles should be of homogeneous color, and (4) those transparent or whitish particles should be inspected with the support of fluorescence at high magnification to exclude an organic origin.

Fourier Transform Infrared Spectroscopy

Fourier transform infrared spectroscopy is applicable to a wide variety of chemical applications, such as the case of polymers and organic compounds. It is the most used technique to identify polymer in sediment samples. It uses the infrared spectrum of emission or absorption generated using infrared radiation to excite the sample, which allows to identify the type of plastic accurately (Frias et al. 2010; Harrison et al. 2012; Ng and Obbard 2006; Reddy et al. 2006; Thompson et al. 2004; Vianello et al. 2013). When the infrared radiation reaches a sample, part of the radiation is absorbed by the sample, and another part passes through it. The resulting information is a characteristic spectrum associated to the chemical structures presented in the sample. In microplastic identification application, one important advantage of Fourier transform infrared spectroscopy is it allows the analysis of polymers without destroying the sample.

Pyrolysis-Gas Chromatography in Combination with Mass Spectrometry

Another technique that allows evaluating the chemical composition of plastic particles is pyrolysis-gas chromatography in combination with mass spectrometry. Currently, this technique is widely applied to synthetic and natural polymers. In this technique the polymers are converted to products of lower molecular weight by the action of heat. The composition and relative abundance of the products obtained in the pyrolysis are characteristic for a given polymer. The correct determination of this information allows the identification of materials that cannot be determined in any other way. Then, this technique is based on the analysis of thermal degradation products generated during the thermal processing of the sample (Fries et al. 2013; Nuelle et al. 2014).

The main disadvantages of this technique are that particles must be placed manually in the pyrolysis tube and lower particles cannot be manipulated manually. In addition, the method lets the analysis of only one sample per test, and, therefore, large quantities of sample are not suitable for processing. Finally, compared with spectroscopic methods, the major disadvantage is that it is destructive.

Raman Spectroscopy

Raman spectroscopy, together with the Fourier transform infrared spectroscopy, is another important and commonly used spectroscopy technique that provides chemical information of microplastics (Araujo et al. 2018; Cole et al. 2013; Imhof et al. 2012, 2013; Murray and Cowie 2011; Van Cauwenberghe et al. 2013). The analysis is based on the examination of light dispersed by sample when a monochromatic laser source (between 500 and 800 nm) impacts on it. The result is a characteristic Raman spectrum that allows the identification of each type of polymer. It is a nondestructive technique allowing the recovery of the sample for further analysis (Shim et al. 2017). In microplastic identification, one of the great advantages of this technique is that it can be coupled with microscopy which lets the identification of smaller microplastics (Strungaru et al. 2019).

Scanning Electron Microscopy and Energy-Dispersive X-Ray Spectroscopy

Scanning electron microscopy generates an image of the surface of the microplastic based on interaction of an electron beam with the sample (Rocha-Santos and Duarte 2015). The scanning electron microscopy technique provides full information about the shape, size, and topography of the plastic particles. According to the provided images, the source of the microplastics, i.e., decomposed fragments of larger plastics or primary microplastics, can be predicted (Zbyszewski and Corcoran 2011). Also, scanning electron microscopy can be combined with energy-dispersive X-ray spectroscopy to determine elemental composition and identify inorganic additives in microplastics fragments. For example, scanning electron microscopy-energy-dispersive X-ray method was used by Fries et al. (2013) to analyze the existence of aluminum, barium, carbon, oxygen, titanium, sulfur, and zinc on microplastic particles.

1.4 Microplastics in Freshwater Environments

Microplastic pollution has gained considerable attention in freshwater systems, despite the fact that a large number of works are still devoted to the study of the marine environment. Freshwaterenvironments are a recognizable way to carry microplastics from land-based sources to the aquatic environment. Studies about microplastics in freshwaterenvironments are increasing in attention due to the great quantities of plastic found in lakes, rivers, and even drinking water and because of its harmful effects on the environment and human health.

1.4.1 Global Microplastic Concentration and Distribution in Different Freshwater Ecosystems

Microplastics vary geographically, depending on environmental factors, especially hydrodynamic conditions and anthropogenic factors (Besseling et al. 2017; Imhof et al. 2017; Kim et al. 2015; Sarafraz et al. 2016). In this section, the most important concentrations of microplastics present in the literature over the last decade have been collected and selected. These data are presented on maps of different locations,

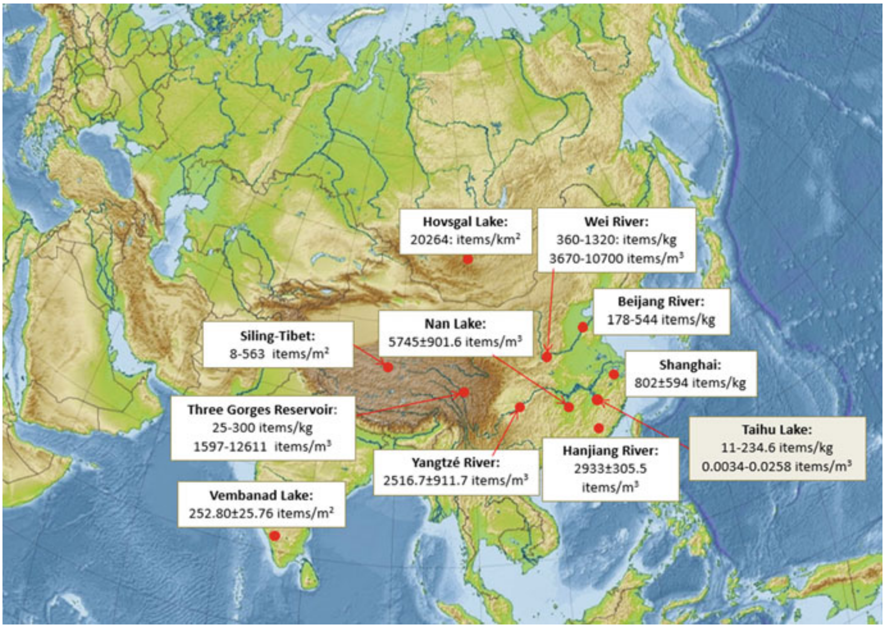


Fig. 1.5 Abundance of microplastics in sediment and water samples from different freshwater systems, i.e., rivers or lakes, across Asia. The abundances present in sediments are expressed in items per m^2 or items per kg, while the abundances in water are expressed in items per m^3 (Sources of data: Di and Wang (2018), Free et al. (2014), Peng et al. (2018), Sruthy and Ramassamy (2017), Su et al. (2016), Wang et al. (2017a, b), Zhang et al. (2016), Ding et al. (2019). Source of figure: Original production)

in Asia, Africa, Europe, and North America, in order to determine their geographical distribution. This information is presented in Figs. 1.5, 1.6, 1.7, and 1.8.

The samples found in rivers and lakes mainly from freshwater sources contain a large amount of microplastics, which is then reflected in the amount of microplastics found in the seas and oceans, as rivers are one of the main transport routes. Based on the sediment typology, it can be observed how in Europe, in Sweden (Lysekil), 8360 items per kg were found (Magnusson and Noren 2014), while in North America, in Canada (St. Lawrence River), 13,832 items per m^2 were found (Castañeda et al. 2014). On the other hand, with focus on the microplastics found in water samples, the highest concentrations are found in North America. In the United States (Los Angeles River), 12,932 items per m^3 were obtained (Moore et al. 2011), while in Chicago River 6.69E6 items per m^2 were obtained (McCormick et al. 2014).

Figure 1.5 represents the microplastic abundance and distribution in Asia. This continent contains the largest contamination by microplastics. The biggest concentrations of these particles are present along river and lakes. Studies have reported high concentrations of microplastics in Wei River, where 360–1320 items per kg of sediment were found (Ding et al. 2019), or Beijing River, where 178–544 items per kg of sediment were counted (Wang et al. 2017a). Other studies have reported high

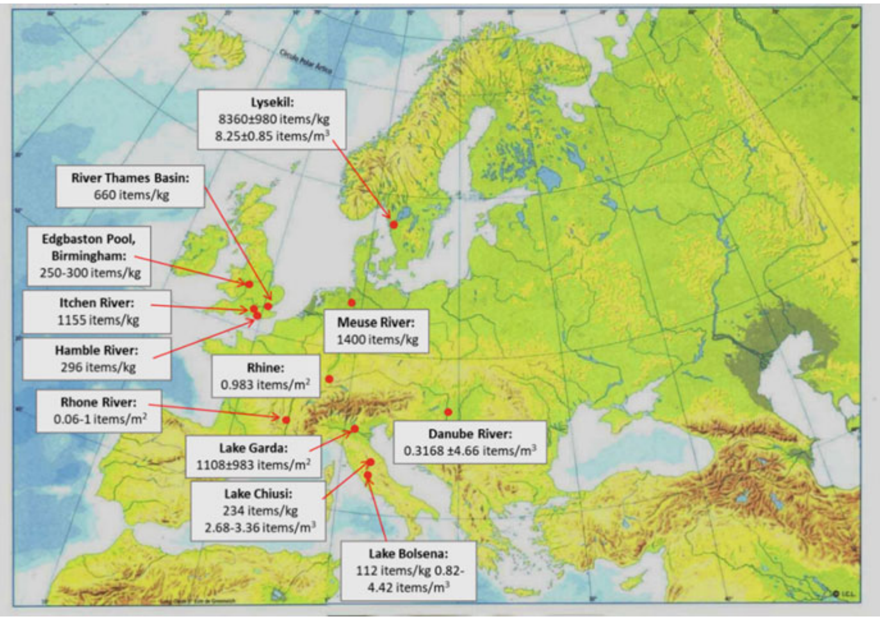


Fig. 1.6 Abundance of microplastics in sediment and water samples from different freshwater systems, i.e., rivers or lakes, across Europe. The abundances present in sediments are expressed in items per m^2 or items per kg, while the abundances in water are expressed in items per m^3 (Sources of data: Fischer et al. (2016), Gallagher et al. (2016), Horton et al. (2017a, b), Imhof et al. (2013), Lechner et al. (2014), Leslie et al. (2017), Magnusson and Noren (2014), Mani et al. (2015), Schmidt et al. (2018), Vaughan et al. (2017). Source of figure: Original production)

concentrations of microparticles in lakes, i.e., in the Nan Lake, where more than 5745 items per m^3 were found (Wang et al. 2017a). Lake Hovsgol and those lakes within the Siling Lake basin (northern Tibet) were studied showing significant concentrations of microplastics, 0.02 items per m^2 and 8–563 items per m^2 (Zhang et al. 2016), respectively, although these locations have little human activity. This may be due to inappropriate waste management in low-density populations.

Figure 1.6 represents a map of Europe with the main accumulations of microplastics. The most contaminated areas were Lysekil (Sweden), where quantities of 8360 items per kg in sediments and 8.25 items per m^3 in water were estimated (Magnusson and Noren). In Meuse River (Netherlands), 1400 items per kg (sediments) were estimated (Leslie et al. 2017), whereas in Itchen River (UK), 1155 items per m^3 (water) were estimated (Gallagher et al. 2016).

North America is represented in Fig. 1.7, with the main areas where microplastics accumulate. The most contaminated areas are Canada and the United States. Chicago River (USA) contained about 6.69E10^6 items per m^2 (McCormick et al. 2014), while St. Lawrence River (Canada) contained 13,832 items per m^2 (Castañeda et al. 2014). There are also other rivers, such as Los Angeles River, that have high concentrations

Fig. 1.7 Abundance of microplastics in sediment and water samples from different freshwater systems, i.e., rivers or lakes, across North America. The abundances present in sediments are expressed in items per m^2, items per km^2, or items per kg, while the abundances in water are expressed in items per m^3 (Sources of data: Anderson et al. (2017), Ballent et al. (2016), Castañeda et al. (2014), Corcoran et al. (2015), Eriksen et al. (2013), McCormick et al. (2014), Moore et al. (2011). Source of figure: Original production)

of microplastics around 12,932 items per m^3. On the other hand, lakes have lower amounts of microplastics than rivers, which may be mainly due to the currents.

Figure 1.8 represents the microplastic abundance and distribution in Africa; there is a great lack of data and studies on microplastics in fresh water. Nel et al. (2018)

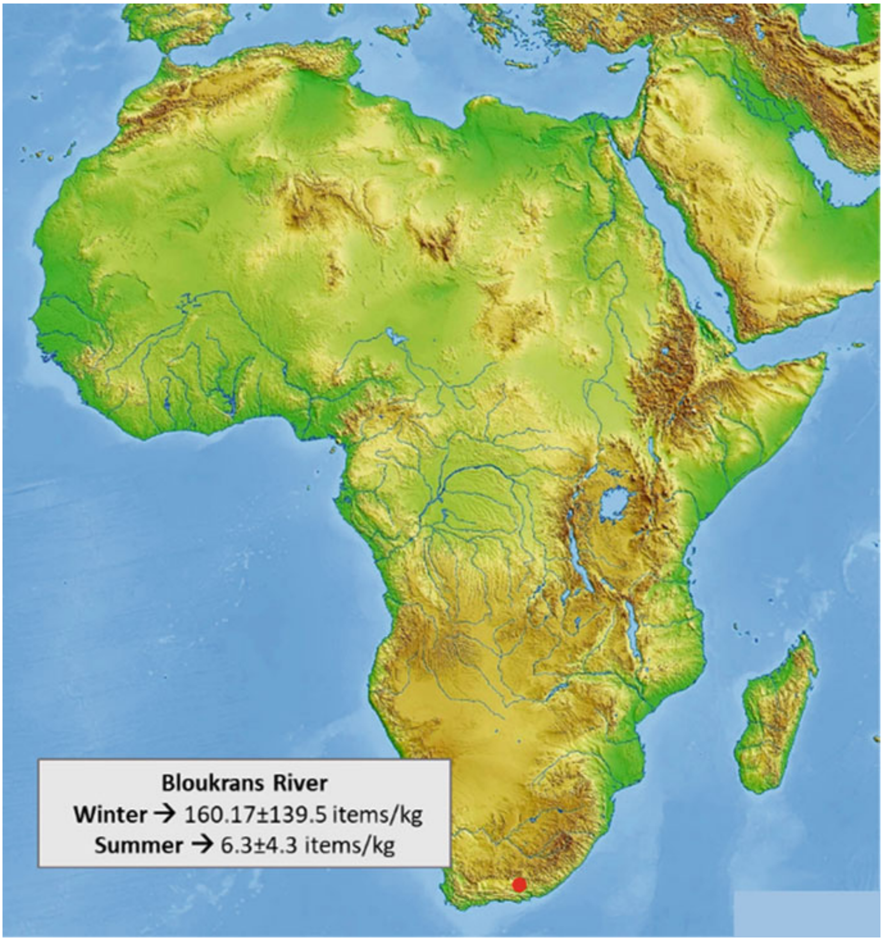


Fig. 1.8 Abundance of microplastics in sediment and water samples from different freshwater systems, i.e., rivers or lakes, across Africa. The abundances present in sediments are expressed in items per kg (Source of data: Nel et al. (2018). Source of figure: Original production)

carried out a study along the Bloukrans River of South Africa and found microplastic densities in beach sediments between 6.3 ± 4.3 items per kg in summer season and 160.1 ± 139.5 items per kg of sediment in winter season. Higher concentrations were obtained in winter, associated with the flow of the river, and this in turn associated with the transport of microplastics.

Microplastics are not only found in rivers and lakes, but there are also studies where significant amounts of microplastics have been detected in potable water. Novotna et al. (2019) collected results of some important studies that found significant amounts of plastic in both the public supply and the bottled water. The public source that contains more microplastics is treated water in Czech Republic with 628 microplastics by liter (Pivokonsky et al. 2018). On the other hand, the bottled water where more microplastics were found in account 6298 microplastics by liter (Oßmann et al. 2018). Also, Schymanski et al. (2018) found 117 microplastics by liter in returnable plastic bottles, and Mason et al. (2018) estimated a concentration of 932 and 1411 microplastics by liter in plastic bottles of brand Nestle Pure Life and Gerolsteiner, respectively.

1.4.2 Type, Size, and Morphology of Microplastics in Freshwater

With respect to microplastic sizes, they can be distributed into six different groups: category 1 (0.5 mm), category 2 (0.5–1 mm), category 3 (1–2 mm), category 4 (2–3 mm), category 5 (3–4 mm), and category 6 (4–5 mm). Figure 1.9 shows the size distribution of the samples both on the water surface and in sediments of the samples collected at Wei River, China.

The most abundant microplastics were of category 1 in all samples including water and sediment samples. Category 2 and category 3 were the second and third most important, while samples belonging to group 4, 5, and 6 were insignificant. Similar results have been obtained in other freshwater locations such as in Qinghai Lake (China), Lake Garda (Italy), Three Gorges (China), Laurentian Great Lakes (USA), and Taihu Lake (China) (Di and Wang 2018; Eriksen et al. 2013; Imhof et al. 2016; Su et al. 2016; Xiong et al. 2018). The most abundant fraction was the size lower than 0.5 mm in all the mentioned locations, especially in water surface. Some of them realized that the predominant fraction in sediments was 0.5–1 mm. In sum,

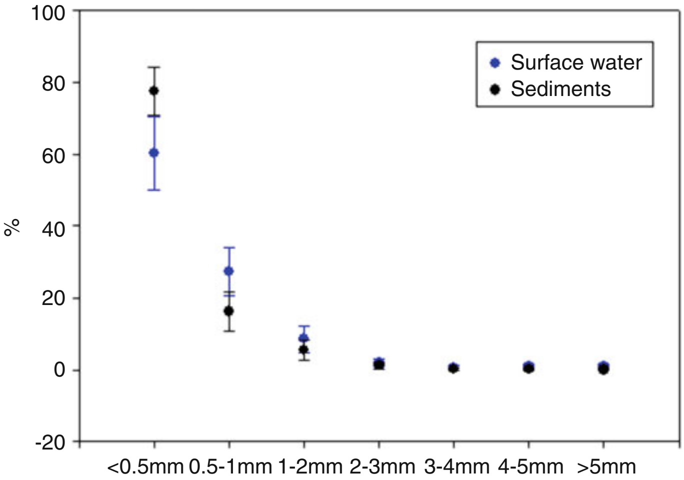


Fig. 1.9 Size distribution of the samples both on the water surface and in sediments of the samples collected in Wei River, China. The data are expressed as a percentage of microplastics within each size group (Source: Modified after Ding et al. (2019))

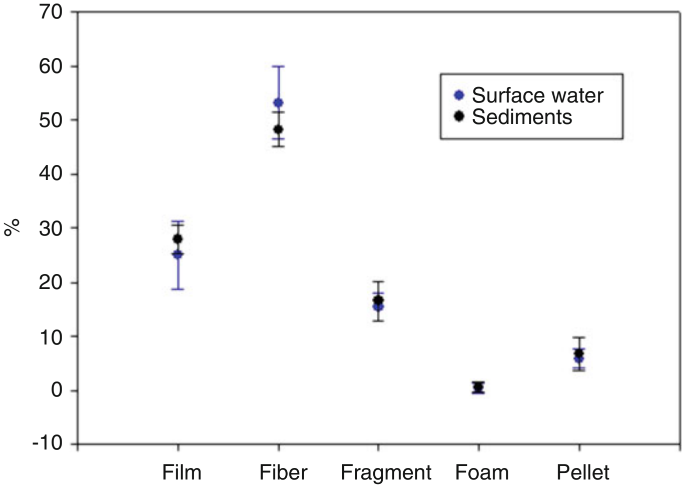


Fig. 1.10 Morphology distribution of the samples both on the water surface and in sediments of the samples collected in Wei River, China. The data are expressed as a percentage of microplastics within each morphology (Source: Modified after Ding et al. (2019))

the most abundant microplastic particles in freshwater had a size less than 1 mm, while it is insignificant with the presence of microplastics greater than 2 mm.

The most studied shapes were fragments, fibers, film, foam, or pellet, but beads, lines, spherules, sheets, flakes, paint, foil, and nurdle can also be found. For example, the results of a study carried out by Ding et al. (2019), which analyzed the morphology of different samples obtained in Wei River in China, are shown in Fig. 1.10.

The difference between the samples obtained in surface water and sediments can be due to the reaction that samples produce in the outdoors with the organic products. Fibers and films were the most dominant, whereas pellets and foams were the less abundant types of microplastics in Wei River. Fiber was the dominant species in surface water and sediment samples, where it represented approximately half of the samples studied. The origin of these microplastics was attributed to the decomposition of agricultural plastics and wastewatereffluents containing fibers from clothes (Claessens et al. 2011). Similar results were obtained in other freshwater locations such as in Tibetan Plateau lakes (China) or in Three Gorges (China), where fiber was dominant, accounted for 28.6–90.5% in water surface and 33.9–100% in sediments (Di and Wang 2018; Zhang et al. 2016).

With respect to microplastic colors, the most common were blue, green, red, transparent, and white (Di and Wang 2018). With regard to the composition of microplastics, the different polymers found in freshwater are due to two main factors: the demand for plastics and the density of the polymers. The annual demand of plastics in Europe is presented in Fig. 1.11, where it can be seen that the most consumed plastics are polyethylene and polypropylene.

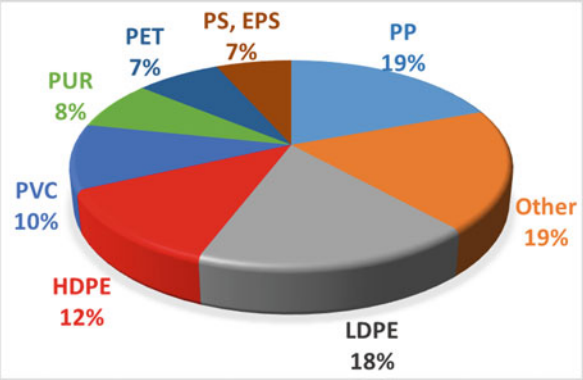


Fig. 1.11 Distribution of demand for different types of plastics in Europe in 2017 (Source: Modified after Plastics Europe (2017))

Polyethylene and polypropylene have densities below 1 g per cm^3; polystyrene has a density close to that of 1 g per cm^3; polyvinyl chloride and polyethylene terephthalate have densities of 1.3–1.7 g per cm^3. The higher the density, the easier the sedimentation occurs, which is the main reason why less polyvinyl chloride and polyethylene terephthalate are found (Koelmans et al. 2019). Table 1.1 shows the different polymers found in some freshwater studies. The most commonly found polymers are polyethylene, polypropylene, and polystyrene.

1.5 Microplastics in Marine Environments

Microplastics are found in almost every marine environment on the Earth. Both research on these particles and concentrations in the marine environment have not ceased to grow. There are citations of the presence of microplastics in all types of environments, including those considered to be the most virgin or distant from the sources of production of these particles, such as the depths of the oceans or Arctic ice (Obbard et al. 2014; Woodall et al. 2014). Microplastics are present in the marine and coastal environments and accessible to ingestion by a wide variety of organisms.

Although the harmful effects of microplastics into the food chain are not yet well known, it has been demonstrated that one of the main problems is the capacity of these particles to absorb hydrophobic compounds on their surface, accumulating them and entering the living organisms that consume them including humans (Brennecke et al. 2016; Llorca et al. 2018; Li et al. 2018; Wu et al. 2019). An important environmental effect derives from the fact that microplastics not only adsorb pollutants from water but they also release additives or persistent organic compounds into the environment (Bakir et al. 2014; Moore 2008). These compounds have been described by the US Environmental Protection Agency as a risk to human health, as they enter and accumulate in the food chain.

Table 1.1 Summary of polymers found in different freshwater locations

Country	Location	Composition	References
China	Shanghai	PP, PE, rayon, cotton+viscose, phenoxy resin, poly (vinyl stearate)	Peng et al. (2018)
China	Three Gorges Reservoir	PE, PP, PS	Di and Wang (2018)
China	Beijing River	PE, PP, copolymer, paint particle	Wang et al. (2017a)
China	Taihu Lake	CP, PET, PE, PA, PP	Su et al. (2016)
China	Hanjiang River	PA, PE, PET, PP, PS	Wang et al. (2017b)
China	Yangtze River	PA, PE, PET, PP, PS	Wang et al. (2017b)
China	Sha Lake	PA, PE, PET, PP, PS	Wang et al. (2017b)
China	Nantaizi Lake	PA, PE, PET, PP, PS	Wang et al. (2017b)
China	Nan Lake	PA, PE, PET, PP, PS	Wang et al. (2017b)
China	Siling, Tibet	PE, PET, PP, PS, PVC	Zhang et al. (2016)
India	Vembanad Lake	HDPE, LDPE, PS, PP	Sruthy and Ramasamy (2017)
UK	River Thames basin	PP, PES, PET, PS, PE	Horton et al. (2017a, b)
UK	Itchen River	PE, PP, CP	Gallagher et al. (2016)
UK	Hamble River	PE, PP, CP	Gallagher et al. (2016)
Italy	Lake Bolsena	PE, PP, PET, PVC	Fischer et al. (2016)
Italy	Lake Chiusi	PE, PP, PET, PVC	Fischer et al. (2016)
Italy	Lake Garda	PA, PE, PP, PS, PVC	Imhof et al. (2013)
Sweden	Lysekil	PE, PP	Magnusson and Noren (2014)
Germany	Rhine	PA, PE, PP, PS, PVC	Mani et al. (2015)
Canada	Ontario Lake	PE, PS, PUR, PP, PVC, PET, PMMA, polyvinyl acetate, PMMA-PS, ABS, nylon, phenoxy or epoxy resin, polymethylsiloxane	Ballent et al. (2016)
Canada	St. Lawrence River	PE, PP, nitrocellulose	Castañeda et al. (2014)

ABS acrylonitrile butadiene styrene, *CP* cyclopentadienyl complex, *HDPE* high-density polyethylene, *LDPE* low-density polyethylene, *PA* polyamide, *PE* polyethylene, *PET* polyethylene terephthalate, *PMMA* polymethyl methacrylate, *PP* polypropylene, *PS* polystyrene, *PSS* poly (styrenesulfonate), *PUR* polyurethane, *PVC* polyvinyl chloride

1.5.1 Global Microplastic Concentration and Distribution in Different Marine Ecosystems

The first study that reported the presence of microplastics in seawater was conducted by Carpenter and Smith (1972). They estimated average microplastic concentrations of 3500 items and 290 g per km^2 in the western Sargasso Sea. With this discovery, the scientists tried to alert society about the problem of that contamination, but their warning was ignored. At present, microplastics are much more abundant and distributed all over the seas, oceans, and beaches, as revealed by numerous studies over the last decade (Auta et al. 2017; Cole et al. 2011; Guo and Wang 2019; Hamid et al. 2018; Hidalgo-Ruz et al. 2012; Kane and Clare 2019).

Microplastics have low density in general, which means that they can easily float on the water surface or in the water column (Piperagkas et al. 2018). Microplastics with density higher than that of seawater tend to sink down in sediments, where they accumulate, while those with low density float on the sea surfaces (Alomar et al. 2016; Suaria and Aliani 2014). Density can change when microplastics are degraded by the action of external agents or when biofouling caused by organisms occurs. In addition, Eriksen et al. (2014) verified that the movement of microplastics is also controlled by marine currents and oceanic gyres. According to that study, ocean margins are zones of plastic migration, while subtropical gyres are areas of accumulation. Therefore, the distribution of microplastics in marine environments is controlled by a wide range of causes.

In this section, the most important concentrations of microplastics present in the literature over the last decade have been collected and selected. These data are presented on maps of the continents of the world, in order to determine the geographical distribution of microplastics. Figure 1.12 represents the microplastic abundance and distribution in Europe. This continent contains the largest contamination by microplastics, along with East Asia. The biggest concentrations of these particles are present along the coast of Algarve (Portugal), in the lagoon of Venice, and in the Rhine estuary (Frias et al. 2016; Vianello et al. 2013; Mani et al. 2015). This can be due to the fact that microplastic particles tend to accumulate in areas characterized by lower water movement, such as an estuary or a lagoon.

Other studies have reported high concentrations of microparticles in beaches, for example, in Canary Islands, where more than 1600 items per m^2 in the beach of Lambra were found (Herrera et al. 2018). The authors reached the conclusion that debris accumulation depended mainly of coastline orientations and meteorological conditions. In addition, the subtropical oceanic gyre affects the way in which the currents vary from the coast to the open ocean during the year (Navarro-Pérez and Barton 2001). The same occur to some remote areas where high amounts of microplastics are recorded, i.e., Scapa Flow (UK), which accounted between 730 and 2300 items per kg of sediment, or Vik (Iceland), with 792 items per kg (Blumenröder et al. 2017; Lots et al. 2017). This is mainly caused by the oceanic currents. Other factors that can affect the pollution distribution are the salinity, temperature, shape of the coast line, or coastal activities (Cincinelli et al. 2019).

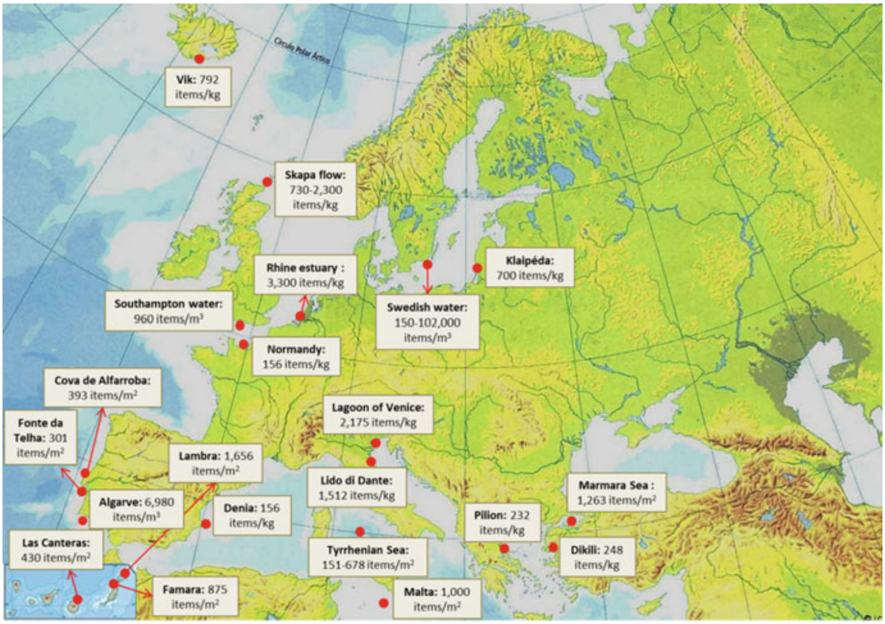


Fig. 1.12 Abundance of microplastics in sediment and water samples from different marine systems, i.e., beaches, estuaries, or marine water, across Europe. The abundances present in sediments are expressed in items per m^2 or items per kg, while the abundances in water are expressed in items per m^3 (Sources of data: Blumenröder et al. (2017), Fastelli et al. (2016), Frias et al. (2016), Herrera et al. (2018), Lots et al. (2017), Mani et al. (2015), Martins and Sobral (2011), Tunçer et al. (2018), Turner and Holmes (2011), Vianello et al. (2013). (Source of figure: Original production)

The first study that reported the abundance of floating plastic debris in the Mediterranean Sea was conducted by Morris (1980), who determined a concentration of about 1300 items per km^2 near Malta. A similar study was conducted later by Turner and Holmes (2011), who reported a concentration of 1000 items per m^2 in the Maltese beaches. The average plastic concentration in Mediterranean surface waters is 243,853 items per km^2 (Cózar et al. 2015). This concentration is much lower in the water column, where a limited number of studies have reported low concentrations of microplastics (Cincinelli et al. 2019; Fossi et al. 2012; Xiong et al. 2018).

Figure 1.13 represents a map of Asia with the main accumulations of microplastic debris. The most contaminated areas are, as in Europe, the estuaries of the rivers Yangtze, Nakdong, and Pearl, where quantities of 4137 items per m^3 in water, 27,606 items per m^2 in sediments, and 5959 items per m^2 in sediments were estimated, respectively (Fok and Cheung 2015; Lee et al. 2013; Zhao et al. 2014). Compared to European marine ecosystems, Asia is much more contaminated with microplastics. China is the third major producer of plastic waste in the world (Plastics Europe 2018). Therefore, it is not surprising that their coastlines are so

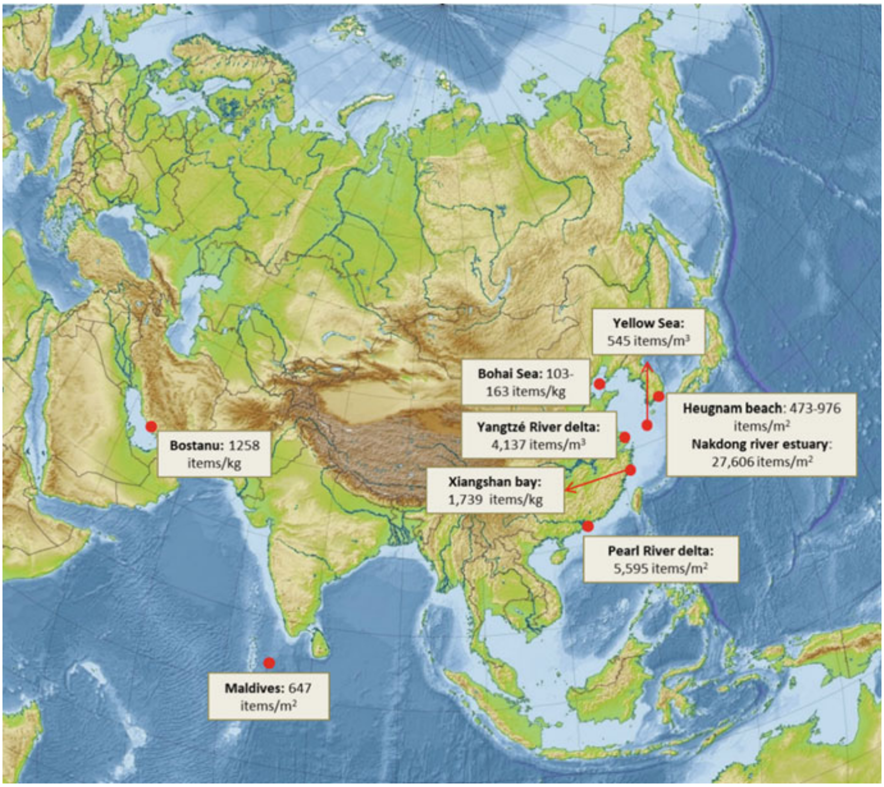


Fig. 1.13 Abundance of microplastics in sediment and water samples from different marine systems, i.e., beaches, estuaries, or marine water, across Asia. The abundances present in sediments are expressed in items per m^2 or items per kg, while the abundances in water are expressed in items per m^3 (Sources of data: Chen et al. (2018), Fok and Cheung (2015), Heo et al. (2013), Imhof et al. (2017), Lee et al. (2013), Naji et al. (2017), Zhao et al. (2014), Zhu et al. (2018). Source of figure: Original production)

polluted by microplastics. Despite this, Kang et al. (2015) have shown that the release of microplastic is higher in raining season than in waterless season.

Beaches in India are not so polluted by microplastics. It was found between 2 and 178 items per m^2, in contrast to the results obtained for the Maldives Islands, where more than 600 items per m^2 were reported (Imhof et al. 2017; Karthik et al. 2018). The origin of the contamination in this isolated island could be generated in the nearby islands in Maldives, where tourism is more frequent. Debris can also enter this island from many coastal areas of the Indian Ocean. Eriksen et al. (2014) estimated the amount of microplastics in surface waters along the Indian Ocean between 7000 and 8000 items per km^2.

On the other hand, average concentrations in open seas have also been measured. Isobe et al. (2015) investigated the concentrations of microplastics in the East Asian Seas around Japan and obtained a total particle concentration of about 1.72 million

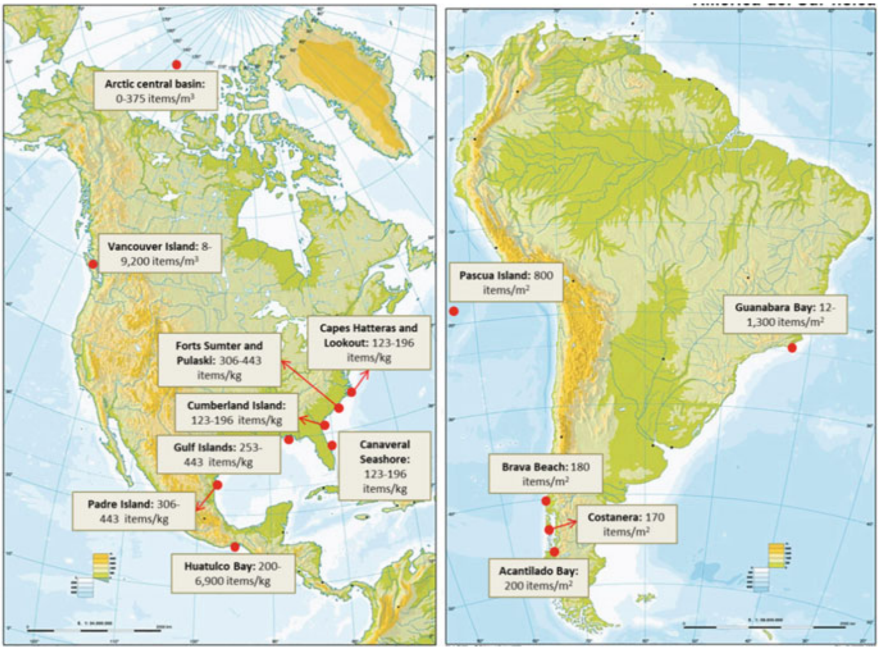


Fig. 1.14 Abundance of microplastics in sediment and water samples from different marine systems, i.e., beaches, estuaries, or marine water, across North and South America. The abundances present in sediments are expressed in items per m^2 or items per kg, while the abundances in water are expressed in items per m^3 (Sources of data: Desforges et al. (2014), Gomes de Carvalho and Baptista (2016), Hidalgo-Ruz and Theil (2013), Kanhai et al. (2018), Retama et al. (2016), Yu et al. (2018). Source of figure: Original production)

items per km^2. Another study conducted in the northwestern Pacific (Pan et al. 2019) recorded about 10,000 items per km^2, a very lower concentration than that obtained in Japanese seas. Compared to Mediterranean data, seas in Asia are much more contaminated.

North and South America are represented in Fig. 1.14, with the main areas where microplastics accumulate. The most contaminated area is the coast along North and South Carolina, where microplastics can account for more than 400 items per kg of sediment (Yu et al. 2018). Authors considered that nearby urbanization core and the presence of large rivers that discharge water into that area are factors that influence the amount of microplastics found. North and South America are bordered by oceans Pacific and Atlantic on the west and the east, respectively. These oceans exhibit strong currents, wave and hurricane action, tides, and in general a high dynamic action, which determine microplastic distribution.

Another contaminated area is the Gulf of Mexico, which accounts for more than 110 items per m^2 in sediment (Wessel et al. 2016). Authors determined that the microplastic composition and abundance were related to the exposition to marine currents. Therefore, the areas more exposed to marine currents have bigger and denser microplastics than that found in locations less influenced by marine activity. On the other side of the Gulf of Mexico is Huatulco Bay, whose beaches exhibit a moderate to high microplastic concentration (Retama et al. 2016). Authors reported that microplastics in these beaches are mostly resulting from intensive tourist activities. With respect to the western coast of North America, Desforges et al. (2014) carried out a quantification of microplastics in the Pacific Ocean and coastal British Columbia. The authors found that the highest concentrations were located in Vancouver Island and nearby locations, whereas Pacific offshore waters exhibited less number of particles per m^3 of water.

Hidalgo-Ruz and Thiel (2013) found an extensive contamination of microplastics along the coast of Chile, in South America. This area presents an average contamination of 30 items per m^2, although in some beaches 200 items per m^2 can be reached. The sources of origin are, as in most beaches and coastal areas, the proximity of urban cores and economic activities such as aquaculture. Easter Island has an abundance of microplastics higher than the rest of the Chilean coast. This is due to the transport of particles by ocean currents, a phenomenon that generates an accumulation zone in the center-east of the South Pacific (Abreu and Pedrotti 2019). On the eastern coast of South America, Gomes de Carvalho and Baptista (2016) and Olivatto et al. (2019) determined the contamination caused by microplastics in beaches and surface water, respectively, of Guanabara Bay (Brazil). During the summer, microplastic concentrations at the beaches ranged from 12 to 1300 items per m^2, whereas this concentration decreased in winter. This is caused by the great inputs of water entering the estuary during the rainy season in summer.

In Africa (Fig. 1.15), there is a great lack of data and studies on microplastics in coasts and marine environments, with the exception of South Africa. This country has a wide plastic manufacturing industry, but recycling is limited and insufficient (Verster et al. 2017). Therefore, it has a huge proportion of waste managed improperly entering the environment. Nel and Froneman (2015) carried out a study along the southeastern coastline of South Africa and found that microplastic densities in beach sediments were between 688 and 3308 items per m^2, whereas in the water column ranged from 257 to 1215 items per m^3. Kanhai et al. (2017) estimated the average amount of microplastics in water of the offshore of Namibia and the west coast of Morocco, but contamination was very scarce in comparison to other areas of the world (between 6 and 8 items per m^3).

1.5.2 *Type, Size, and Morphology of Microplastics in Marine Ecosystems*

The main composition of microplastics present in marine environments is based on polyethylene, polypropylene, and polystyrene, as they represent the majority of the plastic waste generated in the world (Plastics Europe 2018). Thus, it is expected that

Fig. 1.15 Abundance of microplastics in sediment and water samples from different marine systems, i.e., beaches, estuaries, or marine water, across Asia. The abundances present in sediments are expressed in items per m^2, while the abundances in water are expressed in items per m^3 (Sources of data: Kanhai et al. (2017), Nel and Froneman (2015). Source of figure: Original production)

these are the most plastic waste generated and, consequently, the main composition of microplastics. However, the vast majority of microplastic fibers are composed by polyamide or polyester, since they come from the synthetic clothing that people use (Cesa et al. 2017). For example, chlorinated polyethylene, polyamide, and polypropylene predominate (76%) in Arctic sediments (Bergmann et al. 2017). Polyester and acrylic fibers are the most abundant polymers in sediments from the North Atlantic, Mediterranean, and southern Indian Ocean (Woodall et al. 2014). Polyethylene and polypropylene are the predominant polymers in the northern Pacific Ocean (Pan et al. 2019).

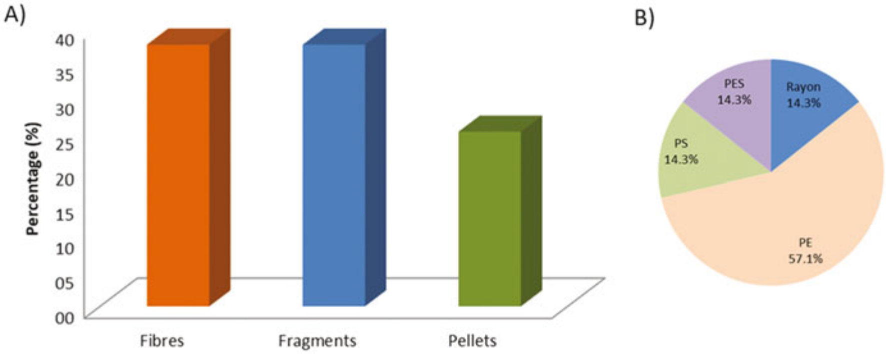


Fig. 1.16 Main shapes and compositions of microplastics from marine ecosystems in Europe. (**a**) Percentage of studies that found fibers, fragments, and pellets as the main shapes among microplastics; (**b**) percentage of studies that found polyethylene (PE), polyether sulfone (PES), polystyrene (PS), and rayon as predominant composition in microplastics (Source: Original production)

These compositional variations reflects not only the wide variety of land and marine sources that can originate microplastics but also the differences in the transport processes caused by the marine currents (Peng et al. 2018), as it is detailed in Sect. 1.4.1. Also important is that PE and PP are polymers with a low relative density, which float in water, unlike polyethylene terephthalate or polyvinyl chloride. This is the main reason why these floating polymers are identified in greater proportion than the others, with higher density. Below are diagrams of the most frequent composition and morphology of microplastics for each continent (Figs. 1.16, 1.17, and 1.18). The data of each diagram are based on information obtained from 10 studies carried out in each continent.

Figure 1.16 represents the most abundant morphologies and composition of microplastics analyzed in seawater and sediments from Europe. Fibers and fragments are the most abundant morphologies, while polyethylene stands out as the main component of these microplastics. Rayon is a semisynthetic fiber used in textile elements and is the most abundant microplastic on the beaches of the Algarve (Portugal) (Frias et al. 2016). On the other hand, granulated pellets come from plastic manufacturing industries. Polyethylene and polypropylene fragments usually come from industrial areas or from the degradation of larger plastic containers (GESAMP 2019). Harbors and vessels have also been identified as sources of fibrous plastic particles (Gewert et al. 2017).

In terms of particle sizes, the smallest detected were 0.06 mm, and the largest were up to 5 mm. Most particles were in the range of 0.1–1 mm, although there are studies that managed larger sizes of 2–5 mm (Martins and Sobral 2011; Turner and Holmes 2011). Increased temperature as a result of prolonged exposure to solar radiation could justify faster disintegration of terrestrial microplastics. Microplastics

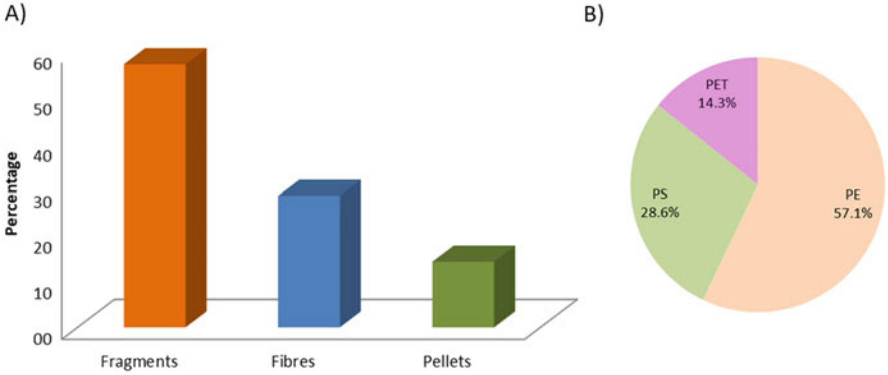


Fig. 1.17 Main shapes and compositions of microplastics from marine ecosystems in Asia. (**a**) Percentage of studies that found fibers, fragments, and pellets as the main shapes among microplastics; (**b**) percentage of studies that found polyethylene (PE), polystyrene (PS), and polyethylene terephthalate (PET) as predominant composition in microplastics (Source: Original production)

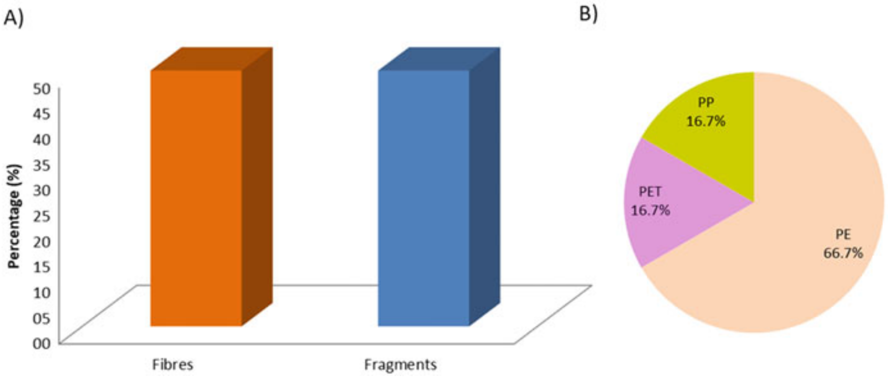


Fig. 1.18 Main shapes and compositions of microplastics from marine ecosystems in North and South America. (**a**) Percentage of studies that found fibers and fragments as the main shapes among microplastics; (**b**) percentage of studies that found polyethylene (PE), polyethylene terephthalate (PET), and polypropylene (PP) as predominant composition in microplastics (Source: Original production)

floating in water do not experience the same temperature increase for the same sun exposure due to the thermoregulatory effect of water. Therefore, size differences between studies can be found (Cooper and Corcoran 2010).

Figure 1.17 shows the main shapes and compositions of microplastics found in waters and coasts along the Asia continent. In contrast to Europe, in Asia fragments are the predominant forms, while polyethylene was once again the most abundant, followed by the polystyrene. At the estuaries of China's main rivers, it is not surprising that the main composition of microplastics is polystyrene, because expanded polystyrene is widely used in cork boxes for the transport of food in southern China and Hong Kong (Fok and Cheung 2015). When this waste is not managed properly, these boxes can be transported to the oceans, seas, and beaches by means of rivers and stormwater drainage systems. The fragments are usually microplastics resulting from the physical-chemical degradation of larger plastics exposed to the action of heat, wind, and waves (Andrady 2015). On the other hand, polyethylene terephthalate is also a fiber very common in textile industry, as polyamide (nylon).

All particle sizes were in the range of 0.1–5 mm. In some areas the smallest microplastics (between 0.5 and 1 mm) were more abundant, as is the case in the northwest Pacific (Pan et al. 2019). In other locations, such as beaches in southern India, larger microplastics between 1.2 and 4.5 mm were more abundant (Karthik et al. 2018). On the other hand, equal abundance of fragments and fibers was found in studies carried out in both North and South America, and the preferred composition is polyethylene, followed by polyethylene terephthalate and polypropylene in equal proportions (Fig. 1.18).

In some areas of North America, the presence of rayon fibers was also detected (Yu et al. 2018), as was the case on the beaches of the Algarve (Portugal). As mentioned above, polyethylene terephthalate is a synthetic fiber widely used in the textile industry. The release of textile fibers into the environment is frequent and abundant, due to the large number of household and industrial washes carried out every day. A standard wash of 5 kg of synthetic clothing can release 6,000,000 fibers into the environment, although it depends on the type of washing machine and detergents used, making it a very difficult source to quantify (De Falco et al. 2018).

Other authors suggested that microplastics in North American waters may also come from fishing, recreational boating, and wastewater effluent (Desforges et al. 2014). On the other hand, in Guanabara Bay, microplastics are mainly fragments, which come from the degradation and breakage of larger plastics on the coast (Gomes de Carvalho and Baptista 2016). Most of the small plastic debris found on beaches from Guanabara Bay possibly come from fishing, rivers, harbor activities, and other local sources. The predominant particle size in these studies is lower than 1 mm, although larger microplastics can be found, especially fragments, with sizes exceeding 2–3 mm (Wessel et al. 2016).

In Africa, the few available studies show a dominance of fibers over other morphologies. The predominant composition in the area of Morocco and Namibia is EPS and PA, probably coming from the detachment of synthetic textile garments (Kanhai et al. 2017).

In sum, the most frequent polymer found in the studies reviewed was polyethylene, which corresponded approximately to 60% of those studies. Polystyrene was the second representative in Europe and Asia, with 14.3% and 28.6%, respectively. It is important to take into account that polypropylene was the second polymer found in almost every reviewed study on every continent. Other components such as rayon or polyether sulfone (PES) were also representative in certain sites such as Portuguese coast, sediments in South Carolina, or coast from Turkey, Greece, Iceland, or France (Lots et al. 2017). These results agreed with the fact that PE, PP, and PS are three polymers very common and account for approximately 90% of the 348 million tons of plastics produced annually (Edo et al. 2019).

1.6 Interactions Among Microplastics and Other Pollutants Presented in Aquatic Environments

Microplastics can adsorb and concentrate a significant number of environmental toxins, which can be transferred to organisms (Mato et al. 2011; Leon et al. 2018). Particles do not only adsorb, but they can also desorb emitting into the environment toxic compounds such as additives or plasticizers, which negatively affect the organisms exposed (Cole et al. 2011; Neves et al. 2015).

There are some environmental factors that affect the balance between chemicals and microplastics as well as accumulation and transport of these pollutants (Murphy et al. 2016). These factors are exposure to sunlight, pH, residence time, and temperature, among others. Between pollutants that microplastics can accumulate, metals are the most studied (Hodson et al. 2017; Brennecke et al. 2016). They are frequently added as catalysts, pigments, and stabilizers during plastic manufacturing (Fahrenfeld et al. 2019; Nakashima et al. 2012). They can also adsorb organic pollutants, especially pharmaceuticals (Li et al. 2018; Llorca et al. 2018). This accumulation of contaminants mainly occurs in freshwater systems, where the concentrations of these chemicals are expected to be higher due to proximity to the sources that produce and discharge them (Horton et al. 2017a, b).

As mentioned above, concentrations of metals in freshwater are generally higher than in coastal areas. These concentrations depend mainly on location, sampling time, and anthropogenic activities (Guo and Wang 2019). Some authors studied the concentration of heavy metals in freshwater from the Beijing River, China (Wang et al. 2017a, b). The average results of this work are shown in Table 1.2.

Table 1.2 Mean concentrations of metals in the microplastics and surface sediments from Beijing River littoral zone

	μg per g (mg element per g sample)	
	Microplastics	Sediments
Nickel	1.326 ± 0.543	0.039 ± 0.012
Cadmium	8.271 ± 5.442	1.146 ± 0.811
Lead	78.975 ± 28.609	41.47 ± 13.007
Copper	258.9 ± 153.654	36.738 ± 23.139
Zinc	8242.525 ± 4020.627	183.863 ± 86.186
Titanium	22841.05 ± 8329.956	20718.913 ± 5836.971

Source: Wang et al. (2017a, b)

The concentrations of cadmium and zinc on microplastic surface get hold of 22841.05 ± 8329.96 μg per g and 8242.52 ± 4020.63 μg per g, respectively.

Organic contaminants such as antibiotics are widespread in aquatic environments. The affinity of these contaminants for microplastics is conditioned in many cases by their polarity and hydrophobicity. The sorption capacities of nonpolar organic contaminants are higher on nonpolar than polar polymers (Hüffer and Hofmann 2016). Some authors synthesized concentrations on freshwater in order to study the adsorption of organic contaminants in microplastics. Some of the published results are shown in Table 1.3.

The sorption capacity of organic compounds on microplastics is high, although the sorption capacities of different antibiotics on a specific type of plastic differed greatly. Sorption of antibiotics studied on microplastics decreased in the following order: ciprofloxacin > amoxicillin > trimethoprim > tetracycline (Li et al. 2018).

Sorption affinities vary depending on the polymer type and the nature of the pollutants. Thus, different types of polymers have different adsorption behaviors for the same pollutant. This could be attributed to the differences in the polarity and the functional groups of each polymer (Guo et al. 2012).

1.6.1 Effects of Microplastics on Freshwater Organisms

There is reasonably extensive evidence related to the harm caused by plastic waste in aquatic ecosystems. This can have a range of negative impacts on infrastructure and fishing. In addition, this could affect a wide range of freshwater organisms as a consequence of entanglement and ingestion. According to Scherer et al. (2017), there are some freshwater species that ingested microplastics with demonstrated effects on them, such as *L. varigatus*, *C. riparius*, *G. pulex*, *Gammarus fossarum*, *P. acuta*, or *D. magna*. Some studies on fish have shown that microplastics and associated toxins are bioaccumulated and cause problems such as intestinal damage and changes in metabolic profiles or are even lethal. Some of these effects on freshwater organisms are presented in Table 1.4.

Table 1.3 Summary of current studies of organic pollutantsorption on microplastics

Types	Organic contaminants	Microplastics	C_0	Sorption capacity	Reference
Polycyclic aromatic hydrocarbons	Phenanthrene	Polyethylene, polystyrene, and polyvinyl chloride (100–150 μm)	10–200 μg per L	303.03–714.29 μg per g	Wang et al. (2018a)
	Phenanthrene	Polypropylene, polyethylene, and polyoxymethylene (2–3 mm)	100 μg per L	–	Karapanagioti and Klontza (2008)
	Pyrene	Polyethylene, polystyrene, and polyvinyl chloride (100–150 μm)	0–100 μg per L	78.7–333 μg per g	Wang et al. (2018a, b)
Polyfluoroalkyl substances	Polyfluoroalkyl substances	High-density polyethylene and polystyrene (10 μm)	1–20 μg per L	34–210 μg per g	Llorca et al. (2018)
Antibiotics	Ciprofloxacin	Polypropylene	50 mg per L	0.615 mg per g	Li et al. (2018)
		Polystyrene		0.416 mg per g	
		Polyvinyl chloride		0.453 mg per g	
		Polyethylene		0.2 mg per g	
		Polyamide		2.2 mg per g	
	Trimethoprim	Polypropylene		0.102 mg per g	
		Polystyrene		0.174 mg per g	
		Polyvinyl chloride		0.481 mg per g	
		Polyethylene		0.154 mg per g	
		Polyamide		0.468 mg per g	
	Amoxicillin	Polypropylene		0.294 mg per g	
		Polyvinyl chloride		0.523 mg per g	
		Polyethylene		0.1131 mg per g	
		Polyamide		22.7 mg per g	
	Tetracycline	Polyamide		3.84 mg per g	

Table 1.4 Effects of microplastic particles on freshwater organisms

Species	Polymer	Parameter	Most significant effects	Reference
Chironomus tepperi	Polyethylene	Mortality	Increase at 1–4, 10–27, and 43–54 μm	Ziajahromi et al. (2018)
		Development	Decrease of body length at 1–4, 10–27, and 43–54 μm	
			Decrease of body parts at 10–27 μm	
			Delay at 10–27 μm	
		Emergence	Decrease of emerging rate	
Gammarus fossarum	Polyamide	Assimilation	Decrease in assimilation efficiency	Blarer and Burkhardt-Holm (2016)
	Polymethylmethacrylate	Development	Decrease in wet weight	Straub et al. (2017)
		Assimilation	Decrease in assimilation efficiency	
	Polyhydroxybutyrate	Development	Decrease	
Gammarus pulex	Polystyrene	Development	Decrease	Redondo-Hasselerharm et al. (2018)
Hyalella azteca	Polyethylene	Mortality	Increase. Dose dependent	Au et al. (2015)
		Reproduction	Decrease	
	Polypropylene	Mortality	Increase. Dose dependent	
		Development	Decrease. Dose dependent	
Thamnocephalus platyrus	Polystyrene	Mortality	Increase (4.03 mg per l)	Booth et al. (2013)
Hyalella azteca	Polyethylene	Mortality	Lethal (217.73 mg per l)	Lenz et al. (2015)
Caernorhabditis elegans	Polyamide	Mortality	Increase (0.5 mg per m^2)	Lei et al. (2018)
		Development	Decrease of body length	
		Reproduction	Decrease of embryo numbers	
		Cellular response	Decrease of calcium concentration	
	Polypropylene	Mortality	Increase (0.5 mg per m^2)	
		Development	Decrease of body length	
		Reproduction	Decrease of embryo numbers	

	Polyethylene	Mortality	Increase (0.5 mg per m^2)	
		Development	Decrease of body length	
		Reproduction	Decrease of embryo numbers. Decrease of brood size	
		Cellular response	Decrease of calcium concentration	
	Polyvinyl chloride	Mortality	Increase (0.5 mg per m^2)	
		Reproduction	Decrease of embryo numbers. Decrease of brood size	
		Cellular response	Decrease of calcium level in intestines	
	Polystyrene	Cellular response	Induction of intestinal reactive oxygen species production and increase in defecation cycle length from up 10 μg per l. Dose dependent	
		Behavior	Decrease of locomotion from up 10 μg per l. Dose dependent	
		Reproduction	Decrease of reproduction from up 1010 μg per l. Dose dependent	
		Development	Transgenerational effects on F1 generation in terms of intestinal ROS production, locomotion, and reproduction form up 100 10 μg per l	
Daphnia magna	Polyethylene	Mortality	Increase (57.43 mg per l)	Raimondo et al. (2007)
	Polystyrene	Mortality	Increase (0.66 mg per l)	Booth et al. (2013)
Brachionus koreanus	Polystyrene	Reproduction	Increase of reproduction time for 0.05 μm at 10 μg per ml	Jeong et al. (2016)
			Decrease of fecundity at 0.5 μm	
		Life span	Life span affected for 0.05 and 0.5 μm	
		Cellular response	Increase in reactive oxygen species level. Increase in phosphorylation status of p-JNK and p-p38 at 0.05 μm	

Sources: Connors et al. (2017), Scherer et al. (2017), Haegerbaeumer et al. (2019)

References

Abreu A, Pedrotti ML (2019) Microplastics in the oceans: the solutions lie on land. Field Actions Sci Rep [Online], Special Issue 19

Alomar C, Estarellas F, Deudero S (2016) Microplastics in the Mediterranean Sea: deposition in coastal shallow sediments, spatial variation and preferential grain size. Mar Environ Res 115:1–10. https://doi.org/10.1016/j.marenvres.2016.01.005

Anderson PJ, Park BJ, Palace VP (2016) Microplastics in aquatic environments: implications for Canadian ecosystems. Environ Pollut 218:269–280. https://doi.org/10.1016/j.envpol.2016.06.074

Anderson PJ, Warrack S, Langen V (2017) Microplastic contamination in Lake Winnipeg, Canada. Environ Pollut 225:223–231. https://doi.org/10.1016/j.envpol.2017.02.072

Andrady AL (2011) Microplastics in the marine environment. Mar Pollut Bull 62(8):1596–1605. https://doi.org/10.1016/j.marpolbul.2011.05.030

Andrady AL (2015) Persistence of plastic litter in the oceans. In: Bergmann M et al (eds) Marine anthropogenic litter. Springer Open, Berlin, pp 57–72. https://doi.org/10.1007/978-3-319-16510-3_3

Araujo CJ, Nolasco MM, Ribeiro AMP, Ribeiro-Claro PJA (2018) Identification of microplastics using Raman spectroscopy: latest developments and future prospects. Water Res 142:426–440. https://doi.org/10.1016/j.watres.2018.05.060

Au Y, Bruce TF, Bridges WC, Klaine SJ (2015) Responses of Hyalella azteca to acute and chronic microplastic exposures. Environ Toxicol Chem 34:2564–2572. https://doi.org/10.1002/etc.3093

Auta HS, Emenike CU, Fauziah SH (2017) Distribution and importance of microplastics in the marine environment: a review of the sources, fate, effects, and potential solutions. Environ Int 102:165–176. https://doi.org/10.1016/j.envint.2017.02.013

Bakir A, Rowland S, Thompson C (2014) Transport of persistent organic pollutants by microplastics in estuarine conditions. Estuar Coast Shelf Sci 140:14–21. https://doi.org/10.1016/j.ecss.2014.01.004

Ballent A, Corcoran PL, Madden O (2016) Sources and sinks of microplastics in Canadian lake Ontario nearshore, tributary and beach sediments. Mar Pollut Bull 110(1):383–395. https://doi.org/10.1016/j.marpolbul.2016.06.037

Bergmann M, Wirzberger V, Krumpen T, Lorenz C et al (2017) High quantities of microplastic in Arctic deep-sea sediments from the Hausgarten Observatory. Environ Sci Technol 51 (19):11000–11010. https://doi.org/10.1021/acs.est.7b03331

Besseling E, Quik JT, Sun M (2017) Fate of nano-and microplastic in freshwater systems: a modeling study. Environ Pollut 220:540–548. https://doi.org/10.1016/j.envpol.2016.10.001

Blarer P, Burkhardt-Holm P (2016) Microplastics affect assimilation efficiency in the freshwater amphipod Gammarus fossarum. Environ Sci Pollut Res 23:23522–23532. https://doi.org/10.1007/s11356-016-7584-2

Blumenröder J, Sechet P, Kakkonen JE et al (2017) Microplastic contamination of intertidal sediments of Scapa Flow, Orkney: a first assessment. Mar Pollut Bull 124:112–120. https://doi.org/10.1016/j.marpolbul.2017.07.009

Booth AM, Justynska J, Kubowicz S, Johnsen H, Frenzel M (2013) Influence of salinity, dissolved organic carbon and particle chemistry on the aggregation behaviour of methacrylate-based polymeric nanoparticles in aqueous environments. Int J Environ Pollut 52:15–31. https://doi.org/10.1504/IJEP.2013.056358

Botterell ZLR, Beaumont N, Dorrington T, Steinke M, Thompson RC, Lindeque PK (2019) Bioavailability and effects of microplastics on marine zooplankton: a review. Environ Pollut 245:98–110. https://doi.org/10.1016/j.envpol.2018.10.065

Bouwmeester H, Hollman PCH, Peters RJB (2015) Potential health impact of environmentally released micro- and nanoplastics in the human food production chain: experiences from nanotoxicology. Environ Sci Technol 49:8932–8947. https://doi.org/10.1021/acs.est.5b01090

Brennecke D, Duarte B, Paiva F, Caçador I, Canning-Clode J (2016) Microplastics as vector for heavy metal contamination from the marine environment. Estuar Coast Shelf Sci 178:189–195. https://doi.org/10.1016/j.ecss.2015.12.003

Browne MA, Crump P, Niven SJ et al (2011) Accumulation of microplastic on shorelines worldwide: sources and sinks. Environ Sci Technol 45:9175–9179. https://doi.org/10.1021/es201811s

Carpenter EJ, Smith KL (1972) Plastics on the Sargasso sea surface. Science 175 (4027):1240–1241. https://doi.org/10.1126/science.175.4027.1240

Castañeda RA, Avlijas S, Simard MA (2014) Microplastic pollution in St. Lawrence river sediments. Can J Fish Aquat Sci 71:1767–1771. https://doi.org/10.1139/cjfas-2014-0281

Catarino AI, Thompson R, Sanderson W, Henry TB (2017) Development and optimization of a standard method for extraction of microplastics in mussels by enzyme digestion of soft tissues. Environ Toxicol Chem 36:947–951. https://doi.org/10.1002/etc.3608

Cesa FS, Turra A, Baruque-Ramos J (2017) Synthetic fibers as microplastics in the marine environment: a review from textile perspective with a focus on domestic washings. Sci Total Environ 598:1116–1129. https://doi.org/10.1016/j.scitotenv.2017.04.172

Chen M, Jin M, Tao P, Wang Z et al (2018) Assessment of microplastics derived from mariculture in Xiangshan Bay, China. Environ Pollut 242:1146–1156. https://doi.org/10.1016/j.envpol.2018.07.133

Cincinelli A, Martellini T, Guerranti C, Scopetani C et al (2019) A potpourri of microplastics in the sea surface and water column of the Mediterranean Sea. TrAC 110:321–326. https://doi.org/10.1016/j.trac.2018.10.026

Claessens M, Meester SD, Landuyt LV, Clerck KD, Janssen CR (2011) Occurrence and distribution of microplastics in marine sediments along the Belgian coast. Mar Pollut Bull 62:2199–2204. https://doi.org/10.1016/j.marpolbul.2011.06.030

Claessens M, Van Cauwenberghe L, Vandegehuchte LB, Janssen CR (2013) New techniques for the detection of microplastics in sediments and field collected organisms. Mar Pollut Bull 70 (1–2):227–233. https://doi.org/10.1016/j.marpolbul.2013.03.009

Cole M, Lindeque P, Halsband C, Galloway TS (2011) Microplastics as contaminants in the marine environment: a review. Mar Pollut Bull 62:2588–2597. https://doi.org/10.1016/j.marpolbul.2011.09.025

Cole M, Lindeque P, Fileman E, Halsband C, Goodhead R, Moger J, Galloway TS (2013) Microplastic ingestion by zooplankton. Environ Sci Technol 47:6646–6655. https://doi.org/10.1021/es400663f

Cole M, Webb H, Lindeque PK, Fileman ES, Halsband C, Galloway TS (2014) Isolation of microplastics in biota-rich seawater samples and marine organisms. Sci Rep 4:4528–4535. https://doi.org/10.1038/srep04528

Connors KA, Dyer SD, Belanger SE (2017) Advancing the quality of environmental microplastic research. Environ Toxicol Chem 36(7):1697–1703. https://doi.org/10.1002/etc.3829

Cooper DA, Corcoran PL (2010) Effects of mechanical and chemical processes on the degradation of plastic beach debris on the island of Kauai, Hawaii. Mar Pollut Bull 60(5):650–654. https://doi.org/10.1016/j.marpolbul.2009.12.026

Corcoran PL, Biesinger MC, Grifi M (2009) Plastics and beaches: a degrading relationship. Mar Pollut Bull 58:1363–1369. https://doi.org/10.1016/j.marpolbul.2008.08.022

Corcoran PL, Norris T, Ceccanese T et al (2015) Hidden plastics of Lake Ontario, Canada and their potential preservation in the sediment record. Environ Pollut 204:17–25. https://doi.org/10.1016/j.envpol.2015.04.009

Cózar A, Sanz-Martín M, Martí E et al (2015) Plastic accumulation in the Mediterranean Sea. PLoS One 10:e0121762. https://doi.org/10.1371/journal.pone.0121762

Crawford CB, Quinn B (2017) Microplastic collection techniques. In: Microplastic pollutants. Elsevier, Amsterdam, pp 179–202. https://doi.org/10.1016/B978-0-12-809406-8.00008-6

Davidson K, Dudas SE (2016) Microplastic ingestion by wild and cultured manila clams (Venerupis philippinarum) from Baynes Sound, British Columbia. Arch Environ Contam Toxicol 71(2):147–156. https://doi.org/10.1007/s00244-016-0286-4

De Falco F, Gullo MP, Gentile G, Di Pace E et al (2018) Evaluation of microplastic release caused by textile washing processes of synthetic fabrics. Environ Pollut 236:916–925. https://doi.org/10.1016/j.envpol.2017.10.057

De Sá LC, Oliveira M, Ribeiro F, Rocha TL, Futter MN (2018) Studies of the effects of microplastics on aquatic organisms: what do we know and where should we focus our efforts in the future? Science of the Total Environment Elsevier BV. https://doi.org/10.1016/j.scitotenv.2018.07.207

Dehaut A, Cassone AL, Frère L, Paul-Pont I (2016) Microplastics in seafood: benchmark protocol for their extraction and characterization. Environ Pollut 215:223–233. https://doi.org/10.1016/j.envpol.2016.05.018

Dekiff JH, Remy D, Klasmeier J, Fries E (2014) Occurrence and spatial distribution of microplastics in sediments from Norderney. Environ Pollut 186:248–256. https://doi.org/10.1016/j.envpol.2013.11.019

Desforges JPW, Galbraith M, Dangerfield N et al (2014) Widespread distribution of microplastics in subsurface seawater in the NE Pacific Ocean. Mar Pollut Bull 79:94–99. https://doi.org/10.1016/j.marpolbul.2013.12.035

Di M, Wang J (2018) Microplastics in surface waters and sediments of the three gorges reservoir, China. Sci Total Environ 616-617:1620–1627. https://doi.org/10.1016/j.scitotenv.2017.10.150

Ding L, Mao RF, Guo X, Yang X, Zhang Q, Yang C (2019) Microplastics in surface waters and sediments of the Wei River, in the northwest of China. Sci Total Environ 667:427–434. https://doi.org/10.1016/j.scitotenv.2019.02.332

Duis K, Coors A (2016) Microplastics in the aquatic and terrestrial environment: sources (with a specific focus on personal care products), fate and effects. Environ Sci Eur 28(1):1–25. https://doi.org/10.1186/s12302-015-0069-y

Edo C, Tamayo-Belda M, Martínez-Campos S, Martín-Betancor K et al (2019) Occurrence and identification of microplastics along a beach in the Biosphere Reserve of Lanzarote. Mar Pollut Bull 143:220–227. https://doi.org/10.1016/j.marpolbul.2019.04.061

Egbeocha CO, Malek S, Emenike CU, Milow P (2018) Feasting on microplastics: ingestion by and effects on marine organisms. Aquat Biol 27:93–106. https://doi.org/10.3354/ab00701

Eriksen M, Mason S, Wilson S et al (2013) Microplastic pollution in the surface waters of the Laurentian Great Lakes. Mar Pollut Bull 77:177–182. https://doi.org/10.1016/j.marpolbul.2013.10.007

Eriksen M, Lebreton LCM, Carson HS, Thiel M et al (2014) Plastic pollution in the World's oceans: more than 5 trillion plastic pieces weighing over 250,000 tons afloat at sea. PLoS One 9(12):111913. https://doi.org/10.1371/journal.pone.0111913

Fahrenfeld NL, Arbuckle-Keil G, Beni NN, Shannon L, Bartelt-Hunt (2019) Source tracking microplastics in the freshwater environment. TrAC 112:248–254. https://doi.org/10.1016/j.trac.2018.11.030

Fastelli P, Blašković A, Bernardi G et al (2016) Plastic litter in sediments from a marine area likely to become protected (Aeolian Archipelago's islands, Tyrrhenian sea). Mar Pollut Bull 113:526–529. https://doi.org/10.1016/j.marpolbul.2016.08.054

Fischer EK, Paglialonga L, Czech E et al (2016) Microplastic pollution in lakes and lake shoreline sediments – a case study on Lake Bolsena and Lake Chiusi (central Italy). Environ Pollut 213:648–657. https://doi.org/10.1016/j.envpol.2016.03.012

Fok L, Cheung PK (2015) Hong Kong at the Pearl River Estuary: a hotspot of microplastic pollution. Mar Pollut Bull 99:112–118. https://doi.org/10.1016/j.marpolbul.2015.07.050

Fossi MC, Panti C, Guerranti C, Coppola D et al (2012) Are baleen whales exposed to the threat of microplastics? a case study of the Mediterranean fin whale (Balaenoptera physalus). Mar Pollut Bull 64:2374–2379. https://doi.org/10.1016/j.marpolbul.2012.08.013

Fries E, Dekiff JH, Willmeyer J, Nuelle MT, Ebert M, Remy D (2013) Identification of polymer types and additives in marine microplastic particles using pyrolysis-GC/MS and marine scanning electron microscopy. Environ Sci Process Impacts 15:1949–1956

Free CM, Jensen OP, Mason SA et al (2014) High levels of microplastic pollution in a large, remote, mountain lake. Mar Pollut Bull 85:156–163. https://doi.org/10.1016/j.marpolbul.2014.06.001

Frias JP, Sobral P, Ferreira AM (2010) Organic pollutants in microplastics from two beaches of the Portuguese coast. Mar Pollut Bull 60(11):1988–1992. https://doi.org/10.1016/j.marpolbul.2010.07.030

Frias JP, Gago J, Otero V et al (2016) Microplastics in coastal sediments from Southern Portuguese shelf waters. Mar Environ Res 114:24–30. https://doi.org/10.1016/j.marenvres.2015.12.006

Fries E, Dekiff JH, Willmeyer J, Nuelle MT, Ebert M, Remy D (2013) Identification of polymer types and additives in marine microplastic particles using pyrolysis-GC/MS and marine scanning electron microscopy. Environ Sci Process Impacts 15:1949–1956. https://doi.org/10.1039/c3em00214d

Gallagher A, Rees A, Rowe R et al (2016) Microplastics in the Solent estuarine complex, UK: an initial assessment. Mar Pollut Bull 102:243–249. https://doi.org/10.1016/j.marpolbul.2015.04.002

Gallo F, Fossi C, Weber R, Santillo D, Sousa J, Ingram I, Nadal A, Romano D (2018) Marine litter plastics and microplastics and their toxic chemicals components: the need for urgent preventive measures. Environ Sci Eur 30(13):13. https://doi.org/10.1186/s12302-018-0139-z

GESAMP (2019) In: Kershaw PJ, Turra A, Galgani F (eds) Guidelines or the monitoring and assessment of plastic litter and microplastics in the ocean, Rep. Stud. GESAMP No. 99. GESAMP, London, 130p

Gewert B, Ogonowskia M, Barth A, MacLeoda M (2017) Abundance and composition of near surface microplastics and plastic debris in the Stockholm Archipelago, Baltic Sea. Mar Pollut Bull 120:292–302. https://doi.org/10.1016/j.marpolbul.2017.04.062

Gomes de Carvalho D, Baptista JA (2016) Microplastic pollution of the beaches of Guanabara Bay, Southeast Brazil. Ocean Coast Manage 128:10–17. https://doi.org/10.1016/j.ocecoaman.2016.04.009

Godoy V, Blázquez G, Calero M, Quesada L, Martín-Lara MA (2019) The potential of microplastics as carriers of metals. Environ Pollut 255. https://doi.org/10.1016/j.envpol.2019.113363

Guo X, Wang J (2019) The chemical behaviors of microplastics in marine environment: a review. Mar Pollut Bull 142:1–14. https://doi.org/10.1016/j.marpolbul.2019.03.019

Guo X, Wang X, Zhou X, Kong X, Tao S, Xing B (2012) Sorption of four hydrophobic organic compounds by three chemically distinct polymers: role of chemical and physical composition. Environ Sci Technol 46:7252–7259. https://doi.org/10.1021/es301386z

Haegerbaeumer A, Mueller MT, Fueser H, Traunspurger W (2019) Impacts of micro- and nano-sized plastic particles on benthic invertebrates: a literature review and gap analysis. Front Eviron Sci 7:17. https://doi.org/10.3389/fenvs.2019.00017

Hamid FS, Bhatti MS, Anuar N, Mohan P, Periathamby A (2018) Worldwide distribution and abundance of microplastic: how dire is the situation? WM&R 36(10):873–897. https://doi.org/10.1177/0734242X18785730

Hanvey JS, Lewis PJ, Jennifer Lavers L, Nicholas Crosbie D, Pozode K, Clarke BO (2017) A review of analytical techniques for quantifying microplastics in sediments. Anal Methods 9:1369–1383

Harrison JP, Ojeda JJ, Romero-González ME (2012) The applicability of reflectance micro-Fourier-transform infrared spectroscopy for the detection of synthetic microplastics in marine sediments. Sci Total Environ 416:455–463. https://doi.org/10.1016/j.scitotenv.2011.11.078

Heo NK, Hong SH, Han GM et al (2013) Distribution of small plastic debris in cross-section and high strandline on Heungnam Beach, South Korea. Ocean Sci 48:225–233. https://doi.org/10.1007/s12601-013-0019-9

Herrera A, Asensio M, Martínez I et al (2018) Microplastic and tar pollution on three Canary Islands beaches: an annual study. Mar Pollut Bull 129:494–502. https://doi.org/10.1016/j.marpolbul.2017.10.020

Hidalgo-Ruz V, Theil M (2013) Distribution and abundance of small plastic debris on beaches in the SE Pacific (Chile): a study supported by a citizen science project. Mar Environ Research 87-88:12–18. https://doi.org/10.1016/j.marenvres.2013.02.015

Hidalgo-Ruz V, Gutow L, Thompson RC, Thiel M (2012) Microplastics in the marine environment: a review of the methods used for identification and quantification. Environ Sci Technol 46:3060–3075. https://doi.org/10.1021/es2031505

Hodson ME, Duffus-Hodson CA, Clark A, Prendergast-Miller MT, Thorpe KL (2017) Plastic bag derived-microplastics as a vector for metal exposure in terrestrial invertebrates. Environ Sci Technol 51:4714–4721. https://doi.org/10.1021/acs.est.7b00635

Horton AA, Svendsen C, Williams RJ et al (2017a) Large microplastic particles in sediments of tributaries of the River Thames, UK – abundance, sources and methods for effective quantification. Mar Poll Bull 114:218–226. https://doi.org/10.1016/j.marpolbul.2016.09.004

Horton AA, Walton A, Spurgeon DJ, Lahive E, Svendsen C (2017b) Microplastics in freshwater and terrestrial environments: evaluating the current understanding to identify the knowledge gaps and future research priorities. Sci Total Environ 586:127–141. https://doi.org/10.1016/j.scitotenv.2017.01.190

Hüffer T, Hofmann T (2016) Sorption of non-polar organic compounds by micro-sized plastic particles in aqueous solution. Environ Pollut 214:194–201. https://doi.org/10.1016/j.envpol.2016.04.018

Imhof H, Schmid J, Niessner R, Ivleva NP, Laforsch C (2012) A novel, highly efficient method for the separation and quantification of plastic particles in sediments of aquatic environments. Limnol Oceanogr Methods 10:524–537. https://doi.org/10.4319/lom.2012.10.524

Imhof HK, Ivleva NP, Schmid J, Niessner R, Laforsch C (2013) Contamination of beach sediments of a subalpine lake with microplastic particles. Curr Biol 23:867–868. https://doi.org/10.1016/j.cub.2013.09.001

Imhof HK, Laforsch C, Wiesheu AC, Schmid J, Anger PM, Niessner R et al (2016) Pigments and plastic in limnetic ecosystems: a qualitative and quantitative study on microparticles of different size classes. Water Res 98:64–74. https://doi.org/10.1016/j.watres.2016.03.015

Imhof HK, Sigl R, Brauer E et al (2017) Spatial and temporal variation of macro-, meso- and microplastic abundance on a remote coral island of the Maldives, Indian Ocean. Mar Pollut Bull 116:340–347. https://doi.org/10.1016/j.marpolbul.2017.01.010

Isobe A, Uchida K, Tokai T et al (2015) East Asian seas: a hot spot for pelagic microplastics. Mar Pollut Bull 101:618–623. https://doi.org/10.1016/j.marpolbul.2015.10.042

Jeong CB, Won EJ, Kang HM, Lee MC, Hwang DS, Hwang UK et al (2016) Microplastic size-dependent toxicity, oxidative stress induction, and p-JNK and p-p38. Activation in the Monogonont Rotifer (Brachionus koreanus). Environ Sci Technol 50:8849–8857. https://doi.org/10.1021/acs.est.6b01441

Kane IA, Clare MA (2019) Dispersion, accumulation, and the ultimate fate of microplastics in deep-marine environments: a review and future directions. Front Earth Sci 7:80. https://doi.org/10.3389/feart.2019.00080

Kang JH, Kwon OY, Lee KW et al (2015) Marine neustonic microplastics around the southeastern coast of Korea. Mar Pollut Bull 96:304–312. https://doi.org/10.1016/j.marpolbul.2015.04.054

Kanhai LDK, Officer R, Lyashevska O et al (2017) Microplastic abundance, distribution and composition along a latitudinal gradient in the Atlantic Ocean. Mar Pollut Bull 115:307–314. https://doi.org/10.1016/j.marpolbul.2016.12.025

Kanhai LDK, Gårdfeldt K, Lyashevska O, Hassellöv M, Thompson RC, O'Connor I (2018) Microplastics in sub-surface waters of the Arctic Central Basin. Mar Pollut Bull 130:8–18. https://doi.org/10.1016/j.marpolbul.2018.03.011

Karapanagioti HK, Klontza I (2008) Testing phenanthrene distribution properties of virginplastic pellets and plastic eroded pellets found on Lesvos island beaches (Greece). Mar Environ Res 65 (4):283–290. https://doi.org/10.1016/j.marenvres.2007.11.005

Karlsson TM, Arneborgb L, Broströmc G, Carney B, Gipperthe L, Hassellöva M (2018) The unaccountability case of plastic pellet pollution. Mar Pollut Bull 129:52–60. https://doi.org/10.1016/j.marpolbul.2018.01.041

Karthik R, Robin RS, Purvaja R, Ganguly D et al (2018) Microplastics along the beaches of southeast coast of India. Sci Total Environ 645:1388–1399. https://doi.org/10.1016/j.scitotenv.2018.07.242

Kim IS, Chae DH, Kim SK et al (2015) Factors influencing the spatial variation of microplastics on high-tidal coastal beaches in Korea. Arch Environ Contam Toxicol 69:299–309. https://doi.org/10.1007/s00244-015-0155-6

Kole PJ, Löhr AJ, Van Belleghem FA (2017) RagasWear and tear of tyres: a stealthy source of microplastics in the environment. Int J Environ Res Public Health 14(10):1265. https://doi.org/10.3390/ijerph14101265

Koelmans AA, Mohamed Nor NH, Hermsen E, Kooi M, Svenja M, De France M, J. (2019) Microplastics in freshwaters and drinking water: critical review and assessment of data quality. Water Res 155:410–422. https://doi.org/10.1016/j.watres.2019.02.054

Lechner A, Keckeis H, Lumesberger-Loisl F et al (2014) The Danube so colourful: a potpourri of plastic litter outnumbers fish larvae in Europe's second largest river. Environ Pollut 188:177–181. https://doi.org/10.1016/j.envpol.2014.02.006

Lee J, Hong S, Song YK et al (2013) Relationships among the abundances of plastic debris in different size classes on beaches in South Korea. Mar Pollut Bull 77:349–354. https://doi.org/10.1016/j.marpolbul.2013.08.013

Lei L, Wu S, Lu S, Liu M, Song Y, Fu Z et al (2018) Microplastic particles cause intestinal damage and other adverse effects in zebrafish Danio rerio and nematode Caenorhabditis elegans. Sci Total Environ 619–620:1–8. https://doi.org/10.1016/j.scitotenv.2017.11.103

Lenz R, Enders K, Stedmon CA, Mackenzie DMA, Nielsen TG (2015) A critical assessment of visual identification of marine microplastic using Raman spectroscopy for analysis improvement. Mar Pollut Bull 100:82–91. https://doi.org/10.1016/j.marpolbul.2015.09.026

Leon VM, Garcia I, Gonzalez E, Samper R, Fernandez-Gonzalez V, Muniategui-Lorenzo S (2018) Potential transfer of organic pollutants from littoral plastics debris to the marine environment. Environ Pollut 236:442–453. https://doi.org/10.1016/j.envpol.2018.01.114

Leslie HA, Brandsma SH, Van Velzen MJM et al (2017) Microplastics en route: field measurements in the Dutch river delta and Amsterdam canals, wastewater treatment plants, North Sea sediments and biota. Environ Int 101:133–142. https://doi.org/10.1016/j.envint.2017.01.018

Li WC, Tse HF, Fok L (2016) Plastic waste in the marine environment: a review of sources, occurrence and effects. Sci Total Environ 566–567:333–349. https://doi.org/10.1016/j.scitotenv.2016.05.084

Li J, Zhang K, Zhang H (2018) Adsorption of antibiotics on microplastics. Environ Pollut 237:460–467. https://doi.org/10.1016/j.envpol.2018.02.050

Liebezeit G, Dubaish F (2012) Microplastics in beaches of the East Frisian islands Spiekeroog and Kachelotplate. Bull Environ Contam Toxicol 89:213–217. https://doi.org/10.1007/s00128-012-0642-7

Llorca M, Schirinzi G, Martínez M, Barceló D, Farré M (2018) Adsorption of perfluoroalkyl substances on microplastics under environmental conditions. Environ Pollut 235:680–691. https://doi.org/10.1016/j.envpol.2017.12.075

Löder MGJ, Gunnar G (2015) Methodology used for the detection and identification of microplastics – a critical appraisal. In: Bergmann M et al (eds) Marine anthropogenic litter. Springer Open, Heidelbderg, pp 201–227. https://doi.org/10.1007/978-3-319-16510-3_8

Lots FA, Behrens P, Vijver MG et al (2017) A large-scale investigation of microplastic contamination: abundance and characteristics of microplastics in European beach sediment. Mar Pollut Bull 123:219–226. https://doi.org/10.1016/j.marpolbul.2017.08.057

Lusher A (2015) Microplastics in the marine environment: distribution, interactions and effects. In: Bergmann M et al (eds) Marine anthropogenic litter. Springer Open, Heidelbderg, pp 245–307. https://doi.org/10.1007/978-3-319-16510-3_10

Lusher AL, McHugh M, Thompson RC (2013) Occurrence of microplastics in the gastrointestinal tract of pelagic and demersal fish from the English Channel. Mar Pollut Bull 67(1–2):94–99. https://doi.org/10.1016/j.marpolbul.2012.11.028

Maes T, Jessop R, Wellner N, Haupt K, Mayes AG (2017) A rapid-screening approach to detect and quantify microplastics based on fluorescent tagging with Nile Red. Nat Sci Rep 7:44501. https://doi.org/10.1038/srep44501

Magnusson K, Noren F (2014) Screening of microplastic particles in and downstream a wastewater treatment plant. IVL Swedish Environmental Research Institute report. http://naturvardsverket.diva-portal.org/smash/record.jsf?pid=diva2%3A773505&dswid=325

Mani T, Hauk A, Walter U et al (2015) Microplastics profile along the Rhine River. Sci Rep 5:17988. https://doi.org/10.1038/srep17988

Martins J, Sobral P (2011) Plastic marine debris on the Portuguese coastline: a matter of size? Mar Pollut Bull 62:2649–2653. https://doi.org/10.1016/j.marpolbul.2011.09.028

Masura J, Baker J, Foster G, Arthur C (2015) Laboratory methods for the analysis of microplastics in the marine environment: recommendations for quantifying synthetic particles in waters and sediments, NOAA Technical Memorandum NOS-OR&R-48. NOAA Marine Debris, Silver Spring

Mason SA, Welch VG, Neratko J (2018) Synthetic polymer contamination in bottled water. Front Chem 6:407. https://doi.org/10.3389/fchem.2018.00407

Mato Y, Isobe T, Takada H, Kanehiro H, Ohtake C, Kaminuma T (2011) Plastic resin pellets as a transport medium for toxic chemicals in the marine environment. Environ Sci Technol 35:318–324. https://doi.org/10.1021/es0010498

McCormick A, Hoellein TJ, Mason SA et al (2014) Microplastic is an abundant and distinct microbial habitat in an urban river. Environ Sci Technol 48:11863–11871. https://doi.org/10.1021/es503610r

McDermid KJ, McMullen TL (2004) Quantitative analysis of small-plastic debris on beaches in the Hawaiian Archipelago. Mar Pollut Bull 48(7–8):790–794. https://doi.org/10.1016/j.marpolbul.2003.10.017

Moore CJ (2008) Synthetic polymers in the marine environment: a rapidly increasing, long-term threat. Environ Res 108(2):131–139. https://doi.org/10.1016/j.envres.2008.07.025

Moore CJ, Lattin GL, Zellers AF (2011) Quantity and type of plastic debris flowing from two urban rivers to coastal waters and beaches of Southern California. Revista de Gestão Costeira Integrada JICZM 11:65–73. https://doi.org/10.5894/rgci194

Morris RJ (1980) Floating plastic debris in the Mediterranean. Mar Pollut Bull 11(5):125. https://doi.org/10.1016/0025-326X(80)90073-9

Murphy F, Ewins C, Carbonnier F, Quinn B (2016) Wastewater treatment works (WwTW) as a source of microplastics in the aquatic environment. Environ Sci Technol 50:5800–5808. https://doi.org/10.1021/acs.est.5b05416

Murray F, Cowie PR (2011) Plastic contamination in the decapod crustacean Nephrops norvegicus (Linnaeus, 1758). Mar Pollut Bull 62(6):1207–1217. https://doi.org/10.1016/j.marpolbul.2011.03.032

Naji A, Esmaili Z, Khan FR (2017) Plastic debris and microplastics along the beaches of the Strait of Hormuz, Persian Gulf. Mar Pollut Bull 114:1057–1062. https://doi.org/10.1016/j.marpolbul.2016.11.032

Nakashima E, Isobe A, Kako SI, Itai T, Takahashi S (2012) Quantification of toxic metals derived from macroplastic litter on Ookushi Beach, Japan. Environ Sci Technol 46:10099–10105. https://doi.org/10.1021/es301362g

Navarro-Pérez E, Barton ED (2001) Seasonal and interannual variability of the Canary Current. Sci Mar 65(Suppl. 1):205–213. https://doi.org/10.3989/scimar.2001.65s1205

Nel HA, Froneman PW (2015) A quantitative analysis of microplastic pollution along the South-Eastern coastline of South Africa. Mar Pollut Bull 101:274–275. https://doi.org/10.1016/j.marpolbul.2015.09.043

Nel HA, Dalu T, Wasserman RJ (2018) Sinks and sources: assessing microplastic abundance in river sediment and deposit feeders in an austral temperate urban river system. Sci Total Environ 612:950–956. https://doi.org/10.1016/j.scitotenv.2017.08.298

Nel HA, Dalu T, Wasserman RJ (2018) Sinks and sources: assessing microplastic abundance in river sediment and deposit feeders in an austral temperate urban river system. Sci Total Environ 612:950–956. https://doi.org/10.1016/j.scitotenv.2017.08.298

Nelms SE, Barnett J, Brownlow A, Davison NJ, Deaville R, Galloway TS, Lindeque PK, Santillo D, Godley BJ (2019) Microplastics in marine mammals stranded around the British coast: ubiquitous but transitory? Sci Rep 9:1–8. https://doi.org/10.1038/s41598-018-37428-3

Napper, Bakir IE, Rowland A, Thompson SJ, Characterisation RC (2015) Quantity and sorptive properties of microplastics extracted from cosmetics. Marine Pollution Bulletin, Volume 99, Issues 1–2, 15 October. https://doi.org/10.1016/j.marpolbul.2015.07.029

Neves D, Sobral P, Ferreira JL, Pereira T (2015) Ingestion of microplastics by commercial fish off the Portuguese coast. Mar Pollut Bull 101:119–126. https://doi.org/10.1016/j.marpolbul.2015.11.008

Ng KL, Obbard JP (2006) Prevalence of microplastics in Singapore's coastal marine environment. Mar Pollut Bull 52(7):761–767. https://doi.org/10.1016/j.marpolbul.2005.11.017

Norén F (2007) Small plastic particles in coastal Swedish waters. N-research report. KIMO, Sweden, p 11

Novotna K, Cermakova L, Pivokonska L, Cajthaml T, Pivokonsky M (2019) Microplastics in drinking water treatment – current knowledge and research needs. Sci Total Environ 667:730–740

Nuelle MT, Dekiff JH, Remy D, Fries E (2014) A new analytical approach for monitoring microplastics in marine sediments. Environ Pollut 184:161–169. https://doi.org/10.1016/j.envpol.2013.07.027

Obbard RW, Sadri S, Wong Y, Khitun AA, Baker I, Thompson RC (2014) Global warming releases microplastic legacy frozen in Arctic Sea ice. Earth's Future 2:315–320. https://doi.org/10.1002/2014EF000240

Oßmann BE, Sarau G, Holtmannspotter H, Pischetsrieder M, Christiansen SH, DickeSmall-sized W (2018) DickeSmall-sized microplastics and pigmented particles in bottled mineral water Water Res 141:307–316

Olivatto CA, Martinsa MC, Montagner C, Henry TB, Carreira R (2019) Microplastic contamination in surface waters in Guanabara Bay, Rio de Janeiro, Brazil. Mar Pollut Bull 139:157–162. https://doi.org/10.1016/j.marpolbul.2018.12.042

Pan Z, Guo H, Chen H, Wang S et al (2019) Microplastics in the Northwestern Pacific: abundance, distribution, and characteristics. Sci Total Environ 650:1913–1922. https://doi.org/10.1016/j.scitotenv.2018.09.244

Peng G, Xu P, Zhu B et al (2018) Microplastics in freshwater river sediments in Shanghai, China: a case study of risk assessment in mega-cities. Environ Pollut 234:448–456. https://doi.org/10.1016/j.envpol.2017.11.034

Piperagkas O, Papageorgiou N, Karakassis I (2018) Qualitative and quantitative assessment of microplastics in three sandy Mediterranean beaches, including different methodological approaches. Estuar Coast Shelf Sci 219:169–175. https://doi.org/10.1016/j.ecss.2019.02.016

Pivokonsky M, Cermakova L, Novotna K, Peer P, Cajthaml T, Janda V (2018) Occurrence of microplastics in raw and treated drinking water. Sci Total Environ 643:1644–1651

Plastics Europe (2017) An analysis of European plastics production, demand and waste data. Plastics – the Facts 2017. Plastics Europe, Brussels

Plastics Europe (2018) An analysis of European plastics production, demand and waste data. Plastics – the facts 2018

Prata JC, Da Costa J, Duarte AC, Rocha-Santos T (2019) Methods for sampling and detection of microplastics in water and sediment: a critical review. TrAC 110:150–159. https://doi.org/10.1016/j.trac.2018.10.029

Quinn B, Murphy F, Ewins C (2017) Validation of density separation for the rapid recovery of microplastics from sediment. Anal Methods 9:1491. https://doi.org/10.1039/C6AY02542K

Raimondo S, Montague BJ, Barron MG (2007) Determinants of variability in acute to chronic toxicity ratios for aquatic invertebrates and fish. Environ Toxicol Chem 26:2019–2023. https://doi.org/10.1897/07-069R.1

Reddy SM, Basha S, Adimurthy S, Ramachandraiah G (2006) Description of small plastics fragments in marine sediments along the Alang-Sosiya ship-breaking yard, India. Estuar Coast Shelf Sci 68:656–660. https://doi.org/10.1016/j.ecss.2006.03.018

Redondo-Hasselerharm PE, Falahudin D, Peeters ETHM, Koelmans AA (2018) Microplastic effect thresholds for freshwater benthic macroinvertebrates. Environ Sci Technol 52:2278–2286. https://doi.org/10.1021/acs.est.7b05367

Retama I, Jonathan MP, Shruti VC et al (2016) Microplastics in tourist beaches of Huatulco Bay, Pacific coast of southern Mexico. Mar Pollut Bull 113:530–535. https://doi.org/10.1016/j.marpolbul.2016.08.053

Rocha-Santos T, Duarte AC (2015) A critical overview of the analytical approaches to the occurrence, the fate and the behavior of microplastics in the environment. TrAC 65:47–53. https://doi.org/10.1016/j.trac.2014.10.011

Rocha-Santos T, Duarte AC (2017) Characterization and analysis of microplastics, vol 75, 1st edn. Elsevier, Amsterdam. 302 pp

Ryan PG, Moore CJ, Van Franeker JA, Moloney CL (2009) Monitoring the abundance of plastic debris in the marine environment. Philos Trans R Soc B: Biol Sci 364:1999–2012. https://doi.org/10.1098/rstb.2008.0207

Sánchez-Nieva J, Perales JA, González-Leal JM, Rojo-Nieto E (2017) A new analytical technique for the extraction and quantification of microplastics in marine sediments focused on easy implementation and repeatability. Anal Methods 9:6371. https://doi.org/10.1039/C7AY01800B

Sarafraz J, Rajabizadeh M, Kamrani E (2016) The preliminary assessment of abundance and composition of marine beach debris in the northern Persian Gulf, Bandar Abbas City, Iran. MBAI 96:131–135. https://doi.org/10.1017/S0025315415002076

Scherer C, Brennholt N, Reifferscheid G, Wagner M (2017) Feeding type and development drive the ingestion of microplastics by freshwater invertebrates. Sci Rep 7:17006. https://doi.org/10.1038/s41598-017-17191-7

Schmidt N, Thibault D, Galgani F et al (2018) Occurrence of microplastics in surface waters of the Gulf of Lion (NW Mediterranean Sea). Prog Oceanogr 163:214–220. https://doi.org/10.1016/j.pocean.2017.11.010

Schymanski D et al (2018) Analysis of microplastics in water by micro-Raman spectroscopy: release of plastic particles from different packaging into mineral water. Water Res 129:154–162. https://doi.org/10.1016/j.watres.2017.11.011

Sci Total Environ. (2019) Jun 1;667:427–434. https://doi.org/10.1016/j.scitotenv.2019.02.332

Shim WJ, Hong SH, Eo SE (2017) Identification methods in microplastic analysis: a review. Anal Methods 9:1384–1391. https://doi.org/10.1039/C6AY02558G

Silva AB, Bastos AS, Justino CIL, Da Costa JP, Duarte AC, Rocha-Santos TAP (2018) Microplastics in the environment: challenges in analytical chemistry – a review. Anal Chim Acta 1017:1–19. https://doi.org/10.1016/j.aca.2018.02.043

Sommer F, Dietze V, Baum A, Sauer J, Gilge S, Maschowski C, Gieré R (2018) Tire abrasion as a major source of microplastics in the environment. Aerosol Air Qual Res 18:2014–2028. https://doi.org/10.4209/aaqr.2018.03.0099

Sruthy S, Ramasamy EV (2017) Microplastic pollution in Vembanad Lake, Kerala, India: the first report of microplastics in lake and estuarine sediments in India. Environ Pollut 222:315–322. https://doi.org/10.1016/j.envpol.2016.12.038

Straub S, Hirsch PE, Burkhardt-Holm P (2017) Biodegradable and petroleum-based microplastics do not differ in their ingestion and excretion but in their biological effects in a freshwater invertebrate Gammarus fossarum. Int J Environ Res Public Health 14:14. https://doi.org/10.3390/ijerph14070774

Strungaru SA, Jijie R, Nicoara M, Plavan G, Faggio C (2019) Micro- (nano) plastics in freshwater ecosystems: abundance, toxicological impact and quantification methodology. TrAC 110:116–128. https://doi.org/10.1016/j.trac.2018.10.025

Su L, Xue Y, Li L et al (2016) Microplastics in Taihu Lake, China. Environ Pollut 216:711–719. https://doi.org/10.1016/j.envpol.2016.06.036

Suaria G, Aliani S (2014) Floating debris in the Mediterranean Sea. Mar Pollut Bull 86:494–504. https://doi.org/10.1016/j.marpolbul.2014.06.025

Sundt P, Schulze P, Syversen F (2014) Sources of microplastics-pollution to the marine environment. Project Report. (108 pp. Norway)

Syberg K, Khan FR, Selck H, Palmqvist A, Banta GT, Daley J, Sano L, Duhaime MB (2015) Microplastics: addressing ecological risk through lessons learned: microplastics ecological risk. Environ Toxicol Chem 34:945–953. https://doi.org/10.1002/etc.2914

Taylor ML, Gwinnett C, Robinson LF, Woodall LC (2016) Plastic microfibre ingestion by deep-sea organisms. Nat Sci Rep 6:33997. https://doi.org/10.1038/srep33997

Thompson RC, Olsen Y, Mitchell RP, Davis A, Rowland SJ, John AWG, McGonigle D, Russell AE (2004) Lost at sea: where is all the plastic? Science 304:838. https://doi.org/10.1126/science.1094559

Tunçer S, Artüz B, Demirkol M, Artüz L (2018) First report of occurrence, distribution, and composition of microplastics in surface waters of the Sea of Marmara, Turkey. Mar Pollut Bull 135:283–289. https://doi.org/10.1016/j.marpolbul.2018.06.054

Turner A, Holmes L (2011) Occurrence, distribution and characteristics of beached plastic production pellets on the island of Malta (central Mediterranean). Mar Pollut Bull 62:377–381. https://doi.org/10.1016/j.marpolbul.2010.09.027

UNEP (2015) report Plastic in Cosmetics: Are We Polluting the Environment Through Our Personal Care?

Van Cauwenberghe L, Vanreusel A, Mees J, Janssen CR (2013) Microplastic pollution in deep-sea sediments. Environ Pollut 182:495–499. https://doi.org/10.1016/j.envpol.2013.08.013

Vandenberg LN, Hauser R, Marcus M, Olea N, Welshons WV (2007) Human exposure to bisphenol A (BPA). Reprod Toxicol 24(2):139–177. https://doi.org/10.1016/j.reprotox.2007.07.010

Vaughan R, Turner SD, Rose NL (2017) Microplastics in the sediments of a UK urban lake. Environ Pollut 229:10–18. https://doi.org/10.1016/j.envpol.2017.05.057

Verster C, Minnaar K, Bouwman H (2017) Marine and freshwater microplastic research in South Africa. Integr Environ Assess Manag 13(3):533–535. https://doi.org/10.1002/ieam.1900

Vianello A, Boldrin A, Guerriero P et al (2013) Microplastic particles in sediments of a lagoon of Venice, Italy: first observations on occurrence, spatial patterns and identification. Estuar Coast Shelf Sci 130:54–61. https://doi.org/10.1016/j.ecss.2013.03.022

Wang W, Wang J (2018) Investigation of microplastics in aquatic environments: an overview of the methods used, from field sampling to laboratory analysis. TrAC 108:195–202. https://doi.org/10.1016/j.trac.2018.08.026

Wang J, Peng J, Tan Z et al (2017a) Microplastics in the surface sediments from the Beijiang River littoral zone: composition, abundance, surface textures and interaction with heavy metals. Chemosphere 171:248–258. https://doi.org/10.1016/j.chemosphere.2016.12.074

Wang W, Ndungu AW, Li Z et al (2017b) Microplastics pollution in inland freshwaters of China: a case study in urban surface waters of Wuhan, China. Sci Total Environ 575:1369–1374. https://doi.org/10.1016/j.scitotenv.2016.09.213

Wang F, Wong CS, Chen D, Lu X, Wang F, Zeng EY (2018a) Interaction of toxic chemicals with microplastics: a critical review. Water Res 139:208–219. https://doi.org/10.1016/j.watres.2018.04.003

Wang Z, Chen M, Zhang L, Wang K, Yu X, Zheng Z, Zheng R (2018b) Sorption behaviors of phenanthrene on the microplastics identified in a mariculture farm in Xiangshan Bay, southeastern China. Sci Total Environ 628–629:1617–1626. https://doi.org/10.1016/j.scitotenv.2018.02.146

Wessel CC, Lockridge GR, Battiste D et al (2016) Abundance and characteristics of microplastics in beach sediments: insights into microplastic accumulation in northern Gulf of Mexico estuaries. Mar Pollut Bull 109:178–183. https://doi.org/10.1016/j.marpolbul.2016.06.002

Woodall LC, Sanchez-Vidal A, Canals M, Paterson G, Coppock R et al (2014) The deep sea is a major sink for microplastic debris. R Soc Open Sci 1:140317. https://doi.org/10.1098/rsos.140317

Wright SL, Kelly FJ (2017) Plastic and human health: a micro issue? Environ Sci Technol 51:6634–6647. https://doi.org/10.1021/acs.est.7b00423

Wright SL, Thompson RC, Galloway TS (2013) The physical impacts of microplastics on marine organisms: a review. Environ Pollut 178:483–492. https://doi.org/10.1016/j.envpol.2013.02.031

Wu P, Cai Z, Jin H, Tang Y (2019) Adsorption mechanisms of five bisphenol analogues on polyvinyl chloride microplastics. Sci Total Environ 650:671–678. https://doi.org/10.1016/j.scitotenv.2018.09.049

Xiong X, Zhang K, Chen X, Shi H, Luo Z, Wu C (2018) Sources and distribution of microplastics in China's largest inland lake – Qinghai Lake. Environ Pollut 235:899. https://doi.org/10.1016/j.envpol.2017.12.081

Yu X, Ladewig S, Bao S et al (2018) Occurrence and distribution of microplastics at selected coastal sites along the southeastern United States. Sci Total Environ 613–614:298–305. https://doi.org/10.1016/j.scitotenv.2017.09.100

Zbyszewski M, Corcoran PL (2011) Distribution and degradation of fresh water plastic particles along the beaches of Lake Huron, Canada. Water Air Soil Pollut 220:365–372. https://doi.org/10.1007/s11270-011-0760-6

Zhang K, Su J, Xiong X et al (2016) Microplastic pollution of lakeshore sediments from remote lakes in Tibet plateau, China. Environ Pollut 219:450–455. https://doi.org/10.1016/j.envpol.2016.05.048

Zhao S, Zhu L, Wang T, Li D (2014) Suspended microplastics in the surface water of the Yangtze Estuary System, China: first observations on occurrence, distribution. Mar Pollut Bull 86:562–568. https://doi.org/10.1016/j.marpolbul.2014.06.032

Zhao S, Zhu L, Gao L, Li D (2017) Methodological limitations for microplastic quantification in the ocean: recommendations for overcoming the defects. WESTPAC Workshop for Marine MP. https://doi.org/10.1016/B978-0-12-813747-5.00002-3

Zhu L, Zhang K, Chen X, Shi H et al (2018) Microplastic pollution in North Yellow Sea, China: observations on occurrence, distribution and identification. Environ Pollut 636:20–29. https://doi.org/10.1016/j.scitotenv.2018.04.182

Ziajahromi S, Kumar A, Neale PA, Leusch FDL (2018) Environmentally relevant concentrations of polyethylene microplastics negatively impact the survival, growth and emergence of sediment-dwelling invertebrates. Environ Pollut 236:425–431. https://doi.org/10.1016/j.envpol.2018.01.094

Chapter 2
Identification and Remediation of Plastics as Water Contaminant

Zaman Tahir, Muhammad Shahid Nazir, Masoom Fatima, Sadaf ul Hassan, Zulfiqar Ali, and Mohd Azmuddin Abdullah

Contents

Z. Tahir · Z. Ali
Department of Chemical Engineering, COMSATS University Islamabad, Islamabad, Pakistan
e-mail: zulfiqar.ali@cuilahore.edu.pk

M. S. Nazir (✉) · M. Fatima · S. ul Hassan
Department of Chemistry, COMSATS University Islamabad, Islamabad, Pakistan
e-mail: shahid.nazir@cuilahore.edu.pk; masoomfatima@cuilahore.edu.pk; sadafulhassan@cuilahore.edu.pk

M. A. Abdullah (✉)
Institute of Marine Biotechnology, Universiti Malaysia Terengganu, Kuala Terengganu, Terengganu, Malaysia
e-mail: azmuddin@umt.edu.my; joule1602@gmail.com

Inamuddin et al. (eds.), *Water Pollution and Remediation: Organic Pollutants*, Environmental Chemistry for a Sustainable World 54,
https://doi.org/10.1007/978-3-030-52395-4_2

Abstract Plastics are major assets for mankind due to their widespread applications in all spheres of life. The major drawbacks are their after-use handling, as it may take hundreds and thousands of years for its biodegradation. While major advancement has been made in the development of nontoxic and eco-friendly plastics, the accumulation of plastics in the environment has been a major concern in landfills, natural ecosystem, and oceans. The deleterious effects of plasticizers, additives, and dioxins from plastic pollutions on human health include endocrine disruption, reproductive disorders, and breast cancer. A well-managed plastic production, consumption, and disposal system must be put in place, to address this global problem. The development and application of biocompatible plastics and incentives on plastic reuse and recycle, within circular economy framework, must be implemented and enforced. This chapter will provide information about plastic; its types, nature and chemistry, consumption, and pollution impact; and the solutions and remedies. Different techniques to process various types of plastic wastes are discussed. Primary recycling of plastic wastes is a low-impact process. Mechanical recycling is widely used due to its effectiveness, where the waste is firstly converted into appropriate shapes and sizes through different processes. Chemical recycling involves the breakdown of polymers by heating in the absence of oxygen. Plastics are also degraded by means of ultraviolet light because these are not naturally degraded even by biotic means. The 3R scheme, which represents reduction, reusability, and recycling of plastic wastes, and the alternative measures through incentives to promote eco-friendly plastic products and a safer environment will be elaborated.

Keywords Plastics · Pollutions · Contaminants · Environmental impacts · Water pollution · Plastic degradation · Biodegradability · Additives · Remediation · Eco-friendly products

Abbreviations

ATR	Attenuated total reflectance
BBP	Butyl benzyl phthalate
BFR	Brominated flame retardants
BPA	Bisphenol A
BTBPE	1, 2-Bis(2,4,6-tribromophenoxy)ethane
CNS	Central nervous system
DBP	Dibutyl phthalate
DEHP	Diethylhexyl phthalate
DEP	Diethyl phthalate

DMP	Dimethyl phthalate
END	Endocrine disruption
EPS	Extended polystyrene
FTIR	Fourier transform infrared spectroscopy
GC/MS	Gas chromatograph/mass spectrometer
HBB	Hexabromobiphenyl
HDPE	High-density polyethylene plastic
LDPE	Low-density polyethylene plastic
MSW	Municipal solid waste
NaCl	Sodium chloride
NPE	Nonylphenol ethoxylates
PAE	Phthalic acid esters
PBDE	Polybrominated diphenyl ethers
PET	Polyethylene terephthalate
PSW	Plastic solid waste
PVC	Polyvinyl chloride
TBBPA	Tetrabromobisphenol A
WPO	Wet peroxide oxidation

2.1 Introduction

Before the discovery of plastics, elephant ivory (teeth and tusks) obtained from the remains of elephants have found applications in the manufacturing of billiard balls, combs, and many products. To meet the market demand for elephant ivory, the killing of the elephants has become widespread such as in the African continent that the elephant population has dramatically decreased. The ivory products consequently become prohibitively expensive. Thus, the alternative material was invented by J. W. Hyatt and his brother from cotton cellulose and named as “Celluloid” (National Museum of American History, Estate of Catherine Walden Myer). The word “Plastic” was coined from the Greek word “Plastikos” which means “moulded or shaped by heat” for the celluloid-like product easily moulded into different shapes. A big disadvantage in the preparation of the cellulose-based products is the exothermic reaction of the mixture which produces high energy and releases heat making it potentially highly flammable and risky.

An American chemist, L. Baekeland, considered as “the Father of the Plastic industry,” has successfully synthesized bakelite, prepared using phenol from coal tar and formaldehyde and reacted together. Bakelite has a good property for insulation. The invention of bakelite opens up a new avenue for the development of plastics, its derivatives, and composite materials for specialized applications in most areas in the fields of material sciences. Plastics are durable and sometimes inert, which can withstand very harsh conditions of temperature and weathering. These properties of plastics make it a burden to the environment later, after use.

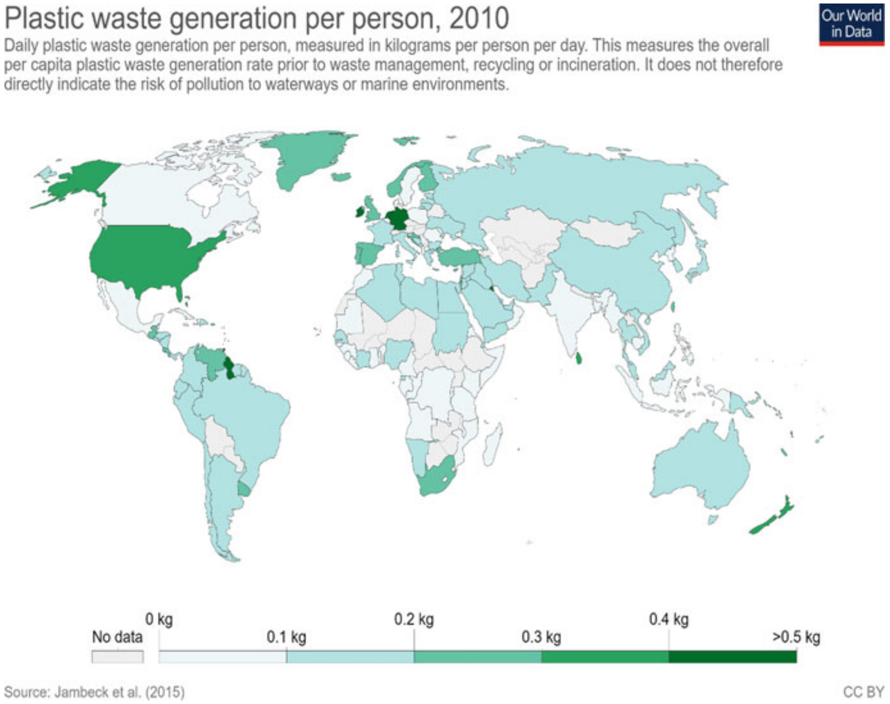
Plastics have become vital parts of human life and provide many advantages and ease the activities and the interactions with the surroundings and ecosystem (Hahladakis et al. 2018). These are due to the diverse properties of plastics which are easily incorporated into a wide range of applications, from domestic to major components in industries, as shown in Fig. 2.1. The production of plastic has increased from 2 to 382 metric tons between 1950 and 2015, with the total of 7800 metric tons in 65 years. Globally, 50% of the plastic manufacturers are located in the Asian region, while only 18–19% are in Europe and North America (Lam et al. 2018). The thermoplastics, which include polypropylene, polyvinyl chloride, and high-density polyethylene, have found diverse applications worldwide; but the thermosetting plastics, such as polystyrene and polyethylene terephthalate, receive higher demand. The plastic polymers are extensively used to make foams, synthetic fibers, adhesives, and coatings for different applications, resulting in increasing global plastic demand annually (Brems et al. 2012). However, plastics are resistance to decomposition and degradation, and can exist for a long time. As a consequence, plastic wastes are filling up the landfills and the municipal solid wastes, and may cause accidental fires and pollution. Made up of many different chemicals and additives, plastics can be the main source of cadmium and lead poisoning. The heterogeneity of the plastic composition may limit the recycling process as it may be costly to produce pure plastics or single polymer composites. Despite these limitations, the application of plastics in everyday human activities is set to continue. Plastics are less bulky and light and more suitable for use in transportation and automobiles as the load and fuel consumption are much

Fig. 2.1 The main market sectors of plastic. 39.9% of plastic is used in packaging; 19.7% in building and construction; 10% in automotive; 6.2% in electrical and electronics; 4.2% in household, leisure, and sports; 3.3% in agriculture; and 16.7% in various other sectors. (Reprinted with permission of [The history of plastics: from the Capitol to the Tarpeian Rock, Chalmin, Attribution 3.0 Unported (CC By 3.0)] from Chalmin 2019)

reduced (Clark et al. 1999). This chapter describes the different types of plastics, the sources and wastes generated, the impacts on human health, environment and marine life, and the different techniques used for the detection and removal of the plastic wastes and toxins.

2.1.1 *The Plastic Consumption per Person*

Figure 2.2 shows the total plastic production per person without taking into account the waste management and recycling. The figure represents the daily basis of plastic wastes generated by a person, measured in kilogram unit per individual. It can be seen that the plastic consumption per individual basis is ten times higher in countries including Guyana, Ireland, Kuwait, the Netherlands, and the United States (US) than other countries like India, Tanzania, and Bangladesh.



Plastic waste generation per person, 2010

Daily plastic waste generation per person, measured in kilograms per person per day. This measures the overall per capita plastic waste generation rate prior to waste management, recycling or incineration. It does not therefore directly indicate the risk of pollution to waterways or marine environments.

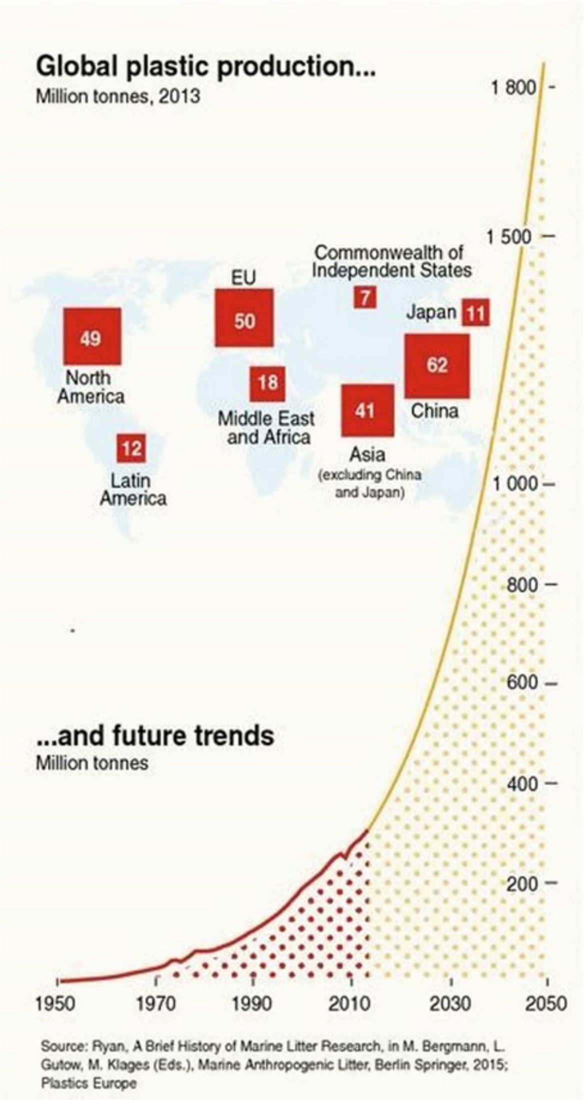
Source: Jambeck et al. (2015)

CC BY

Fig. 2.2 The plastic waste production per person worldwide. The overall plastic waste generated per person before the waste management protocols, or recycling, but not indicating the effects of water pollution. (Reprinted with permission of [Plastic Pollution, Hannah Ritchie, Attribution 4.0 International (CC By 4.0)] from Hannah Ritchie 2018)

2.1.2 The Top 20 River Sources into the Oceans

The total production of plastics globally has been on the rise since the 1950s, with 311 million tons production in 2014, and predicted to be nearly 1800 million tons in 2050. Figure 2.3 illustrates the plastic production worldwide in million tons. China, North America, European Union, and Asia are the biggest cause of plastic pollution. Developed countries like the United States, Europe, Japan, Australia, and New Zealand are the top manufacturing and high consumption countries, but with



Source: Ryan, A Brief History of Marine Litter Research, in M. Bergmann, L. Gutow, M. Klages (Eds.), Marine Anthropogenic Litter, Berlin Springer, 2015; Plastics Europe

Fig. 2.3 The plastic production worldwide in million tons. China, North America, European Union, and Asia are the biggest cause of plastic pollution. (Reprinted with permission of [Marine litter plastics and microplastics and their toxic chemicals components: the need for urgent preventive measures, Gallo et al., Creative Common Attribution (CC by 4.0)] from Gallo et al. 2018)

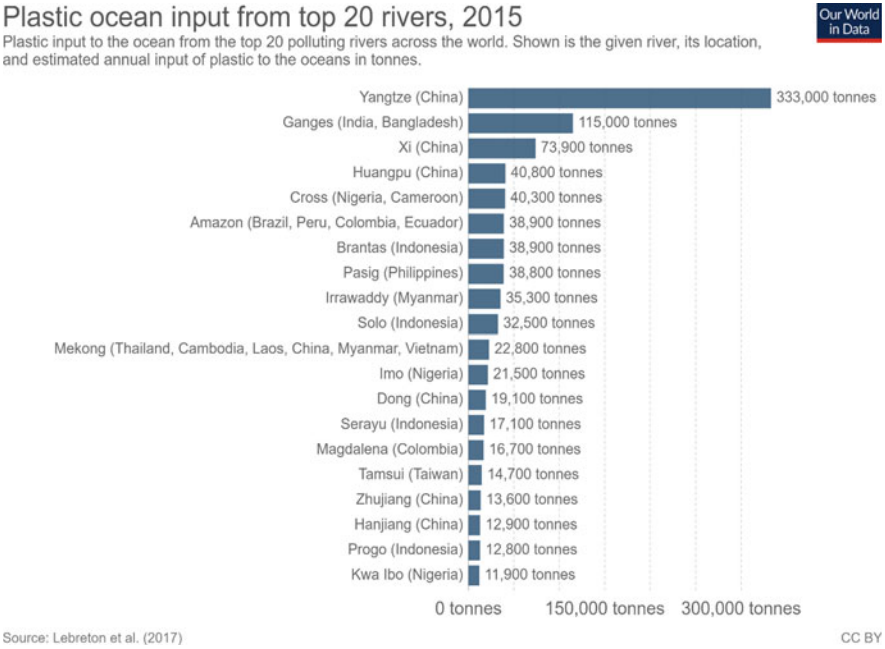


Fig. 2.4 Plastic input in the ocean of top 20 polluted rivers across the world. The river with its location and estimated annual input of plastics (in tons) to the oceans are shown. (Reprinted with permission of [Plastic Pollution, Hannah Ritchie, Creative Common Attribution (CC by 4.0)] from Hannah Ritchie 2018)

excellent waste disposal sytems in place. Many low- to middle-income countries in South Asia and sub-Saharan Africa are facing 80–90% of the plastic pollution with underdeveloped waste management system, resulting in high incidence of river and ocean pollution, and increasing water contamination. The top 20 polluted rivers contribute above 2/3 of the total river wastes and most of these are present in Asia. River Yangtze is at the top for causing pollution, with 333,000 tons of plastic in 2015, contributing up to 4% of the annual marine pollution, as shown in Fig. 2.4. There are different ways that contribute towards the entry of plastics into the aquatic ecosystem such as from the pollution on the beaches, plastic debris floating on the ocean surface, and deposition at the seabeds. One important source is the river that carries plastic effluents from the mainland to the offshore areas.

2.1.3 *Classification of Plastics*

Polymers are long-chained molecules, having unique structures and consisting of repeated subunits called monomers (“mer” means part). The single monomer structure is specifically used to identify chemically or specify any homopolymer. The structure of single monomer (-CH_2-CH_2-)$_n$ describes polyethylene. When the number of repeated units "n" are in hundreds, its consistency becomes like a soft wax or a sticky fluid. When the repeated units are in thousands, it becomes the valuable solid plastic (Andrady 2017). In plastic polymer, the long hydrocarbon chains mainly consist of carbon and hydrogen atoms to form the basic structure. Carbon provides the main backbone of the polymer as it naturally has the ability to attach four other groups. Polymers such as polyethylene, polypropylene, polystyrene, and polymethyl pentane all have the carbon backbone, but there are some polymers that contain other than the carbon backbone including nylon which contains nitrogen atom, and polycarbonates and polyesters which mainly consist of oxygen atom. A few inorganic polymers contain silicon or phosphorus backbone (Vanapalli et al. 2019). The molecular arrangements of polymers can be in the form of amorphous or crystalline structure. The amorphous plastic does not have specific arrangements of atoms in the structure, and are randomly arranged. The amorphous polymer can be formed by controlling the polymerization process and quenching the molten polymer. They are generally transparent and have many applications in food wrappings, windows, contact lenses, and headlight lenses. The crystalline polymer has distinct pattern of atoms and molecules, and through quenching, the polymer structure is crystallized, and the degree of crystallinity controlled. Crystallinity provides strength, chemical resistance, stability, and stiffness. With increase in crystallinity, less light has the ability to pass through and this controls the degree of opaqueness. The work on polymers has increasingly shifted towards exploiting the unique properties for specific applications whilst making them more environmentally-friendly and less polluting to the environment.

Based on the applications, plastics can be classified into different classes:

Thermosetting Plastics

Thermoset plastics conserve their shapes when cooled and cannot be moulded back into their previous state. They are hard and long-lasting. The examples are polyurethanes and epoxy resins.

Thermoplastics

Thermoplastics are flexible as compared to thermosets and can be moulded back to its parent form. They are mostly used in packaging. The examples include polyethylene and polyvinyl chloride.

Plastic Composite

Polyethylene terephthalate or "stomach" plastics are used in the manufacturing of plastic bottles for juice, soft drinks, and liquids. These plastics can be made phthalate free, soft and lightweight-carrying, transparent containers for packaging purposes. It is harmless but, after a long time and at high temperature, may produce carcinogens.

Plastic containers based on polyvinyl chloride are the flexible type of plastics. Phthalates used for its flexibility are harmful chemicals, in addition to bisphenol A, lead, and dioxin. High-density polyethylene plastic has high density and high tensile strength, suitable in the manufacturing of refrigerators and large containers and bags.

Low-density polyethylene plastic is heat resistant and highly brittle, has low tensile strength, may be transparent or opaque, and is used for packaging frozen foods. Polypropylene is a strong, semitransparent, and heat-resistant polymer, usually used for packaging of yogurt, and medicine. Polystyrene is a petroleum-based plastic polymer made from styrene monomer, and is also widely used for food packaging and insulation.

Long exposure to high temperature may produce neurotoxic, hematological, cytogenetic, and carcinogenic by-products.

The plastic material may be composed of different synthetic materials that are malleable when heated, and hardened upon cooling. These include various types of resins, polymer, derivatives, and proteins used instead of the traditional materials such as metals, wood, and glass. Because of this flexible characteristic, the use of plastics is ubiquitous. This has largely contributed to the plastic waste disposal problems seen today that have polluted the marine ecosystem, ocean and seabeds.

2.1.4 Types of Industrial Plastic Wastes

The different types of plastic wastes generated by the plastic industries include macroplastics, microplastics, nanoplastics, platic toxins, and the additives.

Macroplastics

Plastic particles with diameter ranging from 1 to 5 mm are defined as macroplastics. These plastics when ingested by marine animals get stuck in their guts and can be lethal. This type of plastic waste has contaminated the freshwater systems, shorelines, and oceans (Li et al. 2016).

Microplastics

These plastic particles are less than 1 mm. Because of smaller sizes, microplastics can penetrate the body of aquatic life or easily ingested and run through the digestive track, circulatory, or excretory system, and eventually interfere with the proper functioning of the body system. Once settled inside the body and not excreted out, these particles start trickling down the food chain and entering the human body (Li et al. 2016).

Microplastics, though do not seem to be fatal to the livings organism, could still cause acute chronic toxicity. The toxic effects of microplastics can be a result of several mechanisms. Primarily, the toxicity can be caused by the polymeric materials used in the specific plastic goods. For example, polystyrene, commonly utilized as protective packaging, can easily circulate in the blood and induce chronic reproductive disorders in the suspension-feeding animals in the marine water. Microplastics can cause allergy and itchiness due to their tiny sizes with possibly the pointed ends as these materials penetrate into the body tissues. The intake may cause malnourishment and reproductive disruption (Sun et al. 2019). Microplastics are obtained from two different sources: primary and secondary sources. Primary microplastics are synthesized by industrial processes directly, while secondary microplastics are produced from primary microplastics by degradation under the extreme environment of moisture and heat (Li et al. 2016).

Primary Microplastics

This type of microplastic is manufactured on an industrial scale as microbeads of various sizes and shapes. They are mainly used in toiletries and commonly as "exfoliates" in sandblasting media, or as the "plastics pellets" or the raw materials for the manufacturing of these products. These pellets enter and pollute the ecosystem via industrial leakage, transportation, or during utilization. As illustrated in Fig. 2.5, there are different types of chemical structures present in the plastic wastes. Plastic resins are utilized mostly in the packaging, with short life span and found extensively as a part of litters or municipal solid wastes. The major types of thermoplastics that are commonly present in the microplastics are polyethylene,

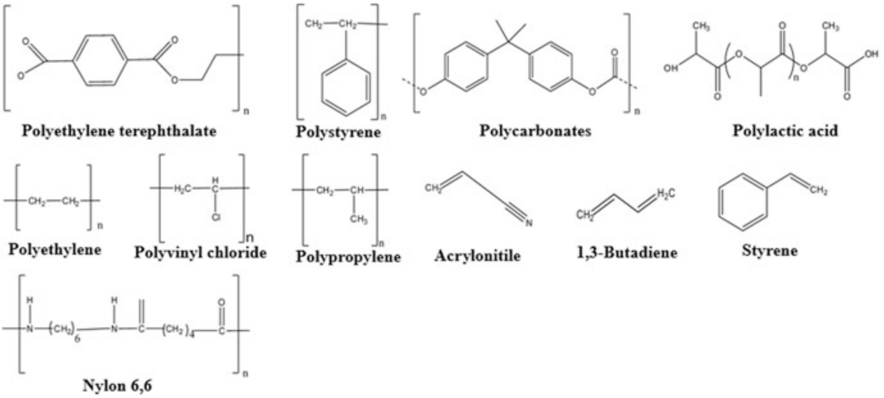


Fig. 2.5 Different types of structures present in the industrial plastic wastes. Carbon provides the backbone to nearly all plastic polymers (Modified from Vanapalli et al. 2019).

polypropylene, polystyrene, polyethylene terephthalate, and polyvinyl chloride. With the increased production rate of around 7–8% annually worldwide between 1950 and 2012, polyethylene and polypropylene have become the major microplastics found in the marine ecosystem (Li et al. 2016).

Secondary Microplastics

Secondary microplastics are derived from the large plastics, converted and fragmented into smaller debris, resulting in the different structures as shown in Fig. 2.5. The estimated lifetime of plastics ranges from months to many thousands of years. As conventional plastic has been produced from the past 60 years, the approximate figure of plastic longevity is unknown (Li et al. 2016). The physical, chemical, and biological factors in the environment affect and reduce the structure, strength, and other properties of the plastics (Li et al. 2016).

Nanoplastic Wastes

There is less knowledge about the threats and risks to humans from nanoplastic wastes ranging from 1 to 100 nm in sizes, as the focus has been those ranging in sizes below 1 mm. Both have different structural makeup and sizes which will influence the rate of uptake and deposition in the living organisms. Once entering the systemic circulation of human body, nanoplastics may be transported to the liver, placenta, brain, heart, and kidney, upset the central nervous system, and could lead to physiological and behavioural changes (Waring et al. 2018).

Plastic Toxins

Additives are defined as the chemicals that are added into plastics to promote specific characteristics and functionalities. These are incorporated during the manufacturing or processing of plastics. These are mainly plasticizers, stabilizers, or flame retardants. Plasticizers are most probably added in comparatively excessive proportion, about 10–50%, to secure the functionality of the plastic. Plastic additives are basically monomers of different polymeric chain but utilized as a stabilizer too. Brominated flame retardants is the monomeric unit of polycarbonate, added as a stabilizing agent in various polymers as shown in Table 2.1. These additives are used mainly to confer stability, antioxidant activity, fire resistance, plastic property, and pigmentation. These additives could be found in the microplastics, originating from the compound plastics (Andrady 2017).

Brominated flame retardants and phthalates are added to the plastics to increase their plasticity and fire-retardant properties. But, these are regarded as endocrine disruptors, which could bioaccumulate in the human body (Sun et al. 2019).

Table 2.1 Statistical data of marine litter (Hannah Ritchie 2018)

Location	Approach	Approximate coverage over the location	Approximate litter density	Global estimate (tons)
Floating	Sea surface sampling data and modeling	361 m/km^2	0.74 kg/km^2	0.27 million
Beach	Beach sampling data by length of coastline	1.4 m/km	1013 kg/km^2	1.4 million
Under beach sand	Proportion of beach surface to the buried litter	0.52 m/km	110 kg/km	0.057 million
Seafloor	Seafloor sampling data collected by the area of sea surface	361 m/km^2	70 kg/km^2	25.3–65 million
Total				27–66.7 million

Brominated flame retardants, alkylphenols, and phthalates, are also extremely toxic to the ecosystem when released into seas, oceans, rivers, and lakes, from the industrial and municipal wastewater, or from the sewage sludge for agricultural purposes. Additives leaking from plastics also contribute to the debris addition in the marine ecosystem and as another major plastic pollution in the oceans (Hermabessiere et al. 2017).

Brominated Flame Retardants

Brominated flame retardants are used to reduce the plastic flammability. These include polybrominated diphenyl ethers, hexabromocyclododecane, and tetrabromobisphenol A. Brominated flame retardants such as 1, 2-bis(2,4,6-tribromophenoxy)ethane, dibutyl phthalate, and hexabromobiphenyl have been found in the ecosystem, organisms, food, and humans. Due to their weak interactions with the polymer, they can readily leak out. Tetrabromobisphenol A however forms strong chemical interaction to the polymeric matrix. Penta-brominated diphenyl ethers, octa-brominated diphenyl ethers, and deca-brominated diphenyl ethers are extremely toxic, persistent, and can accumulate in the ecosystem and pose serious threats to the human health (Hermabessiere et al. 2017).

Phthalates

These additives are also known as phthalic acid esters. Added as plasticizers which can be between 10 and 60% of the plastic content, especially in polyvinyl chloride, additives such as phthalic acid esters could leach into the ecosystem during the manufacturing process, usage, and disposal. Phthalic acid esters exist in a variety of environments, and some of them disturb the endocrine system in even minute concentration (Hermabessiere et al. 2017).

Nonylphenols

Nonylphenols are a class of alkylphenols. These are liberated as the degradation intermediates of some surfactants and antioxidants named as nonylphenol ethoxylates. Both nonylphenol ethoxylates and nonylphenols are mainly used in paints, detergents, pesticides, and toiletries. In the production of plastic, they can also be used as plasticizers and antioxidants. Leaching of nonylphenols from many plastic bottles into the water system may be contributed mainly by the effluents from the wastewater treatment plants. Nonylphenols can seriously disturb the endocrine system, and due to the harmful impacts on the ecosystem and human health, the utilization is banned in the European Union (Hermabessiere et al. 2017).

Antioxidants

Antioxidants are employed as additives in various artificial polymers such as polyolefin (polyethylene and propylene) which may constitute 60% of the total requirement of the antioxidant worldwide. These are meant to increase the shelf-life of plastics and to prevent oxidation. However, these also leach out like other additives of plastic packaging, thus causing various environmental threats and safety concerns (Hermabessiere et al. 2017).

Table 2.2 shows the common additives (brominated flame retardants, phthalates, bisphenol A, nonylphenols, and various antioxidants), their functions, and impacts on health.

Table 2.3 shows the use of additives in general types of plastic such as polyethylene terephthalate, polyvinyl chloride, polystyrene, and many other resins that cause pollution, and also impart toxic effects from the untreated from industrial

Table 2.2 Most common polymers with their plasticadditives (Hermabessiere et al. 2017)

Polymers name	Additive types	Polymer amount (% w/w)	Hazardous chemicals
Polypropylene	Antioxidant	0.05–3	Bisphenol A, Octylphenol, Nonylphenol
High-density polyethylene	Antioxidant	0.05–3	Brominated flame retardant; Boric acid
Low-density polyethylene	Antioxidant	0.05–3	Nonylphenol
Polyvinylchloride	Plasticizer	10–17	Phthalate
Polyurethane	Flame retardant	12–18	Brominated flame retardant; Boric acid

Table 2.3 Some plastic additives with the functions and hazardous effects (Hermabessiere et al. 2017)

Additives	Functions	Effects
Brominated flame retardants	Reduce flammability in plastic	Potential endocrine disorders
Phthalates	Plasticizer mainly in polyvinyl chloride	Endocrine and developmental disorders
Nonylphenol	Antioxidant and plasticizer	Endocrine disturbance
Bisphenol A	Synthesis of polycarbonates, plastics, and epoxy resins	Endocrine disturbance and estrogen mimic

plastic wastes, when discarded into the marine environment (Hermabessiere et al. 2017; Vanapalli et al. 2019).

2.1.5 How Plastic Is Getting into Our Environment

The increased use of plastics, has resulted in uncontrolled waste generation, especially in the developing countries, whose facilities are not able to cope. The availability of different food items in the plastic bags has become a norm, and a lot of plastics end-up flushed into the drainage and water system. Figure 2.6 shows the plastic production by industrial sector, and Fig. 2.7 shows the different forms of plastics introduced into the environment.

The most amount of polluting plastics recorded is the microplastic, produced from the weathering of plastics into smaller particles. This makes the management of plastic becoming more difficult, with the noticeable increase in the amount of microplastics on the surface of the oceans in the last four decades. The aquatic organisms can ingest the microplastics, get accumulated in their bodies, help in the transport of pathogens, and adsorb the toxic substances. Microplastics ingestion could lead to cancer, retard the reproductive ability, and destroy the immune system. The contamination of an aquatic environment by the microplastics may pose serious economic consequences, as their removal is difficult, if not impossible due to their small sizes. The World Economic Forum 2016 postulates that the presence of plastics as pollutants to be more than the fishes in the aquatic ecosystem, in 2050 (White 2016).

Eunomia Research and Consulting has reported that the production of microplastics ranges from 0.5 to 1.4 million tons annually, with an average estimate of 0.95 million tons. The report describes that 94% of plastic ends up on the oceanic floor at a mean of 70 kg/km^2 of plastics. It is reported that only 1% plastic is found floating over the ocean, at the concentration of 1 kg/km^2, with the highest concentration at the North Pacific Gyre at 18 kg/km^2. The amount is 5 times greater on the beaches at 2000 kg/km^2 as illustrated in Fig. 2.8.

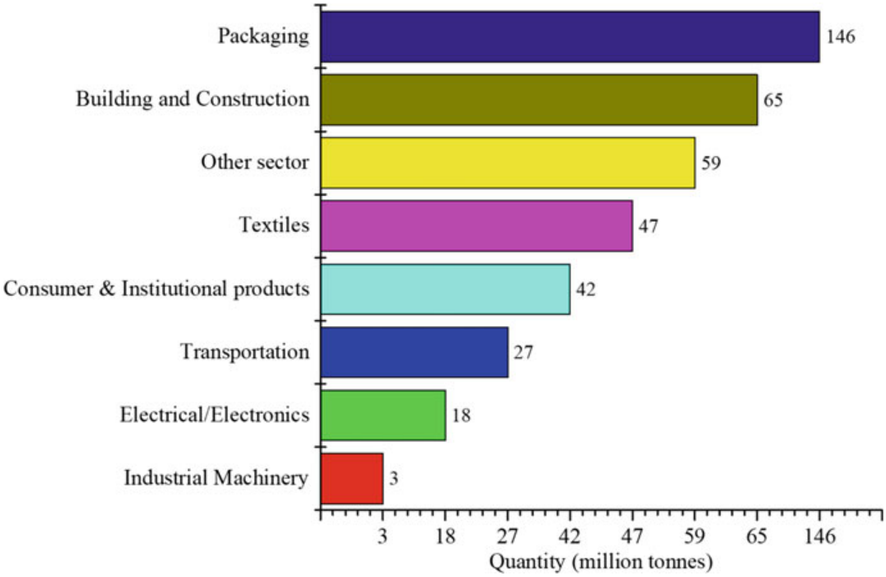


Fig. 2.6 Plastic production by industrial sector. Packaging industry contributes 146 million tons, building and construction 65 million tons, textiles 47 million tons, consumer and industrial products 42 million tons, transportation 27 million tons, electrical and electronics 18 million tons, industrial machinery 3 million tons, and by various other sectors 59 million tons. (Modified from Hannah Ritchie 2018)

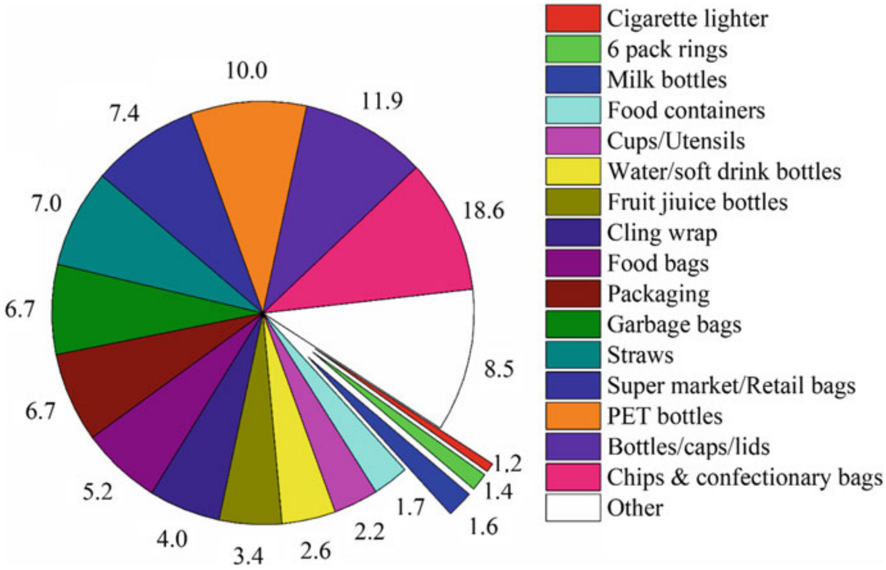


Fig. 2.7 Different forms of plastics introduced into the environment. Maximum contribution of the plastic waste is conributed by the chips and confectionary bags, bottle/caps/lids, polyethylene terephthalate (PET) bottles, supermarket/retail bags, straws, garbage bags, packaging, food bags, and cling wraps. (Modified from White 2016)

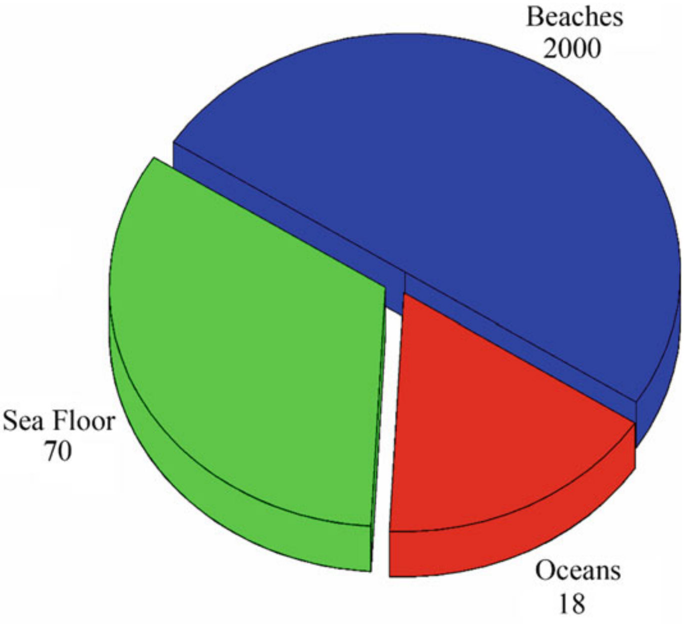


Fig. 2.8 The concentration of plastic per km^2. Oceanic floor has a mean of 70 kg per km^2 of plastics, oceans have around 18 kg per km^2, and beaches have 2000 kg per km^2, of plastics (Modified from Li et al. 2016)

2.1.6 Sources of Water Pollution

The major source of water pollution is the transfer of different household and industrial wastes into the water ways, and then into the oceans. An estimated 2 million tons of different pollutants are flushed into the water systems per day. The situation is more critical in countries where almost 90% of wastes and 70% of industrial wastes are disposed off into the water ways (Wu and Chen 2013).

There are two main classes of water pollution sources – the point and non-point sources. The point sources are simple to detect and easy to control which include the pollutants released by the municipal waste management plant, modern treatment plants, wastewater treatment plants, and also from industries. The industrial wastes can pollute water from any group and of any size. The pollutants change the chemistry of water, alter the oxygen level and temperature, and the population of microorganisms. These can affect the aquatic water bodies and create critical situations (Wu and Chen 2013). The pollution from the non-point sources is not released from any specific source, and can start from many points and places. The toxic substances may be caused by the indiscriminate use of fertilizers, oils, and trash, the horticultural waste movements, the wastes from domesticated animals and the mineralization of soil as shown in Table 2.4. The pollutants can be transferred to the local water sources by drains, or from the rain that flows onto the different

Table 2.4 Comparison of the point and non-point sources

Point sources	Non-point sources
Pollutants from municipal and industries	Effluents from agricultural fields
Filtrate from waste management areas	Waste from pastures
Runoff from animal farms	Waste from drained localities or may be undrained
Waste from oil fields	Pollutants from deserted mines
Population from sewage waste	Different activities of land that produce contaminants
Waste from construction areas	

Modified from Wu and Chen (2013)

sidewalks and lawns, bringing along the particles, dirt, and various pollutants. In many countries, the polluted water runoff is the greatest threat to the supply of fresh water (Wu et al. 2018).

2.1.7 Sources of Plastic Contamination in the Ecosystems

Terrestrial

Most plastic contamination from the terrestrial areas is due to the human activities. Plastics on land may come from the open landfills, wastes from houses, debris by blown wind, plastic bags and boxes. These are macroplastics which upon degradation will release smaller particles into the ecosystem.

In marine ecosystem, 80% of the plastic wastes come from the land populated by humans, or with plastic industries, and with high plastic consumptions. Most of the drifting and stranded plastic flotsam and jetsam, may come from the beach front, and the recreational activities, especially in the northern part of South China Sea. Substantial amounts of trash from the crude assembling wastes are shifted to the shorelines with inadvertent leakages. Others come from the wastewater and site leachate. Plastics from the sources also enter the stream networks and may reach the household, even with the water purification in place, through other indirect means. The climate and weather changes from typhoons could transfer the wastes and pollutants into the ocean. The small-scale plastic contaminants in Californian aquatic ecosystem has been found to increase from 10 to 60 particles (Li et al. 2016), as aresult of these rapid changes in the ecosystem.

Other sources of pollutants may come from indiscriminate dumping of garbages in the municipalities and residential areas, which are released through downpours, floods, or wind (Sheavly and Register 2007).

Aquatic

Rivers transport 70–80% of the plastic wastes or discharged from the fertilizer factories and wastewater treatment plants. Marine plastics may originate from the transportation and activities of the gas and oil, and fishing industries. Samples obtained from the Ross Sea in the Antarctica is found to have plastic particles of 0.3–22 nm in size.

Plastics constitute 20% of the wastes in the sea contributed by the marine flotsam and jetsam, and angling activities. The disposed angling items include the thin single filamentous lines, and the nylon net, which could endanger the aquatic life (Li et al. 2016).

Other marine garbages may originate from the business or military vessels, recreational watercrafts and ships, and oil tankers. Some of the wastes are unlawfully released or extracted from the junks to recover nets, ropes, trawl skims, and other angling-related items (Sheavly and Register 2007).

All plastic products are mostly disposed off after us. As shown in Fig. 2.9, indiscriminate dumping of plastics into the waterways and aquatic ecosystem has reached catastrophic level, especially in the developing world. Among the plastic products produced in the last century, 9% of them are recycled, 12% burned, and

Fig. 2.9 Marine plastic pollution affecting the life of humans and other marine organisms contributed by indiscriminate dumping of plastic garbage and litter in the aquatic environment. (Reprinted with permission of [Planet geography, Codrington, Attribution 2.5 Generic (CC by 2.5)] from Codrington 2005)

Table 2.5 Details of the source and the amount of plastic released

Region	Composition	Source of debris	Quantity
Worldwide	Metal, glass, and plastic containers	Shipping fleet (metal) (glass) (plastic)	Containers 4.8×10^6/day 3×10^5/day
Bays and offshore waters of the United States	"Garbage," including plastics	Sport fishing boats	34,000 t/year
Off Alaska	Gear used to catch fish thrown in water	Commercial fishing ships	1635 t/year
Globally	Broken and discarded fishing gear	Commercial fishing ships	135,000 t/year
Globally	Plastic packaging materials	Commercial fishing ships	>23,000 t/year

Modified from Rezania et al. (2018)

79% disposed off by burying in the land or dumped in the landfill. There are no exact calculations of total marine plastic wastes in comparison to the overall plastic production. However, it has been calculated that 10% of plastic is annually disposed off into the seas and oceans (Mendenhall 2018). Aquatic pollutants can adsorb easily onto the surface of small particles, and persistent organic pollutants are concentrated onto the mats of microplastics. These high concentrations can cause endocrine disorder, and have negative impacts as the combination of the microbial and chemical carriers increases the risk of fish contamination, which would eventually enter the human and animal food chain.

Atmosphere

Polypropylene particles can be transported by the wind. These may come from the cloth fibers, abrasive tires, plastic sheets, and can be breathed in by humans or animals. In urban areas and big cities the air may contain about 200 particles/m^3/day. Polypropylene particles are carcinogens and can concentrate in the brain, lungs, and gastrointestinal track and cause serious problems if present in high amount (Waring et al. 2018). The details of the sources and the amount of plastics released are shown in Table 2.5.

2.2 Techniques for the Identification of Plastic as Water Contaminant

Plastic contaminants are widely distributed in the water systems including in the surface water and groundwater, and marine environment. In order to devise strategies to control plastic pollution, issues related to the plastic degradation, sampling, analysis, migration pathways, and factors influencing the distribution, must be understood. Plastic materials in the ecosystem, with the passage of time, are circulating between the different environmental components – from land to fresh water (ponds, rivers, lakes, or streams), and from fresh water to marine (seas and oceans). This movement will be determined by the distance of travelling within the system such as the river, between the components such from the river to the sea, and the types of land and distanced covered. Plastic trashes on the roadside may be disintegrated by the moving vehicles or grass-cutting equipment. The microplastics are then drained off towards the river system, and are easily distributed among the environmental components, as compared to the macroplastics, before entering the marine environment (Lambert 2018). Many hydrophobic pollutants, such as polychlorinated biphenyls, dichlorodiphenyltrichloroethane, and dioxin, may get adsorbed on the microplastic particles, either by physisorption or chemisorption. This eventually influence the movement and bioavailability of these pollutants, but at the same time, concentrate all the potential toxic components in one area or location. Microplastics are formed in a variety of freshwater matrices, and in organic samples and sediments, the detection and identification can be highly challenging. In fresh water monitoring, the surface water, rivers, beaches, lakes, and sediments of rivers and reservoirs have all been shown to contain an almost consistent concentration of microplastics. The ecotoxicological studies have explored the ingestion of microplastics by different organisms and the side effects on their lives and habitats. Over a short term of exposure, most of the research use primary microspheres of polystyrene and polyethylene at high concentration, to show some evidences that microplastics indeed cause diseases in the freshwater systems. For identification, sensitive detection, and analytical confirmation of the microplastic residues and composition, the combination of physical and chemical techniques with the application of sophisticated equipments, are required (Lambert 2018).

2.2.1 Physical and Chemical Techniques

The conventional physical techniques for preliminary identification of plastics involve sieving, filtration, and density separation. The visual examination of the sample and the isolation of the desired ones may require an in-depth understanding and experience in dealing with the samples containing plastic materials. There are three major sampling techniques – volume reduction, selection, and bulk sampling. Oftentimes in the study of marine eco-system, the sediment samples are collected from the coastlines, and the water samples from the seashores. Sample separation can be achieved through density gradient, sieving, filtering, and optical sorting of the microplastics. The mesh size sieves and filters could estimate the size distribution. The two main size ranges of the microplastics that have been reported are 500 μm–5 mm based on the 500 μm sieve/net; and 1–500 μm or fractions retained on the filter. The optical sorting helps in determining the type, shape, degradation, and color of plastic particles. Most of the studies have identified that the plastic fragments found in abundance in marine environment are polyethylene and polypropylene (Hidalgo-Ruz et al. 2012). In the density separation, sodium chloride is present. The wet peroxide oxidation mixture is added to isolate the plastic debris by the process of floatation. Density separator helps to separate the denser undigested mineral components from the floating solids, by using a custom 0.3 mm filter. The plastic material, after separation, is then weighed to calculate the microplastic concentration. To determine the weight of the separating material, the gravimetric analysis can be used.

For chemical method, the plastic waste in the sample is collected as suspended particles in water. These plastic wastes can be hard plastics and soft plastics like foam, sheets, fibers, lines, and films. Solids can be filtered using 0.335 mm surface sampling net to collect the material of suitable sizes. The separated material is then dried to identify the solid mass, and the microscopic examination is performed with the stereomicroscope (normally with magnification of 40X). Many common plastics can be determined using this technique as a preliminary identification including polyvinylchloride, polyethylene, polystyrene, and polypropylene. The type of microplastics examined normally are in the range 0.3–5 mm, as illustrated in Fig. 2.10 (Nudo 2017). The wet peroxide oxidation is carried out on the dried sample, in the presence of Fe(II) catalyst, to digest the organic matter. There will be no change to the plastic debris, which is collected and analyzed. The physical and chemical methods are simple and easy to execute, but the major limitations are that they can be time consuming and a lot more samples may be wasted than is necessary, whilst the accuracy of the interpretation may be compromised. Advanced technique is a necessity to yield better and accurate analyses, in a shorter period of time (Lehner et al. 2019).

2.2.2 Advanced Instruments

Raman spectroscopy has been used to identify microplastics in microfibers. The monochromatic laser is applied as a source of light, where the sample is illuminated at 500 and 800 nm wavelength. The light interacts with the sample molecules and atoms (low-frequency interactions) and is backscattered, resulting in the frequency differences as compared to the incident light. This is called Raman shift, which is easily identified, and generates the Raman spectra. The large microplastic polymer spectra can be easily identified by comparing with the reference one, called “surface technique.” When Raman spectroscopy is coupled to the microscopy, the particle size of few micrometers can also be determined (i.e., below 1 μm) (Cole et al. 2015; Löder and Gerdts 2015).

Microplastics from different packaging released into mineral water have been analyzed by micro-Raman spectroscopy. The spectra obtained from the blue nitrile gloves, halogen blue, and polypropylene blue bottle cap exhibit almost the same spectra. The main polymers identified are polyethylene terephthalate, polyethylene, polystyrene, and polypropylene. Some of these particles also decompose and disappear due to the high-energy laser. The plastic particles are present at different

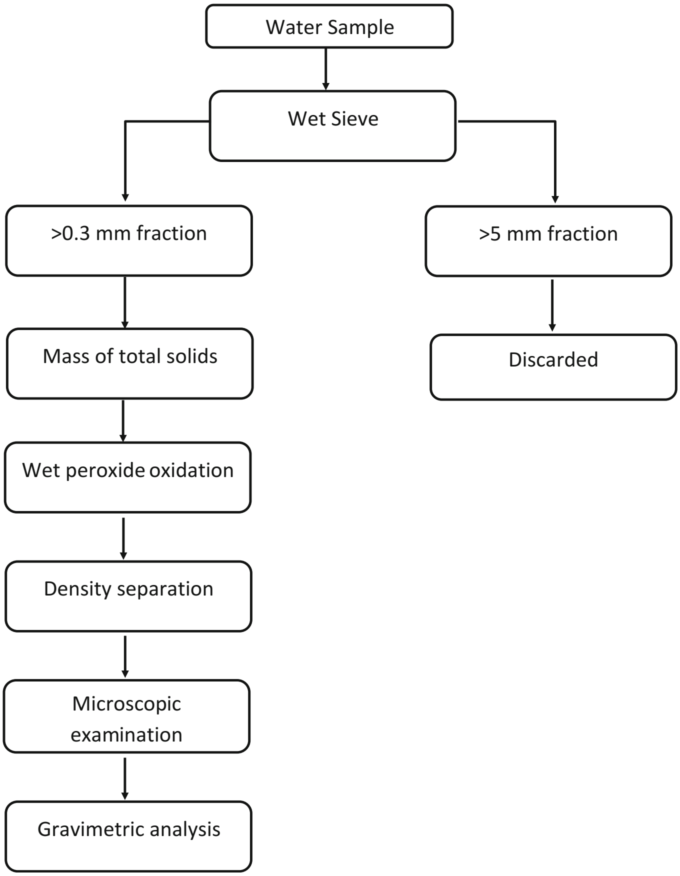


Fig. 2.10 Chemical method for the identification of plastic water contaminants. The type of microplastics examined are normally in the range of 0.3–5 mm (Modified from Nudo 2017)

percentages from different sources but are difficult to differentiate as appeared in the Raman spectroscopy (Fig. 2.11) (Schymanski et al. 2018).

Infrared technique can also be utilized for the determination of plastic particles by visualizing their distinctive infrared spectra. Fourier transform infrared spectroscopy and Raman spectroscopy are also used to provide complementary details of microparticles. Infrared radiations strike with the molecule of the sample and cause vibrational excitations, and these excitations depend upon the molecular structure and composition of the molecules at the specific wavelength. Infrared radiation energy depends upon the wavelength absorbed, which can be used for the determination of characteristic spectra. For the identification of microplastics, plastic polymers possess specific spectra and bands. Fourier transform infrared spectroscopy can be used for the identification of intensity of oxidation that provides information of physiochemical weathering of the sample molecules. Large particles can be

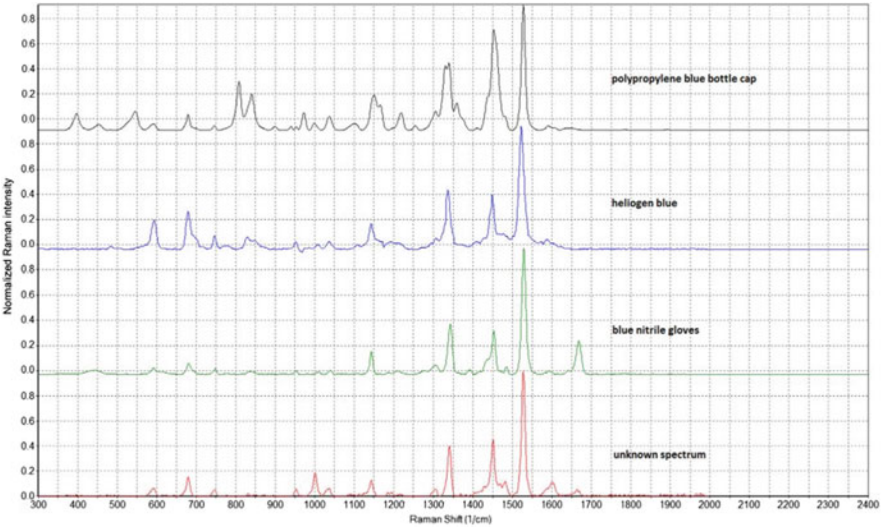


Fig. 2.11 Spectrum of unknown particles and its closest comparison to the databases. Plastic particles are difficult to differentiate and appear as unknown particles in the given Raman spectrum. (Reprinted with permission of [Analysis of microplastics in water by micro-Raman spectroscopy: Release of plastic particles from different packaging into mineral water, Schymanski et al., Elsevier] from Schymanski et al. 2018)

identified by Fourier transform infrared spectroscopy technique with high accuracy. For the identification of small size particles, Fourier transform infrared spectroscopy/microscopy technique is used. But this technique cannot analyze particle less than 20 µm (Löder and Gerdts 2015).

Mass spectroscopy when combined with the pyrolysis-gas chromatography is used to get the chemical arrangement of the microplastics by investigating their thermally-degraded products (Fries et al. 2013). This can be used to determine the type of polymer, by correlating their combustion product with a reference (Fries et al. 2013). Additives can be examined concurrently using a pyrolysis-gas chromatography/mass spectrometry runs, if the thermal desorption occurs before the last step of the pyrolysis. This is suitable for the lower-sized microparticles. The analysis of one particle per run can be done by this technique but not for the bulky particles (Löder and Gerdts 2015). Different techniques can be used to quantify the marine water plastic contaminants (Fig. 2.12) (Kroon et al. 2018), which include the microscopic photography, Fourier transform infrared spectroscopy, stereomicroscopic visual sorting, and attenuated total reflectance.

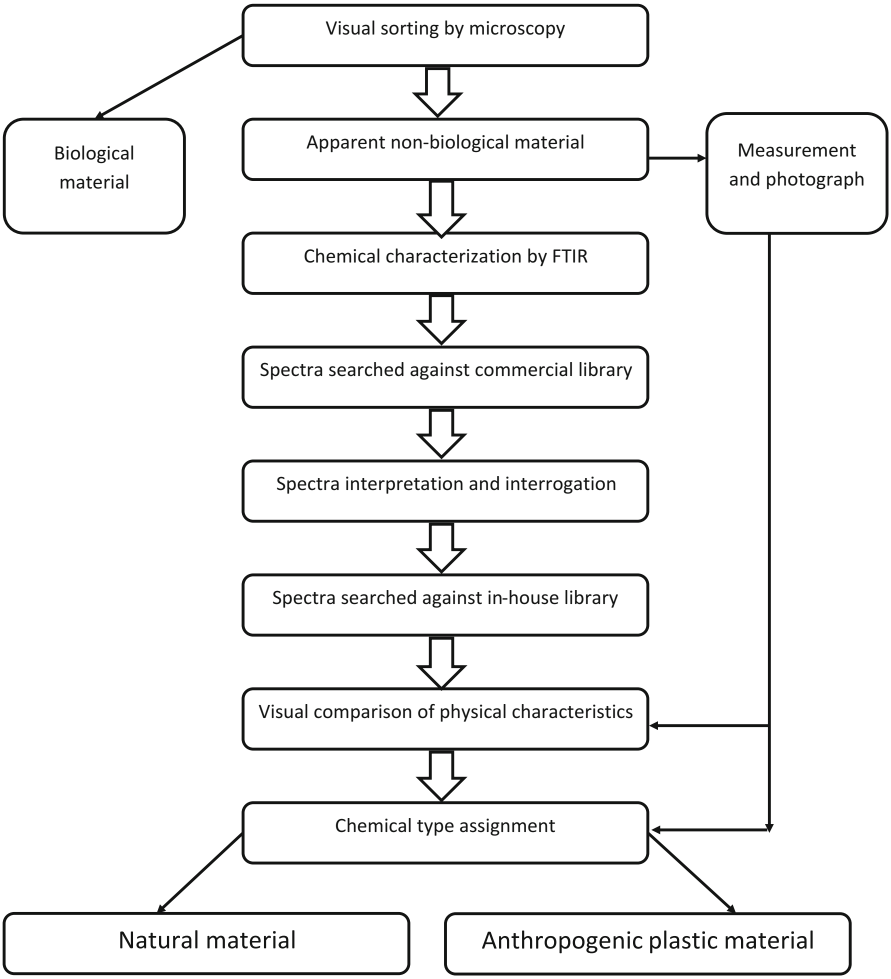


Fig. 2.12 Advanced methods for the analysis of plastic water contaminants. Materials are classified into either natural materials or anthropogenic plastic materials (*FTIR* Fourier transform infrared spectroscopy) (Modified from Kroon et al. 2018).

2.3 The Impacts of Plastic Ingestions

2.3.1 Effects on Human, Wildlife, and the Environment

Many chemicals from which plastics are synthesized, are toxic, and have negative effects on human health. The drinking water bottles are commonly made of polyethylene terephthalate, and these may have the chemicals leached out and mixed with the water (Schymanski et al. 2018). The high-density polyethylene used in the packaging of milk, detergent, and oil, when trashed, could cause pollution and emit harmful chemicals. Furthermore, although cheap and therefore easily available, plastics do not decompose easily (Smith et al. 2018). These toxic chemicals, which include phthalates, bisphenol A, and other by-products or compounds of plastic degradations, may be ingested, or taken up through skin contact. When a plastic particle is introduced into the atmosphere, there is a possibility that other contaminants may get attached to the particles and act as carriers because of their large surface areas. To understand the impacts of plastics, the exposure to plastics and the diverse exposure pathways that affect human health must be understood (Fig. 2.13). Figure 2.14 shows the impact of plastic pollution which can cause the pollution of soil, air, and water and eventually affects human health. The harmful effects of plastics may depend upon the plastic types and shapes, the sizes such as the macro-, micro-, and nanoplastics, the degree of hydrophobicity and the source of exposure. Nanoplastics for example can penetrate the digestive tract, affect the reproductive system, nervous system and the lung, leading to respiratory diseases or cancer (Isangedighi et al. 2018). The microplastics are not degradable and could remain in the body until secreted. When penetrating the gastrointestinal tract, microplastics could damage the epithelial human cells, affect the immune system and enhance the inflammation in the gut (Waring et al. 2018). The contamination in aquatic environment

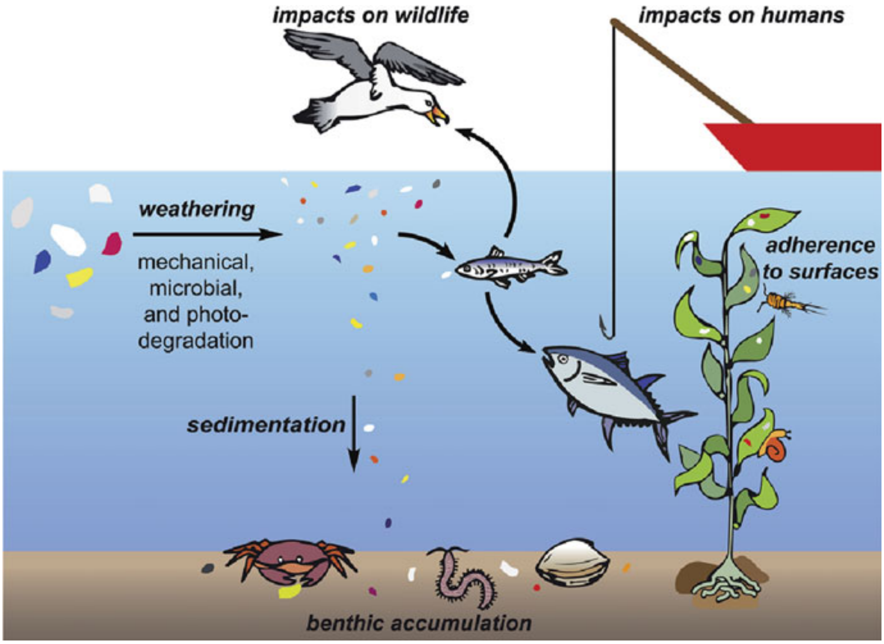


Fig. 2.13 Effect of microplastic and nanoplastic. Plastic due to weathering via mechanical or photodegradation sediments as well as taken up by aquatic life which will affect human health. (Reprinted with permission of [Research highlights: impacts of microplastics on plankton, Lin, RSC publisher] from Lin 2016)

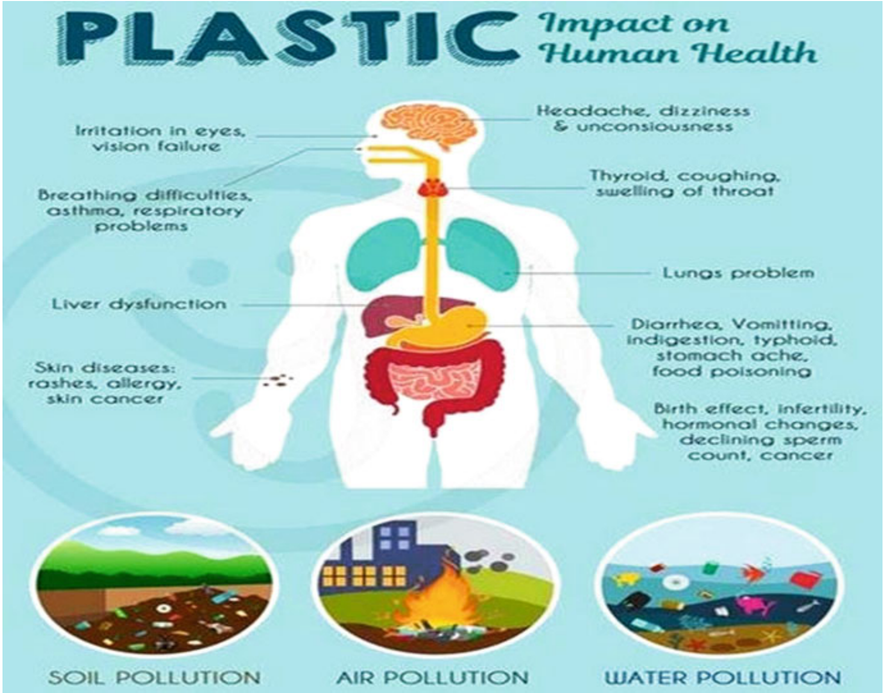


Fig. 2.14 Plastic pollution which causes the pollution of soil, water, and air that affects human health. (Reprinted with permission of [Toxic effects of plastic on human health and environment : A consequences of healthrisk assessment in Bangladesh, Proshad et al., Attribution 3.0 Unported (CC by 3.0)] from Proshad et al. 2017)

leads to the generation of reactive oxygen species, with the capacity to damage the internal organs, liver, and circulatory systems in the fishes and other marine organisms. The consumption of the contaminated seafood by humans, consequently paves the way for the interaction of the toxic elements with the human body and his surroundings. The more concentrated plastic particles are exhibiting more harmful effects (Hahladakis et al. 2018), as there are higher possibilities for the common additives such as Bisphenol A (BPA) or Phthalates to leak out in higher doses in specific tissues or organs. BPA has been first prepared in 1891, and the commercial production starts in the 1950s. It has found large scale applications in the manufacturing of engineering plastics, food cans, metal equipment, dental items, cosmetics, toys, and as additives in polyvinyl chloride (Table 2.6). BPA may be leached out during the washing processes, and when kept in the containers, the BPA may get mixed with the food. The main pathway of interaction with BPA is therefore through food, although inhalation is also a possibility, which can all lead to fatality if absorbed in high doses (Halden 2010). BPA is an endocrine disruptor (END), affects the reproductive system and immune system, and damages the neurological developmental

Table 2.6 Concentration of Bisphenol A (BPA)

Food items	Food composite	BPA (ng/g)
Dairy	Milk (evaporated, canned), cheese, butter	15.3, 2.24, 0.53
Meat	Meat, canned	10.50
Vegetables	Baked beans, canned	23.5
Fish	Fish, canned	106.00

Modified from Almeida et al. (2018)

Table 2.7 The well-known phthalates, their source of exposure, and health-related issues (Kumar 2018)

Phthalates	Source of exposure	Health-related issues
Dimethyl phthalate	Industrial-scale production of petroleum In bug sprays, plasticizer	Acute toxicity (fetal) Musculoskeletal system disturbance Ear and eye anomalies
Diethyl phthalate	Toiletries, e.g., soaps, shampoos, beauty creams, and cosmetics Medicines Industrial solvent Insects killer	Growth rate reduction Minimize food intake ability
Dibutyl phthalate	Adhesives Toiletries Industrial solvents Medicines	Lower sperm production (until exposed to additives and returned to near normal after closure) Rashes, itchiness, redness
Butyl benzyl phthalate	Vinyl composition tiles Viscous binders and adhesives Toiletries Artificial leather	Testicular toxicity Defects of the male genital tract Less anogenital distance Accentuate steroid hormone levels
Diethylhexyl phthalate	Soft plastics for household items, toys, and lightweight floor tiles (velvety touch) Blood bags Utensils for food storage and packing	Liver cancer Testicular toxicity Polycystic ovary syndrome (PCOS) Intrauterine growth restriction (IUGR)

especially during early prenatal developmental stages when organs are forming, or causing hormonal imbalance and low fertility (Proshad et al. 2017). Phthalates is another additive, used as plasticizer. There are three isomers – ortho-isomer isophthalic acid, meta-isomer phthalic acid, and terephthalic acid of phthalic acid. The well-known phthalates, their source of exposure, and the health-related issues are shown in Table 2.7 (Benjamin et al. 2015), and the structural formulas are illustrated in Fig. 2.15. Phthalic acid esters are commonly added during the manufacturing of polyvinyl chloride, terephthalic acid esters are used in the making of bottles for drinks and juices, and isophthalic acid esters are used in resins (Pecht et al. 2018). These may also later find wide application in cosmetics and personal care, food packaging, plastic pipes, raincoats, vinyl flooring, and adhesives. Phthalates can get into the human body through ingestion and also contaminated

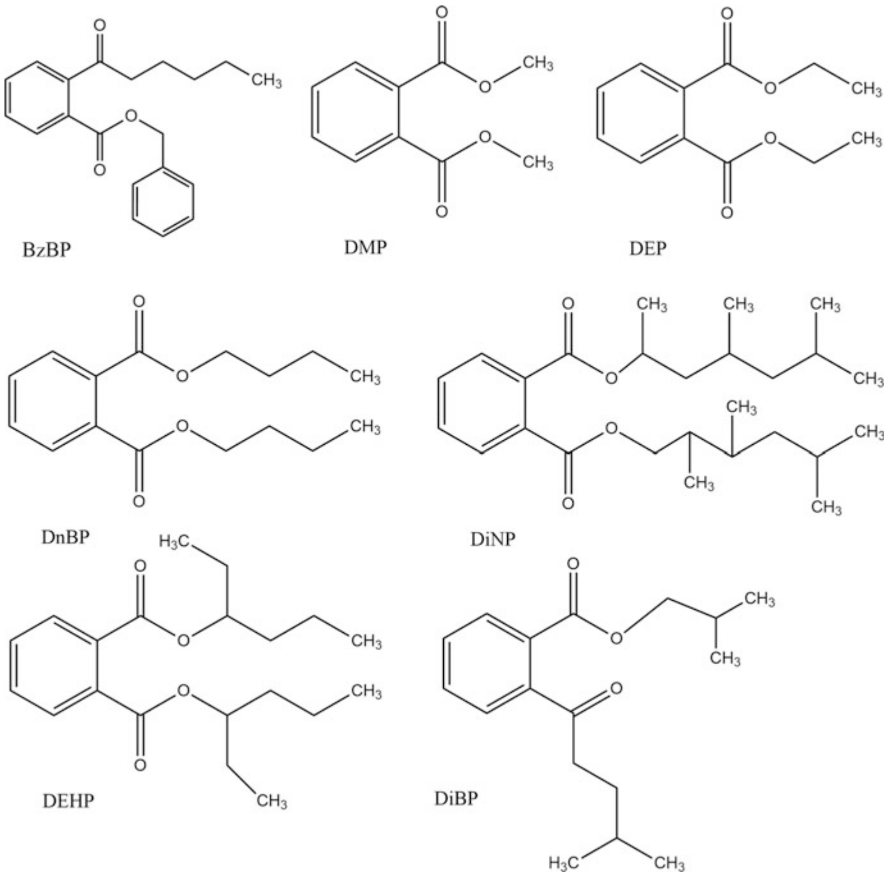


Fig. 2.15 Different types of phthalates with their structural formulas (BzBP, benzyl butyl phthalate; DMP, dimethyl phthalate; DEP, diethyl phthalate; DnBP, di-n-butyl phthalate; DiNP, diisononyl phthalate; DEHP, diethylhexyl phthalate; DiBP, di-isobutyl phthalate). (Modified from Pecht et al. 2018)

soil and air. Phthalates are carcinogenic and can affect the immune sytem, reproduction and development in the human body. The well-known endocrine disruptor is diethylhexyl phthalate (Lu et al. 2018), and the compounds causing endocrine disruption, including BPA, have also been linked to causing hormonal imbalance and increased breast cancer incidence (Shafei et al. 2018). The tubes and catheters used during hemodialysis are often made up of polyvinyl chloride and additives are used to enhance the utility of the polymer. As a result, dialysis patients may interact with phthalates because the tubes and containers used during the blood transfusion also contain considerable amount of phthalates (Tereshchenko and Posnack 2018). Fig. 2.16 shows the types of diseases caused by various plastic additives. These additives mainly target reproductive/endocrine, brain/nervous, and pulmonary cardiovascular organs (Shafei et al. 2018).

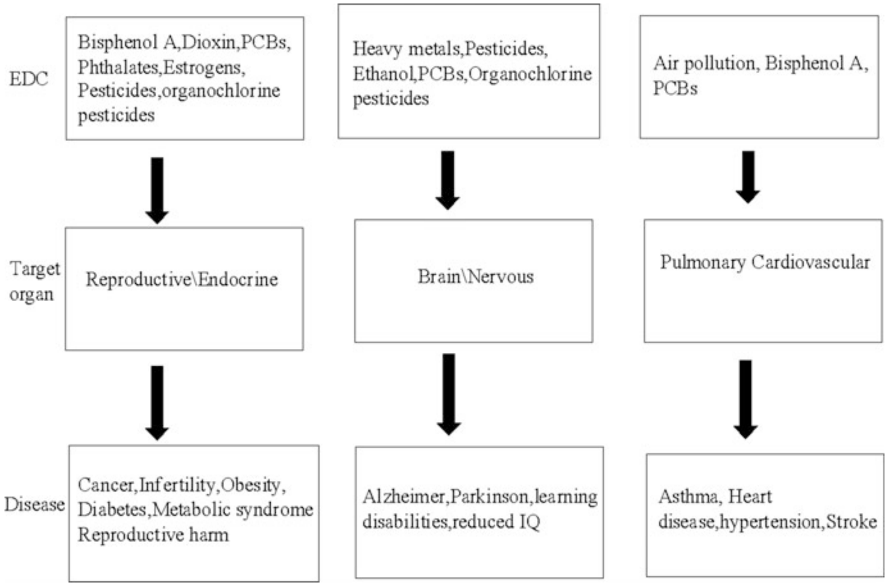


Fig. 2.16 Types of diseases caused by various plastic additives. These additives mainly target reproductive/endocrine, brain/nervous, and pulmonary cardiovascular organs. (*ECD* Erdheim-Chester disease, *PCBs* polychlorinated biphenyls, *IQ* intelligence quotient). (Modified from Shafei et al. 2018)

Living organisms and animals may ingest plastics like active feeding or through the foods containing plastic. Macroplastics are harmful for large animals like turtles as they eat the plastic bags and sheets which later block their intestinal track. The animals may be entangled and unable to free themselves. The slow degradation of plastic may be helpful in the surgical implantation of different tools in the bones of rat and bone marrow, coated with radioactive material, which have resulted in less problem after 8–12 months, and 25% losses over 2 years of life span (Waring et al. 2018). Plastic wastes have direct impact on the fishing and tourism industries (Mee et al. 2007). The unused nets from fishing industries have become plastic wastes which are floating on the water source, and later colonized by the marine organisms and other alien species (Barnes 2005; Brown and Macfadyen 2007; David et al. 1985; Gregory 2009; Moore 2008). The ingestion of plastic wastes by the sea birds may eventually cause the extinction of the species (Thompson et al. 2009).

2.3.2 *Effects on Marine Life*

Different water samples taken from different sources show that the distribution of plastics may also depend upon the area where there are air and water currents even in the absence of wastewater disposal system nearby (Hidalgo-Ruz et al. 2012; Van

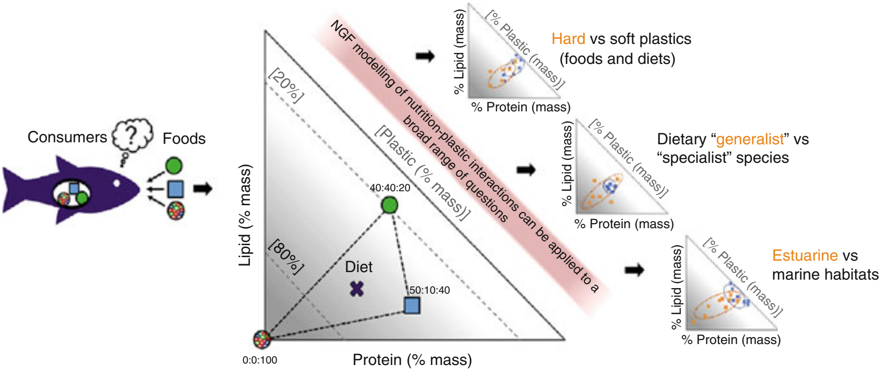


Fig. 2.17 Plastic ingestion in wild aquatic organism through active feeding or the foods containing plastics (*NGF* Nutritional Geometric Framework). (Reprinted with permission of [A nutritional perspective on plastic ingestion in wildlife, Machovsky et al., Elsevier Publisher] from Machovsky Capuska et al. 2019)

Cauwenberghe et al. 2015). Marine animals are active feeders of plastic as shown in Fig. 2.17 (Machovsky Capuska et al. 2019; Wright et al. 2013).

Plastic waste materials have been ingested by small organisms to larger animals of the aquatic ecosystem like whales. It causes many problems like reduced reproduction and growth of the aquatic life and reduced eating and feeding rates, and eventually death. Table 2.8 describes the impacts of plastics on the aquatic life.

Microalga are the primary food source of some marine organisms. The effects of 2 µm particle size of polystyrene on microalgae (*Tisochrysis lutea*, *Heterocapsa triquetra*, and *Chaetoceros neogracile*) have been investigated where the combinations of the cells with the polystyrene particles have been observed. Microparticles of the plastic and lead may also be ingested by the aquatic life (Long et al. 2017; Lagarde et al. 2016).

Zooplankton are the aquatic animals which feed on the plants in the aquatic ecosystem which is called the phytoplankton. They all have a significant role in the recycling of carbon and nitrogen. The microplastics may affect the recycling process by disturbing the tiny food web. The microplastics have impacts on the growth, feeding, and the reproduction of *Calanus helgolandicus* (Cole et al. 2013; 2015).

When the plastics are in contact with human food web, this could directly or indirectly affect human health as illustrated in Fig. 2.13.

When plastics are in the depth or on the surface of water bodies, they are converted into smaller particles and go to the sediments of the water bodies and are ingested by the plants through their root system. These microparticles have been detected in the plant tissues (Auta et al. 2017; Carbery et al. 2018).

The aquatic animals and birds may take up the plastic particles by drinking water or through the food chain. Then plastics become an integral part of the living organisms associated with the aquatic food web.

Table 2.8 Effects of different polymers on the aquatic organisms

Organisms	Type of polymer	Effects	References
Daphnia magna	Polystyrene	Small plastic particles are present in the intestine and transferred to the oil storages	Rosenkranz et al. (2009)
_	Polyethylene	It increases their life span but decreases their recovery	Jemec et al. (2016)
_	Polyethylene terephthalate	Intake of microparticles causes inactivaty with time	Rehse et al. (2016)
_	Polystyrene	Their body size reduced, reproduction level changed, and also causing a decrease in size and formation of neonates	Besseling et al. (2014)
Daphnia magna (planktonic crustacean)	Methyl methacrylate	Ingestion and removal of significant amount of nanoparticles	Booth et al. (2016)
Copepod and decapod crustaceans *Calanus helgolandicus*, *Oithona similis*	Polystyrene Polyethylene Nylon	Energy deficit in all species except *O. similis*	Cole et al. (2013)
Marine copepod (*Paracyclopina nana*)	Polystyrene	Developmental delays and delayed molting, increased reactive oxygen species (ROS) levels	Jeong et al. (2017)
Euryhaline wheel animalcules (*B. plicatilis*)	Polystyrene	Reduction in growth, reproduction and life span	Jeong et al. (2016)
Warm-temperate copepod (*C. helgolandicus*)	Polystyrene	Changes in feeding and reproduction	Cole et al. (2015)
Tigriopusa japonicus	Polystyrene	Death and reduction in fertility	Lee et al. (2013)
Amphipod (*Hyalella azteca*)	Polypropylene	Reduction in reproduction and growth	Talley et al. (2015)
Platorchestia smithi	Polyethylene	Taking longer time to change their habitats	Tosetto (2016)
Arenicola marina	Polyethylene, polyvinyl chloride	Metabolism rate increased, decreased biomass	Green et al. (2016)
Barnacles (*Megabalanus azoricus*)	Polyvinyl chloride	Reduced oxygen consumption	Hentschel (2015)
Artemia franciscana	Polystyrene	Inactivitiy and long-lasting microparticle retention time	Bergami et al. (2016)
Blue mussel (*Mytilus edulis*)	Polystyrene	Increase in urine and reduction in filtration	Wegner et al. (2012)
Pacific oyster (*Crassostrea gigas*)		Reduced number of oocytes and reproduction from affected parents	Sussarellu et al. (2016)

(continued)

Table 2.8 (continued)

Organisms	Type of polymer	Effects	References
Ostrea edulis	Polyethylene, Polylactic acid	Total number of living organisms decreased	Green (2016)
Shore crabs (*Carcinus maenas*)	Polystyrene	Microparticles present in gills, Na ion concentration is less than normal, and Ca ion concentration is increased	Watts et al. (2016)

The microplastics have been found in the scats of the seal *Arctocephalus tropicalis* as well as in *Arctocephalus gazella* which are eating the pelagic fish *Electrona subaspera* that has ingested the microplastic (Eriksson and Burton 2003; Van Cauwenberghe and Janssen 2014).

The aquatic animals eaten up by humans without removing the digestive track, may also inadvertently ingest the microplastic as in the case of eating *Nephrops norvegicus,* a crustacean from the Glyde Sea (Alomar and Deudero 2017; Murray and Cowie 2011; Wang et al. 2019).

2.4 Remediation

2.4.1 Primary Recycling

For recycling and reprocessing of plastic litter, the four main techniques are mechanical reprocessing (primary and secondary), thermal recuperation, and chemical depolymerization. It is actually difficult to recycle plastic technically and economically due to the poor waste separation, high cost of energy, lack of fiscal incentives, contamination by several other materials, and unstable market outlook (Hahladakis et al. 2018). For industrial-scale production of recycled industrial plastic, the thermoplastic waste is recycled through mechanical recycling process. This method gives reliable quality control, and consistent source of feedstocks. The propylene wastes have been mechanically recycled into propylene granules as shown in Fig. 2.18. Melt spinning process is another production process to recycle the industrial plastic wastes as illustrated in Fig. 2.19. The recycled plastic pellets are melted in a special compartment called extruder where the temperature ranges from 218 to 235 °C (Tuladhar and Yin 2019). Molten filaments from the extruder are then cooled and solidified using cold-water bath. At 120–150 °C, these fibers are converted into tiny cross-sectional parts through an oven. These monofilament fibers are further processed by passing through the rollers, and their surfaces are further processed using the special indent roller. These indents improve the characteristics of the fibers such as the compatibility (bonding ability) with the concrete matrix. When the indentation process is completed, the fibers are then sliced into appropriate length of 50 mm. Through the melt spinning process, the polypropylene

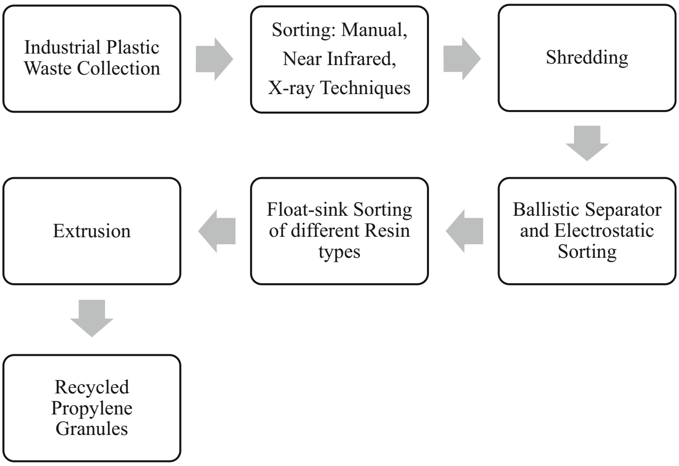


Fig. 2.18 Mechanical reprocessing of industrial plastic wastes into propylene. This method gives reliable quality control, and the polypropylene wastes are 100% recycled. (Modified from Tuladhar and Yin 2019).

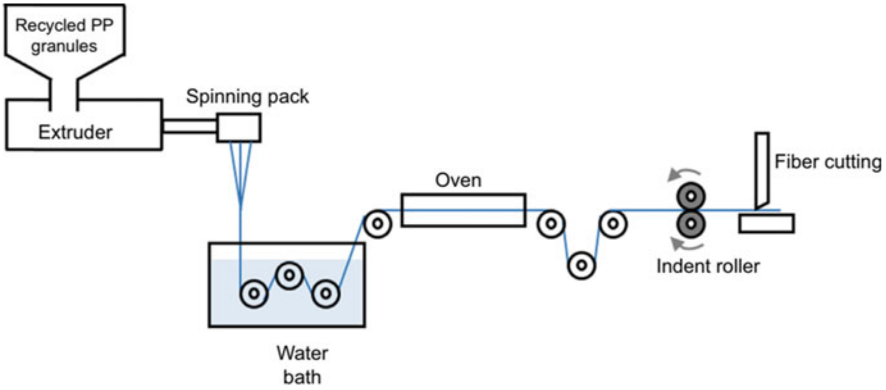


Fig. 2.19 Production of recycled plastic fiber by melt spinning. Recycled PP (polypropylene) are extruded by extruder with a spinning pack and then cooled and solidified before forming cross-sectional fibers in the oven and are further processed by indent roller and fiber cutter. (Reprinted with permission of [Production of recycled polypropylene fibers from industrial plastic waste through melt spinning process, Tuladhar et al., Attribution 3.0 Unported (CC by 3.0)] from Tuladhar and Yin 2019)

granules from the industrial plastic wastes are 100% recycled into the polypropylene fibers (Tuladhar and Yin 2019). Essential recycling is also called re-expulsion, which means re-modeling the waste materials into a new shape. Different methods of plastic moulding into its original shape, or giving the new version of the used plastics having the same characteristics. In the United Kingdom, about 250,000 tons of used plastic have been made to be re-used especially for the used-plastics from shopping. The challenge is in getting the family and community units to develop collection centre with waste segregation in place especially when involving mixed plastic wastes from various sources. A workable framework can be devised considering the social, economic and environmental benefits as a whole that can be gained (Al Salem et al. 2009; Pruter 1987).

2.4.2 Mechanical Recycling

Mechanical recycling methods have been used to reduce the time in getting the recycled fresh-products and the resources required which are the old plastics. The three important steps involved are processing, granulating, and cutting. The homogeneous plastic wastes are used to produce the products with almost similar or slighly lower in terms of durability and mechanical strength, than the original product. During cutting process, bigger plastics are broken down into smaller plastics using a saw or shear. Strong blower is used to remove impurities from plastics. The plastic drops are separated in a skimming container based on sizes and thickness. Those plastics which consist of only one type of polymer are further ground. The plastics are washed and dried as to the form required. In the synthesis process, washing is done in specific cases with different chemicals for that special surface characteristic of the plastic. With the appearance of colors, the whole batch is ready to be marketed. Otherwise, the recycled plastics can turned into pellets and beads, packed and sold (Putun et al. 2008). Mechanical recycling is a green but can be expensive due to the high energy requirement for cleaning, transportation, and raw material or product sorting (Panda et al. 2010).

The polyethylene terephthalate wastes have been converted into smaller particles, washed several times with water, before being put into the centrifugal machine. The waste products like dust are removed in several steps. During crushing, particle sizes of 10–14 mm, and powdered forms of plastics are formed. Then, heating at the prescribed conditions further remove all the pollutants. In the vibratory separator, extra water is removed and a few modifiers and chemicals are added to get the specific plastic properties. The recycled plastic materials are cooled in the air, and the smaller particles are removed by using a sifter (Saikia and de Brito 2012).

2.4.3 Degradation of Thermoplastic Polyolefin and Additives

Generally, polyolefin cannot be decomposed by microorganisms as they are hydrophobic in nature, and their breakdown in the absence of water cannot take place. The antioxidants introduced during the manufacturing prevent the plastics from being broken down into smaller particles. Furthermore there are additives that could further confer mechanical strength to some plastics. Those compounds which can cause oxidation can convert the plastics to be water-loving carbon chains. In the presence of water, polyolefin is broken down. Polyethylene for example is broken down easily in the presence of oxidative agents at the right conditions (Zheng et al. 2005). The removal of bisphenol A from the environment can be carried out using the nonthermal plasma technique, for the degradation and breaking the chemical bond and functional groups. Solution plasma process is reported to be an effective way and implementable in the industrial scale to degrade bisphenol A, and the byproducts are simple (MubarakAli et al. 2019).

2.4.4 Photodegradation and Biodegradation

Plastics are resistant to breakage and biodegradation due to the long-chain hydrocarbons with not so many functional groups. Due to the lack of double bonds and other functionalities, plastics cannot be used as the source of food by microorganisms. However, photooxidation can convert plastics into smaller fractions, from macroplastic to microplastic and then to nanoplastic (Mason et al. 2018). With the passage of time, the ultraviolet light could also convert plastics into simpler fragments. The photodegradation of plastics nonetheless could affect the land fertility as the plastic fragments pollute the environment, soil and water (Jambeck et al. 2015), especially so in the marine ecosystem (Lambert 2018).

Biodegradable plastics could reduce the pollution caused by the non-biodegradable plastics. Environment-friendly plastics like biosynthesized polyhydroxyalkanoate, starch-based, or cellulosic polymers should be developed as alternatives to fossil-based plastics. Biodegradable plastic utilization and safety, at the end, requires proper waste management and community involvement (Rujnic Sokele and Pilipovic 2017). Some microorganisms such as fungi as well as bacteria could degrade both bio-based and fossil-based plastics, utilizing enzymes such as lipases, proteases, and cutinases. The microorganisms convert the plastic polymers into monomers or simpler units. These monomers can be further utilized in various reactions and proved less harmful to the environment than the untreated plastic polymers (Ahmed et al. 2018). Phthalates can be degraded by both biotic and abiotic systems. The abiotic degradation involves photochemical degradation and hydrolysis which are quicker. Biodegradation can also efficiently degrade phthalates in the environment but at slower rate. Many bacteria, some fungi, algae, and yeast are proven to be effective for phthalate degradation under both aerobic and anaerobic conditions. Diethylhexyl phthalate is another harmful additives which may find its way through air, water, and packaged food products. The alternative to diethylhexyl phthalate is the use of polyvinyl chloride-free products or softeners that are flexible without any leaching, or toxicity, but higher durability (Rowdhwal and Chen 2018).

2.4.5 Solutions to Marine Plastic Debris

To solve the marine plastic debris in the long term, policies must be formulated, implemented, monitored, and applied in different areas of management and daily life such as law and regulation on use of safe chemicals, product design, coastal management, waste management, and consumer whistle blowing and protection. To minimize or reduce plastic garbage in the marine ecosystem, concerted efforts must be made to lessen the quantity of plastics entering the ocean, reduce the damage caused by plastics, and clean up the plastic debris already present in the ocean and the coastlines. Further research in the greener production, consumption, disposal, and impacts of plastics on the surrounding areas, and the environment, must be stepped-up. Latest technology can be harnessed for the reduction of harms caused by plastics, or for the collection, identification and cleaning of plastics to mitigate any potential hazards.

The origin of aquatic plastic wastes is the customer products and plastic packing and containers. Production-consumption-waste chain is a linear, one way track, which ends in the ocean. A significant surge of interest can be seen in the recycling of wastes and plastics, but the recycled material is perceived as having inferior and substandard quality when compared to the new or virgin material. The shift of focus to the development of biopolymers that are biodegradable and as alternatives to plastics is one of the strategy. There is however a genuine concern about the economics of the bioplastic production. Also the possibility of the by-products from the degradation of the bioplastics into micro- and nano-bioplastics later may also pose a threat to the living organisms and eco-system, especially if exceeding the threshold levels. Hence, the emphasis should be on the biocompatible, non-toxic and degrable plastics. Another potential route is to change the design of products, such that it will lower the plastic content, but with increased durability, reusability and recyclability. The product design should incorporate those elements without affecting the product quality and usability, such as producing textile that sheds less fibers and dyes in the washing process to reduce the environmental load.

Putting a complete ban or limiting the availability of plastic goods, or imposing high taxes on plastic products are the best methods to lessen the plastic debris. The use of microbeads, plastic straws, and non-environmentally-friendly shopping begs and utensils should be met with some form of economic penalties, on the producers and the customers alike. Incentives should be provided for the recovery, recycling, and deposition of the used plastic products such as the plastic containers and bottles, at the community-based collection centers. The monitoring and evaluation standards should be put in place on waste segregation and the scale of the debris inputs. Research on the waste control before and after the product ban, the use of definite sampling and statistics, with record and documentation, should be promoted and supported, to ensure the success of the policy implemented.

2.4.6 *Plastic Waste Management*

Plastics have become an essential part of our lives, but the marine plastic pollution are now slowly taking its toll with great potential for the global ecological, social, and economic disaster, if not handled properly (Beaumont et al. 2019). To make the environment free of plastic toxicity, it is necessary to use proper disposal methods and to spread awareness regarding the toxicity and proper plastic handling. Wastes of anthropogenic origin, especially plastics, dumped into the water bodies, directly and indirectly, disturbs the marine organisms and marine ecosystem. The first step towards remediation and control measures is the knowledge and understanding of the impacts and damage caused by the marine litter (Barboza et al. 2019). Most of the household organic waste and plastic wastes may be buried in landfills or incinerated, and recycling constitutes only a small percentage, or probably better in the developed world. Landfilling is no longer practical as some facilities can no longer cope with the high volume to weight ratio of the wastes generated on the daily basis. There are associated hazards with the production of greenhouse gases and methane released into the atmosphere, unpleasing odour, and the leachates that may seep into the groundwater and small rivers. The facilities as shown in Fig. 2.20, for the disposal of municipal and industrial plastic debris based on energy recovery, chemical recovery, and reprocessing (Panda et al. 2010), should be developed to replace landfilling, taking into account plastic sorting and recycling.

Simple and immediate daily practices on Reduce, Reuse, Recycle (3R) concept should be promoted and popularized. These include avoiding food items and beverages that are available in plastic bottles/packing; using products having minimum or recyclable packing; purchasing in whole sum to lessen the nessity for extra packaging; purchasing recycled products and using recyclable shopping bags; and bringing own mug and container, instead of using disposable items (Wabnitz and Nichols 2010). There is a significant scope for plastic recycling, especially for

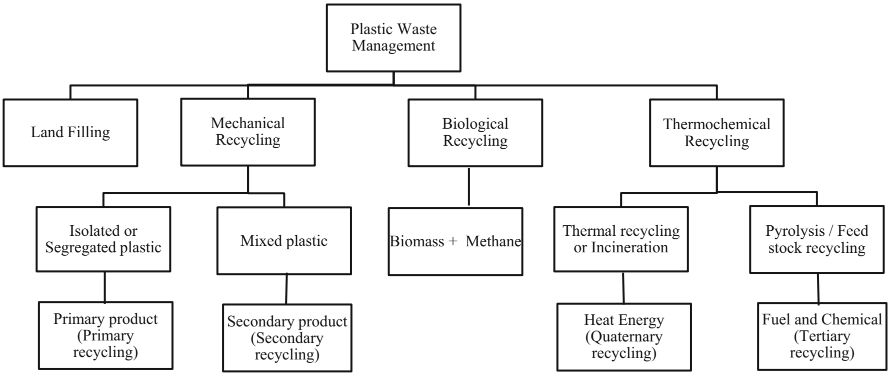


Fig. 2.20 Different paths for the management of plastic litter such as landfilling, mechanical recycling, biological recycling, and thermochemical recycling (Modified from Panda et al. 2010).

the manufacturing of materials for utilization in vehicles and electronic equipments, without compromising the safety and quality aspects. Clear labeling of recyclable plastics could result in efficient separation by the consumers. This would minimize expenditures on waste sorting and separation. In this way, the recycling program efficiency can be enhanced, and the amount that gets recycled can be maximized. In western Europe, mechanical reprocessing of plastics increases at 7% rate annually (Thompson et al. 2009). Scientific data from the field can provide estimation on the thresholds of the ecosystem disturbance, as evidence-based strategy for the creation of binding international agreements with broad acceptability to tackle the plastic crisis (Mendenhall 2018). Measures such as restriction on entering highly polluted areas, control of the sea border, and outreach program to raise ecological awareness of the local populations are now a must to safeguard the ecosystem (Tursi et al. 2018). Some oceanic mammals are bioindicators that could provide clues on the extent of pollution and for eventual steps to be taken in the marine ecosystem remediation and conservation (Germanov et al. 2018). General public must be engaged for them to be aware of the seriousness and extent of the marine plastic pollution, and also on issues related to the chemical pollution and ocean acidification (Panti et al. 2019).

2.5 Conclusion

Plastics play a crucial role in our daily life. However, uncontrolled use and human consumption and activities have generated problems with plastic pollution, impacting human health, environment, and marine ecosystem. The harmful, toxic effects of plastics are dependant upon the sizes, shapes, and source of exposure. Nanoplastics could penetrate and cause disruption to human body functions. Plastic additives such as bisphenol A and phthalates can cause endocrine disruption, leading to many deadly diseases. The remedies may lie in turning to a more biodegradable and biocompatible plastics based on biopolymers that are safer and nontoxic to the environment. Proper plastic disposal methods must be put in place and greater awareness should be made with regards to the toxicity and handling of plastics. Plastic recycling and reuse must be promoted and minimizing the use of plastics must be encouraged. Clear policy should be formulated, implemented, and enforced with the incentives for plastic reduction, reuse and recycle, within circular economy framework. This small ripple on creating awareness about plastic pollution and remediation could hopefully turn into small waves, the small waves into big waves, the big waves into giant waves, and the giant waves later turn the tides, and wash the pollutants and contaminants away.

References

Ahmed T, Shahid M, Azeem F, Rasul I, Shah AA, Noman M, Hameed A, Manzoor N, Manzoor I, Muhammad S (2018) Biodegradation of plastics: current scenario and future prospects for environmental safety. Environ Sci Pollut Res Int 25(8):7287–7298. https://doi.org/10.1007/s11356-018-1234-9

Al Salem SM, Lettieri P, Baeyens J (2009) Recycling and recovery routes of plastic solid waste (PSW): a review. Waste Manag 29(10):2625–2643. https://doi.org/10.1016/j.wasman.2009.06.004

Almeida S, Raposo A, Almeida Gonzalez M, Carrascosa C (2018) Bisphenol a: food exposure and impact on human health. Compr Rev Food Sci Food Saf 17(6):1503–1517. https://doi.org/10.1111/1541-4337.12388

Alomar C, Deudero S (2017) Evidence of microplastic ingestion in the shark Galeus melastomus Rafinesque, 1810 in the continental shelf off the western Mediterranean Sea. Environ Pollut 223:223–229. https://doi.org/10.1016/j.envpol.2017.01.015

Andrady AL (2017) The plastic in microplastics: a review. Mar Pollut Bull 119(1):12–22. https://doi.org/10.1016/j.marpolbul.2017.01.082

Auta HS, Emenike CU, Fauziah SH (2017) Distribution and importance of microplastics in the marine environment: a review of the sources, fate, effects, and potential solutions. Environ Int 102:165–176. https://doi.org/10.1016/j.envint.2017.02.013

Barboza LGA, Cózar A, Gimenez BCG, Barros TL, Kershaw PJ, Guilhermino L (2019) Macroplastics pollution in the marine environment. In: World seas: an environmental evaluation. Academic, Cambridge, MA, pp 305–328. https://doi.org/10.1016/b978-0-12-805052-1.00019-x

Barnes DK (2005) Remote islands reveal rapid rise of southern hemisphere, sea debris. ScientificWorldJournal 5:915–921. https://doi.org/10.1100/tsw.2005.120

Beaumont NJ, Aanesen M, Austen MC, Börger T, Clark JR, Cole M, Hooper T, Lindeque PK, Pascoe C, Wyles KJ (2019) Global ecological, social and economic impacts of marine plastic. J Mar Pollut Bull 142:189–195. https://doi.org/10.1016/j.marpolbul.2019.03.022

Benjamin S, Pradeep S, Josh MS, Kumar S, Masai E (2015) A monograph on the remediation of hazardous phthalates. J Hazard Mater 298:58–72. https://doi.org/10.1016/j.jhazmat.2015.05.004

Bergami E, Bocci E, Vannuccini ML, Monopoli M, Salvati A, Dawson KA, Corsi I (2016) Nano-sized polystyrene affects feeding, behavior and physiology of brine shrimp Artemia franciscana larvae. Ecotoxicol Environ Saf 123:18–25. https://doi.org/10.1016/j.ecoenv.2015.09.021

Besseling E, Wang B, Lurling M, Koelmans AA (2014) Nanoplastic affects growth of S. obliquus and reproduction of D. magna. Environ Sci Technol 48(20):12336–12343. https://doi.org/10.1021/es503001d

Booth AM, Hansen BH, Frenzel M, Johnsen H, Altin D (2016) Uptake and toxicity of methylmethacrylate-based nanoplastic particles in aquatic organisms. Environ Toxicol Chem 35(7):1641–1649. https://doi.org/10.1002/etc.3076

Brems A, Baeyens J, Dewil R (2012) Recycling and recovery of post-consumer plastic solid waste in a European context. Therm Sci 16(3):669–685. https://doi.org/10.2298/Tsci120111121b

Brown J, Macfadyen G (2007) Ghost fishing in European waters: impacts and management responses. Mar Policy 31(4):488–504. https://doi.org/10.1016/j.marpol.2006.10.007

Carbery M, O'Connor W, Thavamani P (2018) Trophic transfer of microplastics and mixed contaminants in the marine food web and implications for human health. Environ Int 115:400–409. https://doi.org/10.1016/j.envint.2018.03.007

Chalmin P (2019) The history of plastics: from the Capitol to the Tarpeian Rock. J Field Actions Science Reports. J Field Actions (Special Issue 19), 6–11, http://journals.openedition.org/factsreports/5071

Clark JH, Aguado J, Serrano DP (1999) Introduction. In: Feedstock recycling of plastic wastes, pp 1–29. The Royal Society of Chemistry, https://doi.org/10.1039/9781847550804-00001

Codrington S (2005) Planet geography (6th edn). Solid Star Press. https://doi.org/10.1073/pnas.1602404113

Cole M, Lindeque P, Fileman E, Halsband C, Goodhead R, Moger J, Galloway TS (2013) Microplastic ingestion by zooplankton. Environ Sci Technol 47(12):6646–6655. https://doi.org/10.1021/es400663f

Cole M, Lindeque P, Fileman E, Halsband C, Galloway TS (2015) The impact of polystyrene microplastics on feeding, function and fecundity in the marine copepod Calanus helgolandicus. Environ Sci Technol 49(2):1130–1137. https://doi.org/10.1021/es504525u

David KA, Barnes FG, Thompson RC, Barlaz M (1985) Accumulation and fragmentation of plastic debris in global environments. Philos Trans R Soc B Biol Sci 364:1526. https://doi.org/10.1098/rstb.2008.0205

Eriksson C, Burton H (2003) Origins and biological accumulation of small plastic particles in fur seals from Macquarie Island. Ambio 32(6):380–384. https://doi.org/10.1579/0044-7447-32.6.380

Fries E, Dekiff JH, Willmeyer J, Nuelle MT, Ebert M, Remy D (2013) Identification of polymer types and additives in marine microplastic particles using pyrolysis-GC/MS and scanning electron microscopy. Environ Sci Process Impacts 15(10):1949–1956. https://doi.org/10.1039/c3em00214d

Gallo F, Fossi C, Weber R, Santillo D, Sousa J, Ingram I, Nadal A, Romano D (2018) Marine litter plastics and microplastics and their toxic chemicals components: the need for urgent preventive measures. Environ Sci Eur 30(1):13. https://doi.org/10.1186/s12302-018-0139-z

Germanov ES, Marshall AD, Bejder L, Fossi MC, Loneragan NR (2018) Microplastics: no small problem for filter-feeding megafauna. Trends Ecol Evol 33(4):227–232. https://doi.org/10.1016/j.tree.2018.01.005

Green DS (2016) Effects of microplastics on European flat oysters, Ostrea edulis and their associated benthic communities. Environ Pollut 216:95–103. https://doi.org/10.1016/j.envpol.2016.05.043

Green DS, Boots B, Sigwart J, Jiang S, Rocha C (2016) Effects of conventional and biodegradable microplastics on a marine ecosystem engineer (Arenicola marina) and sediment nutrient cycling. Environ Pollut 208(Pt B):426–434. https://doi.org/10.1016/j.envpol.2015.10.010

Gregory MR (2009) Environmental implications of plastic debris in marine settings—entanglement, ingestion, smothering, hangers-on, hitch-hiking and alien invasions. Philos Trans R Soc B Biol Sci 364(1526):2013–2025. https://doi.org/10.1098/rstb.2008.0265

Hahladakis JN, Velis CA, Weber R, Iacovidou E, Purnell P (2018) An overview of chemical additives present in plastics: migration, release, fate and environmental impact during their use, disposal and recycling. J Hazard Mater 344:179–199. https://doi.org/10.1016/j.jhazmat.2017.10.014

Halden RU (2010) Plastics and health risks. Annu Rev Public Health 31:179–194. https://doi.org/10.1146/annurev.publhealth.012809.103714

Hannah Ritchie MR (2018) Plastic pollution. Retrieved from https://ourworldindata.org/plastic-pollution

Hentschel LH (2015) Understanding species-microplastics interactions: a laboratory study on the effects of microplastics on the Azorean barnacle. Megabalanus azoricus. https://doi.org/10.1016/j.envpol.2015.10.010

Hermabessiere L, Dehaut A, Paul Pont I, Lacroix C, Jezequel R, Soudant P, Duflos G (2017) Occurrence and effects of plastic additives on marine environments and organisms: a review. Chemosphere 182:781–793. https://doi.org/10.1016/j.chemosphere.2017.05.096

Hidalgo-Ruz V, Gutow L, Thompson RC, Thiel M (2012) Microplastics in the marine environment: a review of the methods used for identification and quantification. Environ Sci Technol 46(6):3060–3075. https://doi.org/10.1021/es2031505

Isangedighi IA, David GS, Obot OI (2018) Plastic waste in the aquatic environment: impacts and management. Environment 2:1–31. https://doi.org/10.31058/j.envi.2018.21001

Jambeck JR, Geyer R, Wilcox C, Siegler TR, Perryman M, Andrady A, Narayan R, Law KL (2015) Plastic waste inputs from land into the ocean. Science 347(6223):768. https://doi.org/10.1126/science.1260352

Jemec A, Horvat P, Kunej U, Bele M, Krzan A (2016) Uptake and effects of microplastic textile fibers on freshwater crustacean Daphnia magna. Environ Pollut 219:201–209. https://doi.org/10.1016/j.envpol.2016.10.037

Jeong CB, Won EJ, Kang HM, Lee MC, Hwang DS, Hwang UK, Zhou B, Souissi S, Lee SJ, Lee JS (2016) Microplastic size-dependent toxicity, oxidative stress induction, and p-JNK and p-p38 activation in the monogonont rotifer (Brachionus koreanus). Environ Sci Technol 50 (16):8849–8857. https://doi.org/10.1021/acs.est.6b01441

Jeong CB, Kang HM, Lee MC, Kim DH, Han J, Hwang DS, Souissi S, Lee SJ, Shin KH, Park HG, Lee JS (2017) Adverse effects of microplastics and oxidative stress-induced MAPK/Nrf2 pathway-mediated defense mechanisms in the marine copepod Paracyclopina nana. Sci Rep 7:41323. https://doi.org/10.1038/srep41323

Kroon F, Motti C, Talbot S, Sobral P, Puotinen M (2018) A workflow for improving estimates of microplastic contamination in marine waters: a case study from North-Western Australia. Environ Pollut 238:26–38. https://doi.org/10.1016/j.envpol.2018.03.010

Kumar P (2018) Role of plastics on human health. Indian J Pediatr 85(5):384–389. https://doi.org/10.1007/s12098-017-2595-7

Lagarde F, Olivier O, Zanella M, Daniel P, Hiard S, Caruso A (2016) Microplastic interactions with freshwater microalgae: hetero-aggregation and changes in plastic density appear strongly dependent on polymer type. Environ Pollut 215:331–339. https://doi.org/10.1016/j.envpol.2016.05.006

Lam CS, Ramanathan S, Carbery M, Gray K, Vanka KS, Maurin C, Bush R, Palanisami T (2018) A comprehensive analysis of plastics and microplastic legislation worldwide. Water Air Soil Pollut 229(11):345. https://doi.org/10.1007/s11270-018-4002-z

Lambert MWS (2018) Freshwater Microplastics. Springer, Cham. https://doi.org/10.1007/978-3-319-61615-5

Lee KW, Shim WJ, Kwon OY, Kang JH (2013) Size-dependent effects of micro polystyrene particles in the marine copepod Tigriopus japonicus. Environ Sci Technol 47 (19):11278–11283. https://doi.org/10.1021/es401932b

Lehner R, Weder C, Petri Fink A, Rothen Rutishauser B (2019) Emergence of nanoplastic in the environment and possible impact on human health. Environ Sci Technol 53(4):1748–1765. https://doi.org/10.1021/acs.est.8b05512

Li WC, Tse HF, Fok L (2016) Plastic waste in the marine environment: a review of sources, occurrence and effects. Sci Total Environ 566–567:333–349. https://doi.org/10.1016/j.scitotenv.2016.05.084

Lin VS (2016) Research highlights: impacts of microplastics on plankton. Environ Sci Process Impacts 18(2):160–163. https://doi.org/10.1039/c6em90004f

Löder MGJ, Gerdts G (2015) Methodology used for the detection and identification of microplastics—a critical appraisal. In: Bergmann M, Gutow L, Klages M (eds) Marine anthropogenic litter. Springer, Cham, pp 201–227. https://doi.org/10.1007/978-3-319-16510-3_8

Long M, Paul Pont I, Hegaret H, Moriceau B, Lambert C, Huvet A, Soudant P (2017) Interactions between polystyrene microplastics and marine phytoplankton lead to species-specific hetero-aggregation. Environ Pollut 228:454–463. https://doi.org/10.1016/j.envpol.2017.05.047

Lu H, Mo CH, Zhao HM, Xiang L, Katsoyiannis A, Li YW, Cai QY, Wong MH (2018) Soil contamination and sources of phthalates and its health risk in China: a review. Environ Res 164:417–429. https://doi.org/10.1016/j.envres.2018.03.013

Machovsky Capuska GE, Amiot C, Denuncio P, Grainger R, Raubenheimer D (2019) A nutritional perspective on plastic ingestion in wildlife. Sci Total Environ 656:789–796. https://doi.org/10.1016/j.scitotenv.2018.11.418

Mason SA, Welch VG, Neratko J (2018) Synthetic polymer contamination in bottled water. Front Chem 6:407. https://doi.org/10.3389/fchem.2018.00407

Mee A, Rideout BA, Hamber JA, Todd JN, Austin G, Clark M, Wallace MP (2007) Junk ingestion and nestling mortality in a reintroduced population of California Condors Gymnogyps californianus. Bird Conservation Int 17(2):119–130. https://doi.org/10.1017/S095927090700069x

Mendenhall E (2018) Oceans of plastic: a research agenda to propel policy development. Mar Policy 96:291–298. https://doi.org/10.1016/j.marpol.2018.05.005

Moore CJ (2008) Synthetic polymers in the marine environment: a rapidly increasing, long-term threat. Environ Res 108(2):131–139. https://doi.org/10.1016/j.envres.2008.07.025

MubarakAli D, Park J, Han T, Srinivasan H, Lee SY, Kim JW (2019) Solution plasma process: an option to degrade bisphenol A in liquid-phase to non-toxic products. J Mol Liq 276:605–610. https://doi.org/10.1016/j.molliq.2018.12.041

Murray F, Cowie PR (2011) Plastic contamination in the decapod crustacean Nephrops norvegicus (Linnaeus, 1758). Mar Pollut Bull 62(6):1207–1217. https://doi.org/10.1016/j.marpolbul.2011.03.032

Nudo F (2017) Quantification of microplastic in the Caloosahatchee River during three different hydrological periods. https://doi.org/10.1146/annurev.publhealth.012809.103714

Panda AK, Singh RK, Mishra D (2010) Thermolysis of waste plastics to liquid fuel: a suitable method for plastic waste management and manufacture of value added products—a world prospective. Renew Sust Energ Rev 14(1):233–248. https://doi.org/10.1016/j.rser.2009.07.005

Panti C, Baini M, Lusher A, Hernandez-Milan G, Bravo Rebolledo EL, Unger B, Syberg K, Simmonds MP, Fossi MC (2019) Marine litter: one of the major threats for marine mammals, Outcomes from the European Cetacean Society workshop. Environ Pollut 247:72–79. https://doi.org/10.1016/j.envpol.2019.01.029

Pecht MG, Ali I, Carlson A (2018) Phthalates in electronics: the risks and the alternatives. Ieee Access 6:6232–6242. https://doi.org/10.1109/Access.2017.2778950

Proshad R, Kormoker T, Islam MS, Haque MA, Rahman MM, Mithu MMR (2017) Toxic effects of plastic on human health and environment : a consequences of health risk assessment in Bangladesh. Int J Health 6(1):1. https://doi.org/10.14419/ijh.v6i1.8655

Pruter AT (1987) Sources, quantities and distribution of persistent plastics in the marine-environment. Mar Pollut Bull 18(6b):305–310. https://doi.org/10.1016/S0025-326x(87)80016-4

Putun E, Ates F, Putun AE (2008) Catalytic pyrolysis of biomass in inert and steam atmospheres. Fuel 87(6):815–824. https://doi.org/10.1016/j.fuel.2007.05.042

Rehse S, Kloas W, Zarfl C (2016) Short-term exposure with high concentrations of pristine microplastic particles leads to immobilisation of Daphnia magna. Chemosphere 153:91–99. https://doi.org/10.1016/j.chemosphere.2016.02.133

Rezania S, Park J, Md Din MF, Mat Taib S, Talaiekhozani A, Kumar Yadav K, Kamyab H (2018) Microplastics pollution in different aquatic environments and biota: a review of recent studies. Mar Pollut Bull 133:191–208. https://doi.org/10.1016/j.marpolbul.2018.05.022

Rosenkranz P, Chaudhry Q, Stone V, Fernandes TF (2009) A comparison of nanoparticle and fine particle uptake by Daphnia magna. Environ Toxicol Chem 28(10):2142–2149. https://doi.org/10.1897/08-559.1

Rowdhwal SSS, Chen JX (2018) Toxic effects of Di-2-ethylhexyl phthalate: an overview. Biomed Res Int 2018. https://doi.org/10.1155/2018/1750368

Rujnic Sokele M, Pilipovic A (2017) Challenges and opportunities of biodegradable plastics: a mini review. Waste Manag Res 35(2):132–140. https://doi.org/10.1177/0734242X16683272

Saikia N, de Brito J (2012) Use of plastic waste as aggregate in cement mortar and concrete preparation: a review. Constr Build Mater 34:385–401. https://doi.org/10.1016/j.conbuildmat.2012.02.066

Schymanski D, Goldbeck C, Humpf HU, Furst P (2018) Analysis of microplastics in water by micro-Raman spectroscopy: release of plastic particles from different packaging into mineral water. Water Res 129:154–162. https://doi.org/10.1016/j.watres.2017.11.011

Shafei A, Matbouly M, Mostafa E, Al Sannat S, Abdelrahman M, Lewis B, Muhammad B, Mohamed S, Mostafa RM (2018) Stop eating plastic, molecular signaling of bisphenol A in breast cancer. Environ Sci Pollut Res Int 25(24):23624–23630. https://doi.org/10.1007/s11356-018-2540-y

Sheavly SB, Register KM (2007) Marine debris & plastics: environmental concerns, sources, impacts and solutions. J Polym Environ 15(4):301–305. https://doi.org/10.1007/s10924-007-0074-3

Smith M, Love DC, Rochman CM, Neff RA (2018) Microplastics in seafood and the implications for human health. Curr Environ Health Rep 5(3):375–386. https://doi.org/10.1007/s40572-018-0206-z

Sun J, Dai X, Wang Q, van Loosdrecht MCM, Ni BJ (2019) Microplastics in wastewater treatment plants: detection, occurrence and removal. Water Res 152:21–37. https://doi.org/10.1016/j.watres.2018.12.050

Sussarellu R, Suquet M, Thomas Y, Lambert C, Fabioux C, Pernet ME, Le Goic N, Quillien V, Mingant C, Epelboin Y, Corporeau C, Guyomarch J, Robbens J, Paul Pont I, Soudant P, Huvet A (2016) Oyster reproduction is affected by exposure to polystyrene microplastics. Proc Natl Acad Sci U S A 113(9):2430–2435. https://doi.org/10.1073/pnas.1519019113

Talley K, Au S, Klaine S (2015) The effect of microplastic fibers on the freshwater amphipod, Hyalella azteca. Springer, https://tigerprints.clemson.edu/cgi/viewcontent.cgi?article=1198&context=grads_symposium

Tereshchenko LG, Posnack NG (2018) Does plastic chemical exposure contribute to sudden death of patients on dialysis? Heart Rhythm. https://doi.org/10.1016/j.hrthm.2018.08.020

Thompson RC, Moore CJ, vom Saal FS, Swan SH (2009) Plastics, the environment and human health: current consensus and future trends. Philos Trans R Soc Lond Ser B Biol Sci 364(1526):2153–2166. https://doi.org/10.1098/rstb.2009.0053

Tosetto L (2016) Impacts of microplastics on coastal biota and the potential for trophic transfer. Macquarie University, Sydney, Australia: https://doi.org/10.1016/j.anbehav.2016.10.035

Tuladhar R, Yin S (2019) Production of recycled polypropylene (PP) fibers from industrial plastic waste through melt spinning process. In: Use of recycled plastics in eco-efficient concrete, pp 69–84, Elsevier, https://doi.org/10.1016/b978-0-08-102676-2.00004-9

Tursi A, Corbelli V, Cipriano G, Capasso G, Velardo R, Chimienti G (2018) Mega-litter and remediation: the case of Mar Piccolo of Taranto (Ionian Sea), Rendiconti Lincei. Scienze Fisiche e Naturali 29(4):817–824. https://doi.org/10.1007/s12210-018-0738-z

Van Cauwenberghe L, Janssen CR (2014) Microplastics in bivalves cultured for human consumption. Environ Pollut 193:65–70. https://doi.org/10.1016/j.envpol.2014.06.010

Van Cauwenberghe L, Devriese L, Galgani F, Robbens J, Janssen CR (2015) Microplastics in sediments: a review of techniques, occurrence and effects. Mar Environ Res 111:5–17. https://doi.org/10.1016/j.marenvres.2015.06.007

Vanapalli KR, Samal B, Dubey BK, Bhattacharya J (2019) 12 – Emissions and environmental burdens associated with plastic solid waste management. In: Al-Salem SM (ed) Plastics to energy. William Andrew Publishing, pp 313–342. https://doi.org/10.1016/B978-0-12-813140-4.00012-1

Wabnitz C, Nichols WJ (2010) Plastic pollution: an ocean emergency. Mar Turt Newsl 129:1. https://doi.org/10.1007/s11270-014-2184-6

Wang W, Gao H, Jin S, Li R, Na G (2019) The ecotoxicological effects of microplastics on aquatic food web, from primary producer to human: a review. Ecotoxicol Environ Saf 173:110–117. https://doi.org/10.1016/j.ecoenv.2019.01.113

Waring RH, Harris RM, Mitchell SC (2018) Plastic contamination of the food chain: a threat to human health? Maturitas 115:64–68. https://doi.org/10.1016/j.maturitas.2018.06.010

Watts AJ, Urbina MA, Goodhead R, Moger J, Lewis C, Galloway TS (2016) Effect of microplastic on the gills of the Shore Crab Carcinus maenas. Environ Sci Technol 50(10):5364–5369. https://doi.org/10.1021/acs.est.6b01187

Wegner A, Besseling E, Foekema EM, Kamermans P, Koelmans AA (2012) Effects of nanopolystyrene on the feeding behavior of the blue mussel (Mytilus edulis L.). Environ Toxicol Chem 31(11):2490–2497. https://doi.org/10.1002/etc.1984

White W (2016) The role of water in the production of energy, Review of Current Knowledge

Wright SL, Thompson RC, Galloway TS (2013) The physical impacts of microplastics on marine organisms: a review. Environ Pollut 178:483–492. https://doi.org/10.1016/j.envpol.2013.02.031

Wu Y, Chen J (2013) Investigating the effects of point source and nonpoint source pollution on the water quality of the East River (Dongjiang) in South China. J Ecol Indic 32:294–304. https://doi.org/10.1016/j.ecolind.2013.04.002

Wu S, Liu H, Liu S, Wang Y, Gu B, Jin S, Lei Q, Zhai L, Wang H (2018) Review of current situation of agricultural non-point source pollution and its prevention and control technologies. J Strategic Study Chin Acad Eng 20(5):23–30. https://doi.org/10.15302/J-SSCAE-2018.05.004

Zheng Y, Yanful EK, Bassi AS (2005) A review of plastic waste biodegradation. Crit Rev Biotechnol 25(4):243–250. https://doi.org/10.1080/07388550500346359

Chapter 3
Remediation of Water Pollution by Plastics

Faizan Muneer, Muhammad Hussnain Azam, Muhammad Zubair, Tahir Farooq, Muhammad Ibrahim, Ijaz Rasul, Muhammad Afzal, Amna Ahmad, and Habibullah Nadeem

Contents

Faizan Muneer and Muhammad Hussnain Azam contributed equally with all other contributors.

F. Muneer · M. H. Azam · M. Zubair · I. Rasul · M. Afzal · A. Ahmad · H. Nadeem (✉)
Department of Bioinformatics and Biotechnology, Government College University Faisalabad, Faisalabad, Pakistan
e-mail: habibullah@gcuf.edu.pk

T. Farooq · M. Ibrahim
Department of Applied Chemistry, Government College University Faisalabad, Faisalabad, Pakistan

Inamuddin et al. (eds.), *Water Pollution and Remediation: Organic Pollutants*, Environmental Chemistry for a Sustainable World 54,
https://doi.org/10.1007/978-3-030-52395-4_3

Abstract The global production of plastic has raised to 330 billion tons per year, which is a huge concern in terms of environmental crisis and health issues. Currently there are no devised mechanisms available on industrial scale and in nature by which plastics can be degraded completely into harmless residues. Water constitutes two-thirds of the planet, and almost 70–80% of it is polluted by plastic debris. Marine organisms are facing alarming situations and awful scenarios due to the water pollution caused by plastics. Micro- and macroplastics are the main entities involved in polluting the water bodies, which besides the generation of different health issues are a direct threat to the destruction of natural habitats to marine and fresh water flora and fauna. Human activities, industrialization, and population burst in recent years has contributed to high demands of plastics for the manufacturing of different products most of which end up in oceans and fresh water bodies resulting in their pollution.

We have reviewed that a three domains solution strategy can be employed to fight plastic pollution and for the remediation of water pollution by plastics, which includes (1) the implementation of science and technology to produce bioplastics to replace the synthetic plastics saving our oceans and lakes from becoming plastic repositories, (2) biodegradation of plastics using different microorganisms which produces plastic degrading enzymes to degrade plastics is another excellent strategy, and (3) community awareness and governmental policies. International agencies, nongovernmental organizations, universities, and research institutes can help create awareness in our society to combat water pollution by helping governments around the globe to effectively formulate and implement new policies to counter water pollution by plastics.

Keywords Biodegradation · Plastic pollution · Macroplastics · Microplastics · Nanoplastics · Bioplastics · Polyethylene terephthalate · Mono-(2-hydroxyethyl) terephthalate · Biorefinery · Marine organisms

3.1 Introduction

Plastics are organic polymers which are synthesized or derived from natural sources like organic substances for example crude oil, natural gas, and coal by polymerization processes (Dang et al. 2018). The finding of first synthetic plastic, i.e. Bakelite in 1907, revolutionized our understanding of polymer science and technology, by initiating the development of a number of polymers or plastic formulations and techniques for their development (Frias and Nash 2019). Plastics are the top most commonly used products in our daily life. Hand bags, shopping bags, water bottles, and different products are all packed in some types of plastics; hence, our daily encounter with plastic is far more than any other specific material (Porta 2019). Invention of plastic was once seen as a marvelous victory, which has now turned into an environmental crisis by causing pollution not only on land but also in our water reservoirs such as lakes, ponds, rivers, seas, and oceans. Packaging, construction, automobile, and electronics together makeup the largest sectors that almost require 70% of the world's plastic (Dang et al. 2018). In Europe, packaging constitutes one third of the plastic demand annually. Only 10% or less of the plastic is reprocessed; the remaining plastics are sent to landfills or burnt (Thevenon and Carroll 2015). Plastics are the most severe and major causes of environmental pollution that have been evident by the present research conducted around the globe.

Water is a universal solvent; almost all the biological and chemical reactions within the body of living organisms need water. Up to 60% of the adult human body is water. We cannot survive without water for a longer duration; however, we can somehow manage to live without food for a longer period of time as compared to water. The survival of biological species in the biosphere is impossible without the availability of water. Agricultural and industrial progress are vital for economic growth; however, poor water supplies, water scarcity, or polluted water can lead to serious economic challenges such as poor infrastructure development, low income per capita, and other factors that hinder and affect grand domestic product of a state facing these problems that resulted just because of water pollution (Lamb et al. 2018). It has been well estimated that two-thirds of the surface of planet Earth is covered by water while the remaining is land. Oceans make up 98% of the total water of the globe which cannot be used for drinking purposes without treatments such as filtration at water filtration facilities which no doubt cost a lot to fulfil the growing demand of population. Today, as much as 40% of our seas are intensely affected by human activities. Fresh water constitutes about 2% of the total water available on earth. This water, however, is still limited to only 0.4% in freely usable form as the rest 1.6% is locked as glaciers and polar ice caps, which are beyond our access to use which indicates us for a dark future if we don't save these water resources. Today, human activities such as plastic pollution have intensely affected as much as 40% of our seas and oceans.

Pollution caused by plastics in the world's oceans is at record levels and it is rising to an alarming level day by day. If urgent action is not taken, the problem will become progressively more dangerous over the coming years. Plastic litter is already damaging many aquatic species and may probably have an impact on human health in ways we do not yet fully understand (Villarrubia-Gómez et al. 2018). The initial scientific articles highlighting the plastic pollution in our seas and oceans first appeared in 1969, which discussed the presence of plastics in the bodies of seabirds and other marine species (Pietrelli et al. 2018).

3.2 Water Pollution

Water pollution means that one or more substances have built up or exceeded their normal levels in water such that they can cause problems for aquatic organisms, animals, plants, and human beings (Mrowiec 2017). Plastics have been located worldwide in the marine environment. It has been estimated through a number of studies that approximately 5 trillion plastic debris (over 250,000 tons) stay afloat on the seas (Barboza et al. 2018). United Nations department for the environment estimates that approximately 800 species are affected by ocean debris globally and nearly 75–80% of which is plastic or products derived from plastics. It is measured and evaluated that almost 67% of marine plastic is coming from land-based sources while the remaining comes from ocean-based sources (Karbalaei et al. 2018). It is calculated that nearly 13 million metric tons of plastics enter the ocean every year. Seabirds, fish, sea turtles, and sea mammals can ingest plastic debris, which ultimately results in suffocation, starvation, and drowning of these marine creatures. Scientists have estimated that nearly 60% of all the seabird species have eaten fragments of plastics at some point in their life. The point of concern here is a study that foresees this figure to increase to 99% by 2050 (Sharma and Chatterjee 2017).

Different states around the globe are taking strict measures to diminish the adverse impacts caused by plastic pollution. For this purpose, governments have banned single use of plastics, shifting petroleum-based plastics to alternative bio-benign products such as glass, paper, or biodegradable plastics and enhance waste collection systems to confirm that all waste is properly collected and recycled or carefully disposed of. The United Nation's environmental program gives guidance on actions that the private, public sector entities, and governments can take to minimize the use of single-use plastics and production (Godfrey 2019). These guidelines and directions include;

(i) Improvement of the waste management systems.
(ii) Voluntary decline strategies and agreements.
(iii) Public pressure and social awareness.
(iv) Promotion of eco-friendly replacements.

According to the Ocean Unite website, approximately 8 million tons of plastics enter into the ocean every year, and at this rate, we will see more plastics in the ocean as compared to fish by 2050. The global production rate of plastics has been continuously increasing for the last five decades at a speed far more than estimated. In spite of the recent economic crisis, the amount of plastic waste is rising year by years. Nearly 4.8–12.7 million metric tons of plastics that entered into the oceans comes from land-based sources in 2010 alone (Geyer et al. 2017). It is estimated that about 4–5% of the global annual production of petroleum is converted into plastics, whereas the same amount of energy resources i.e. petroleum, electricity is used for the production of these plastics. The worldwide production of plastics is now about 320 billion tons per year. Pollution can be a result of either point source or nonpoint source when pollution originates from a single source, it is called point source pollution. For example, wastewater (also called effluent) is released legally or illegally by a manufacturer, oil refinery, or wastewater treatment plants. Point sources of pollution include wastewater effluent (both industrial or municipal) and storm sewer release that affect mostly the zone nearby it (Sigler 2014). While point source pollution initiates from a specific place, it can affect miles of waterways and ocean. Nonpoint sources of pollution are those which comes from different sources of origin and number of ways by which pollutants enter into groundwater or surface water and reach the environment from diverse nonidentifiable sources. These may include storm water runoff or agricultural or debris that is blown into waterways from the land. Nonpoint source pollution is the prime and undeniable cause of water pollution in the United States waters, but it's difficult to regulate since there's no single, identifiable culprit.

3.3 Causes of Water Pollution

Water pollution is caused by multiple factors such as untreated industrial waste, municipal waste, and leaching of heavy metals from soil into the ground water. Ocean and most of the land-based water systems are polluted mainly because of human activities. Industrialization has resulted in the development of products that have turned to pollutants due to their overproduction, use, and nondisposable conditions. Plastic is one of the major causes of water pollution around the globe. This chapter is concerned with the water pollution caused by plastics, so we will be concerned here in detail about how plastics pollute our marine and fresh water sources. The solutions and remedies to counter water pollution are also discussed.

3.3.1 Plastic as a Water Pollutant

The term plastic came from the Greek word "plastikos", meaning ability to change into different shapes (Shah et al. 2008). Plastics consist of various elements such as carbon, oxygen, nitrogen, hydrogen, chlorine, and sulfur. Plastics are synthetic organic polymers similar to naturally existing biopolymers such as wool or wood which are chemically large molecules called polymers composed of repetitive units, called monomers, with carbon backbones. To produce polymers, petrochemicals, and their derivative products are heated under controlled conditions and broken down into simpler residues or small molecules known as monomers (Halden 2010). Different types of monomers make plastic resins with different characteristics, such as molding capability or strength. That monomers can be extracted from oil, natural gas, or coal. The five major classes of plastics (90% of polymer production) more common in the ocean comprise polypropylene, polyvinyl chloride, polystyrene, polyethylene, and polyethylene terephthalate (Thevenon and Carroll 2015).

On the basis of thermal properties, plastics can be divided into two major categories: thermoplastics and thermosets. Thermoset plastic hardens or sets irreversibly when heated at a considerable temperature. These plastics are important for their strength and durability. Therefore, they are used primarily in automobiles and construction applications. Plastic also finds some applications in adhesives, inks, and coatings. On the other hand, molecules in thermoplastic polymer have weaker bonds, hence the plastic softens when heated on flame and restores its original shape at room temperature; hence, these plastics can easily be molded and shaped into products such as carpet fibers, credit cards, milk jugs, and floor coverings (Halden 2010). Plastic fragments vary in size which further classifies them as macrofragmented, with size 5 mm, microfragmented with size range of 1 μm to 5 mm, and nanofragmented with size <2 mm. All these are briefly discussed below.

Macroplastics

Macroplastics are the larger units of plastics found especially in marine environment typically more than about 5 mm. Andrady 2011 showed that the time that macroplastics stays in the ocean can differ, for example, plastic bag (50 years), polyethylene bottle (450 years), cigarette ends (1–5 years), polystyrene cups (50 years), plastic six-pack rings (400 years), and fishing lines (600 years).

Microplastics

Microplastics like most of the other synthetic plastics are solid particles. These synthetic polymers might have an organized or random shape with size limits ranging between 1 μm to 5 mm. These are not soluble in water (Frias and Nash 2019). Sharma and Chatterjee 2017 separated microplastics, based on their sources, into primary and secondary microplastics. The primary microplastics have microscopic dimensions while the plastic formed as result of plastic degradation of larger particles to smaller ones is known as secondary microplastics. According to the definition of the joint group of experts on the scientific aspects of marine environmental protection, "plastic particles <5 mm in diameter, which includes particles in the nano-size range i.e. 1 nm are termed as microplastics" (Beaumont et al. 2019).

Ogunola et al. 2018; Andrady 2011 stated that marine microplastic pollution is due to primary and secondary sources. Primary microplastics are coming from different sources, like daily life products, such as toothpaste, cosmetic products, detergents, cleaning and maintenance products for commercial and industrial use, shampoos, shower gels, and fibers from the laundry. About 90% of microplastics might be reserved in wastewater treatment plants (Law 2017; Rhodes et al. 2018) Within a very short time frame microplastics have tremendously spread into several different ecosystems such as terrestrial habitats to the depth of the mighty ocean. The polar regions have also shown positive results for the presence of microplastics. A number of marine species are at risk of getting entangled in microplastics owing to their small size which eventually results in physical trauma, starvation, and suffocation. As a result the huge environmental concerns and growing threats to flora and fauna are raised. Secondary microplastics arise due to the breakdown of larger plastic materials. Most of the secondary microplastics come from the degradation of larger plastic substances into microscopic pieces when exposed to high solar radiations and abrasion by process of physical, chemical, and biological decay, which results in the direct transfer of these particles into the marine environments (Wang et al. 2018).

Nanoplastics

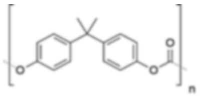
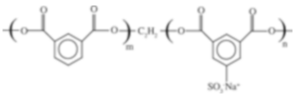
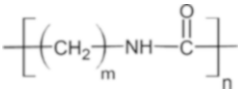
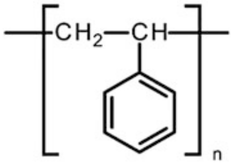
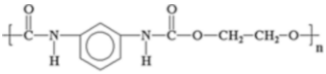
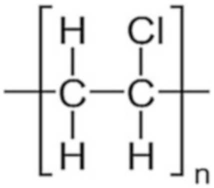
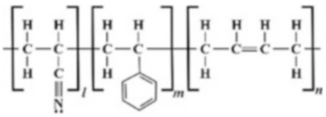
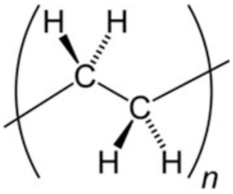
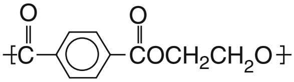
Nanoplastics are defined as the particles formed as a result of degradation of plastic objects within a size range of 1 nm to 1 μm (Frias and Nash 2019). The plastic breakdown process does not stop at the micro level, instead it will continue to become smaller in size turning into nano-sized plastic particles. Almost all the microplastics coming from washing clothes or microbeads present in make-ups (cosmetics) are further broken down into nanoplastics. Limited research and scientific studies are available on nanoplastics which are currently unclear with respect to their health risks for aquatic organisms. A number of long-term scientific studies in oceanic environment have shown that the plastic particles can get ingested by a number of different marine organisms including fish and tortoises which can pass from the intestines reaching into the animal's circulatory system eventually generating an immune response (Barboza et al. 2018; Ivanova et al. 2018). Bioaccumulation as a result of ingesting these nano size particles is possible. As a result of bioaccumulation of plastic particles in different organisms inhabiting a wide range of water bodies the food web can get disturbed. Bioaccumulation usually starts from simpler microorganisms and reaches higher animals in the food web, for example, algae to zooplankton and then to fish. It has been studied that these nano sized plastic particles that are accumulated inside the bodies of different organisms can get access to the brain and incite behavioral disorders. In nature, however, many animals throughout their life time are rarely exposed to nanoparticles. Most commonly used plastics are enlisted in Table 3.1 (Rhodes et al. 2018).

Plastics and Marine Debris as Pollutants

Plastic waste is a long-lasting contaminant or pollutant that is resistant to environmental degradation. It can easily adhere with water repellent organic pollutants which are persistent and are highly associated with fatality in many aquatic animals (Karbalaei et al. 2018). The huge debris piles around us are evidence of their excess in modern society. Marine or aquatic debris consists of solid materials that are released into the aquatic habitat, for example, glass, metallic particles, paper, textile products, wood, rubber, and plastics. Some of these materials are biodegradable, whereas the rest are persistent and long-lived in the marine environment. Sunken wooden vessels and their artifacts made up of ceramic material are non-plastic debris in water bodies with limited effects (Ahmed et al. 2018). Plastics on the other hand are different in that they are persistent to biodegradation and readily transportable by wind and water due to their light weight (Law 2017).

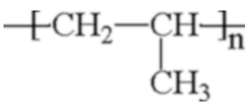
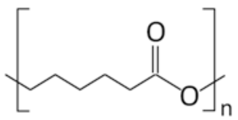
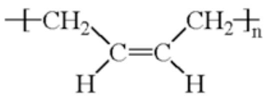
Production of plastics has increased around the globe. The prevalence and risks of plastics in the sea environment possess serious threats to aquatic life which

Table 3.1 Most commonly used plastics with their general structure and common uses

Sr. No	Plastics	Structure	Uses
1.	Polycarbonate		Medical, electronic, packaging, cars, optical storage
2.	Polyester		Used in film, rope, and also in making a variety of textile products such as sarees, dress materials, curtains.
3.	Polyamides		Fibers, toothbrush bristles, tubing, gun frames, or engine parts.
4.	Polystyrene		Ovens, microwaves, vacuum cleaners, air conditioners, refrigerators, foodservice, and electronics
5.	Polyurethanes		Home furnishings furniture, bedding and carpet underlay.
6.	Polyvinyl chloride		Water pipes, doors, frames and windows, flooring material, and shower curtains
7.	Acrylonitrile butadiene styrene		In computer monitors, printers, drain pipes, keyboard, and the plastic face-guard on wall sockets
8.	Polyethylene		Cheap packaging wrapping materials, plastic bottles, and shopping bags
9.	Polyethylene terephthalate		Beverage bottles, jars, plastic films, and packaging used for microwaving purposes.

(continued)

Table 3.1 (continued)

Sr. No	Plastics	Structure	Uses
10.	Polypropylene	 $\left[CH_2-\underset{CH_3}{\underset{\mid}{CH}} \right]_n$	For manufacturing caps for bottles, straws, containers, different appliances, chairs tables, and bumpers for vehicles.
11.	Polycaprolactone		Implants and controlled drug release applications
12.	Polybutadiene		For manufacturing car tires, as a mixture with other plastics such as styrene and for making golf balls

encourages new research not only to quantify plastic pollution and its economic, ecological, biological, and social impacts but also to unmask its remedies. Urban beaches and coastal waters can be seen full of plastic debris. Microplastics are found in every habitat including surface waters, beaches, the deep seafloor and the water column. Impacts of plastic on the environment include habitat damage, health risks and effect on aquatic life (Bråte et al. 2017).

Microplastics and Microorganisms

Microorganisms such as bacteria and archaea are natural biodegraders and recyclers; they could also play a role in breaking down chemical residues of plastics (Yu et al. 2018). Microorganisms can break down plastics by converting the carbon that constitutes the plastics into carbon dioxide (CO_2), water, and biomass. Microplastics floating on water have the capability of providing raft substrates for various epifauna and microbes i.e., bacteria, algae, and diatoms and moving them to zones where they were not present before; this in turn can change the marine ecosystem by disturbing the natural habitat of these microbes which eventually effects food chain (Mrowiec 2017).

3.4 Plastic Pollution in Oceans

Coastlines of some developed countries like China and the United States are responsible for the most of plastic pollution. Nearly one-third of the plastic waste is mishandled, as a result of which its movement into the oceans becomes feasible. It is estimated that approximately 90% of this plastic waste came only from 10 rivers in the world out of which 8 rivers, i.e. the Yangtze, Yellow, Mekong, Indus, Ganges, Pearl, Hai He, and Amur, are in Asia and two, the Niger and Nile, are in Africa (Godfrey 2019).

Three main industrial sectors are responsible for the most plastic waste production which are textiles (13.9% of total plastic waste), packaging (46.7%), and the consumer-institutional product (12.3%). It is estimated that each year, approximately 0.11 million metric tons of waterborne plastic garbage comes from the United States which is heavily polluting our environment and oceans (Wang et al. 2018).

3.4.1 How Plastics Enter into Oceans

Plastic from various sources enter into oceans through different paths; however, the diverse sources that result in ocean pollution remain unknown. It is impossible at the moment to produce trustworthy quantitative contrasts between plastic input loads, bases, and originating sectors, and this indicates a significant knowledge gap (UNEP, 2016). Among the land-based sources, plastics usually enter the oceans from shorelines, wastewater pipelines, or rivers. Waste management process and certain weather conditions such as storms and high-speed winds can also take a huge amount of plastic materials into the oceans and such problems are difficult to be dealt with. Ocean-based sources at sea may be from normal accidental losses, from shipping operations such as cargo ships that transport goods, oil tanker, and other sea liners or vessels or deliberate discarding of plastic wastes during sea- or ocean-based journeys (Bråte et al. 2017).

Food, packaging, tourism, household goods, constructions, and drink containers are the land-based sources of macroplastics. A large amount of aquatic plastic contamination that occurs in ocean and sea arises from sources based on land which is approximately 4.8–13 million metric tons per year. Marine-based causes of macroplastics consist of shipping sectors and fisheries. Moreover, aquaculture structures are mainly made up of plastic materials and if structures are not managed or are spoiled by the environmental conditions, they can result in plastic contamination of water (Haward 2018).

3.4.2 Effects of Plastic Pollution

Plastic pollution has the most adverse effects on the marine biodiversity and habitat about tens of thousands of aquatic animal species like turtles, whales, seals, and birds that feed on these creatures are killed each year due to rising plastic pollution. Plastic bag litter in the marine environment is seen in the dead body of these animals washed off by the oceans at the coast. The presence of plastic debris in water causes damage to aquatic environment and natural habitats of organisms living in such ecosystems. As a result of these factors economic repercussions for tourism and life threats to the marine animals is at the height of its maximum value (Avio et al. 2017). Many aquatic organisms such as molluscs, birds, fish, crustaceans, and mammals mix up microplastics with diet or selectively feed on them instead of food. This not only has a direct effect on the creatures feeding on microplastics but also seriously disturbs all trophic levels in food web. Studies have shown that due to mistreatment and misperception of some sea animals like whales, fish, seabirds, and turtles they feed on plastic particles present in their habitat, which results in adverse side effects on their normal physiology and sometimes prove fatal to their lives. Plastic consumption can be either direct or indirect. For example, in case of direct consumption plastics like polyethylene bags that float in water look like jellyfish and are misunderstood by turtles as their natural prey. While a mussel feeds on plastics resulting in direct plastic consumption, but when a crab feeds on the same mussel, it will end up having the plastic inside its gastrointestinal canal resulting in indirect consumption. It has been confirmed that only a fraction of consumed plastic pass through the digestive tract, while the rest is stored or retained in the body resulting in a number of health issues (Lamb et al. 2018).

Microplastics that are taken up by living organisms hinder or effect normal physiological functions of an organism. For example, the ability of an animal to feed might be affected, which eventually results in malfunctioning of normal growth and reproduction. Experiments performed in controlled environment have shown that ingestion of microplastics by different aquatic organisms has serious health concerns. Oysters have shown a sharp reduction in energy uptake, offspring performance, and reproduction as result of polystyrene microparticles. Egg hatching success and algal feeding was shown to diminish in copepods due to polystyrene ingestion with negative consequences for its survival. Polyvinylchloride microplastics have affected soil-dwelling worms by reducing their energy reserves and normal physiology and functions (Eerkes-Medrano et al. 2015) Hence our discussion here clearly shows the impact of synthetic plastics on organisms which can completely alter the functioning of marine ecosystem.

3.4.3 Species Affected by Plastic Pollution

Plastic pollution has endangered the lives of different organisms both on land and in water, and the results are alarming for the sea life. The reason that sea ecosystem is affected worse than the land is the fact that almost 80% of the land-based plastic is destined to enter water resources. Once in the water the plastic breaks apart into fragments and particles of a wide range of residual sizes due to water currents and other marine water factors. Different organisms have been studied for the effects of plastics on their normal life, physiological activities and also its impacts on their habitat in the water. We will discuss here some of the sea animals in order to grasp the idea of the bad consequences the sea life is facing and how difficult is the war of survival between the life and plastics in the oceans.

Sea Turtles

Sea turtles are widely studied for the estimation of adverse effects of the plastic possess for the sea life. A large number of autopsies and biological samples have clearly shown that the most common and basic culprits behind stress and nonnatural death of sea turtles are plastic and tar which are ingested by the living organisms living in polluted water resources, mainly in oceans. Plastic debris present in water such as plastic bags, polyethylene terephthalate bottle fragments, and plastic ropes have been found in turtles' digestive tract. Studies have also shed light on the phenomenon that the sea turtles usually mistake polyethylene bags with jelly fish, which is their natural prey. This misunderstanding leads plastic into the digestive system of turtles, which ultimately counts for the death (Sigler 2014).

The international union for conservation of nature has placed leather back sea turtles on its critically endangered organisms list because of a sharp reduction in its population over the last two decades. In a research, autopsies were conducted on leatherback turtles which showed that out of 371 turtles that were collected from their natural habitat sites 137 had plastic in their alimentary canal but it was not confirmed beyond doubt that the ingested plastic was the sole cause of death or were there any other factors involved. It has been evaluated through studies that 8.7% of the turtles that died due to plastic pollution had a plastic or polyethylene bag blocking the esophagus and preventing the food passage to stomach which eventually resulted in the death (Vegter et al. 2014) Apart from the treats possessed to sea life, a sharp reduction has been seen in the reproduction of these animals. Some studies on female turtles have clearly shown plastic to block the passage of female eggs. Researchers have isolated and recovered 14 different types of plastic pieces from a turtle female cloaca which eventually resulted and enabled it to lay the eggs (Sigler 2014).

Fish

Different species of fish like *Squalus acanthias, Mullus barbatus, Chelidonichthys lucerna,* and *Sardina pilchardus* have been studied by Avio et al. 2017 to evaluate and discover the presence of microplastics in their bodies, the results were positive for all these species. Polyethylene particles constituted 65% of the total plastics in their stomachs. Mrowiec 2017 showed that in the gastrointestinal tracts of 504 fish that were studied in an experiment, 36.5% had plastic pieces in their stomachs. Data collected as a result of studies conducted in the North Pacific region of central Gyre gathered some results according to which almost 38% of nearly 700 fish tested had a sum of 1380 plastic particles in their body tissue and stomachs, which means that each fish had an average of 2.5 plastic pieces. It should be noted here that most of the plastic pieces ingested by fish had colors white, blue, or transparent nature as exhibited by plankton, this causes a misinterpretation to fish whose primary food source is planktons. Knowledge about the effects of plastics eaten and ingested by the fish is of great concern because the small pieces of plastic may become part of the food chain as a result of bioaccumulation and biomagnification in higher organisms that feed on these smaller fish (Sigler 2014).

Humans

Sea food is considered a delicacy around the globe and people like to eat different types of sea foods like lobster, crabs, oysters and fish. Almost 19% of the global population depend on sea food in order to meet their animal protein intake (Beaumont et al. 2019). Human beings hold the highest level in food web and trophic level hence they consume plastics indirectly for example by consuming seafood more commonly shellfish and small fish which are eaten as a whole including their gut on the other hand larger fish has more flesh hence human consume only their meat and are therefore less affected by them. It has been estimated and evaluated through experiments that nanoplastics have more mobility rates in the tissues of living organisms as compare to other types hence their larger surface to volume ratio increases their concentration in the tissue causing mass concerns of health and reproduction if such sea food is taken which ingest nanoplastics, humans can damage the overall general health with some unknown and uncharacterized effects. Plastic nanoparticles are widely distributed in marine environment with relatively unknown sources of origin. As a result of plastic pollution in aquatic reservoirs as indicated by a large number of studies human beings have to be conscious about their love for the delicious seafood (Rhodes 2018).

3.5 Measurement of Water Pollution

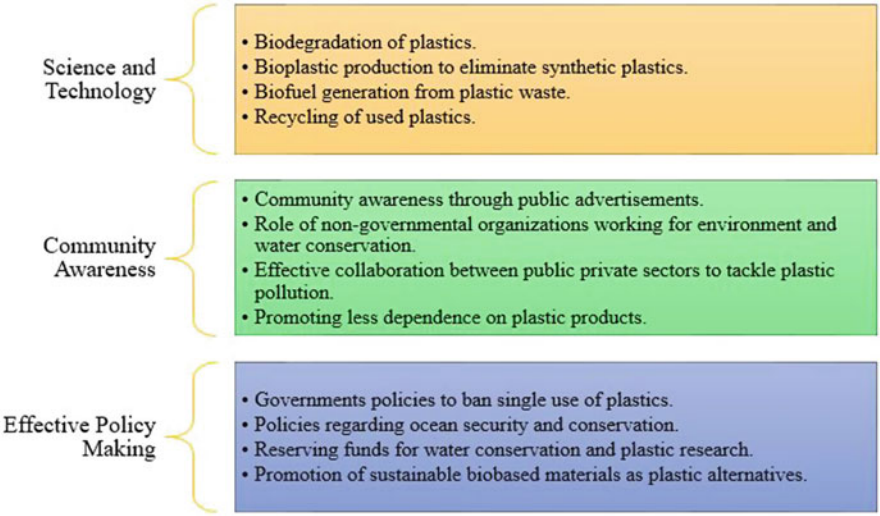
In order to measure the water pollution chemical, physical and biological methods can be used. In the physical testing process, solid concentrations, temperature, turbidity, color, odor and taste are measured. Fresh water has no taste and odor but sea water has a bitter taste due to higher concentration of different salts, the presence of any plastic on any level can be detected using physical tests, for this purpose samples from different sources are compared with standard samples for their physical characteristics any difference or variation from the normal limits indicates the contamination level. Color can also help to physically judge the samples. Turbidity is the haziness or cloudiness of a liquid caused by large number of particles present in the liquid, hence if the water is turbid it gives indication that water is polluted while clear water absorbs light and is free of pollutants. Chemical methods use, analytical chemistry principal for testing the concentrations of different pollutants in water samples, it can also determine the types and qualities of such contaminants. If the concentration of chemicals like industrial dyes, heavy metals like lead, chromium, or plastic is too high it can affect aquatic life or those who consume it for drinking purposes. Some chemical indicators can be used to determine the water purity and quality. These indicators include pH measurement, chemical oxygen demand and biochemical oxygen demand. In the biological methods**,** we use different animals, plants and microbes as biological indicators to monitor different parameters of a marine or fresh water ecosystem. The quality is likely to be very good, if many different types of organisms can live in a river, and if the fish can't live or survive in the river, then the quality is very poor. Which shows the presence of different pollutants that can affect a wide variety of organisms living in or depend on such water resources.

3.6 Solution and Remedies for Water Pollution Caused by Plastics

In December 2017 the United Nations Environment Assembly gathered in Nairobi, Kenya, to discuss the significant issues of water pollution caused as a result of plastic debris in the seas and oceans. Eleven resolutions were taken up at the meeting for effective discussion, one of the main being the pollution of ocean and water bodies due to synthetic plastics. A ministerial declaration was adopted unanimously during the meeting. It was noted and agreed by all the participants that each year at least 5 to 13 million tons of plastic is dumped into oceans (Haward 2018). This huge amount of plastic that is being washed away into the oceans and other water bodies is an alarming situation that needs to be addressed as soon as possible without any further delay.

Plastic pollution has serious effects on the environment and the atmosphere. It has disturbed not only the ecosystem but also the whole biosphere. Although plastic pollution has affected land, air, and water, we will discuss here only the solutions and remedies for water pollution caused by plastic, as it is the main purpose of this chapter. But the solutions given here can be somehow applied to all types of pollutions caused by plastics. The United Nations sustainable development goals put forward certain actionable plans which involve 17 sustainable development goals. It further includes an active agenda to prevent, eliminate and effectively reduce marine pollution including ocean debris and solid waste. The goal 6 is related to clean water and sanitation whose target 6.3 is to deal with untreated water so that our water reserves don't get exhausted with pollutants. Similarly, point 14 is related to life below water whose target 14.1 aims for the reduction of waste generation so that we can use the oceans and other water resources in a more sustainable and efficient way (Löhr et al. 2017).

Plastics can pollute both fresh and marine sources of water. Rivers, lakes, and ponds are the worst affected water bodies as human activities directly affect them. These fresh water sources are polluted by plastics because these are surrounded by populations. People throw garbage like plastic bottles of different beverages and products in rivers and ponds. Untreated municipal waste of developing cities carries a large number of plastic particles or even the whole plastic products into such sources of water; all this happens mostly in underdeveloped or third-world countries which have either poor or no sanitation system at all. The ocean is the ultimate sink for all types of water pollutants that may be heavy metals, toxic chemical compounds, industrial waste, or plastics because almost all the major rivers empty in oceans (Haward 2018). The ocean acts as a repository for increasing quantities of plastics and microplastics. There is a widespread recognition of the fact that these pollutants of the ocean must be addressed in a sustainable way (Avio et al. 2017). In 2010 alone the estimated plastic that entered oceans was somewhat between 4 to 13 million tons (Van Sebille et al. 2016). Plastic pollution has not only endangered more than 250 marine species but it has also put the future of this planet at risk. Marine litter ingestion by aquatic life has seriously affected the ocean biodiversity. Therefore, there is a serious demand to tackle plastic pollution in oceans and seas. The solution and remedies for water pollution caused by plastics are mentioned in Fig. 3.1 which shows that there are three main strategies or solution domains that can be adopted to counter plastic pollution in oceans and fresh water reservoirs. The first strategy used is science and technology, the second being education and community awareness, and the last is government policies and laws implementations. All these strategies employed together can give a positive solution for this problem. We will discuss here briefly all these strategies one by one; however, our main approach shall be the use of science and technology to find sustainable solution to water pollution caused by plastics.



- Biodegradation of plastics.
- Bioplastic production to eliminate synthetic plastics.
- Biofuel generation from plastic waste.
- Recycling of used plastics.

- Community awareness through public advertisements.
- Role of non-governmental organizations working for environment and water conservation.
- Effective collaboration between public private sectors to tackle plastic pollution.
- Promoting less dependence on plastic products.

- Governments policies to ban single use of plastics.
- Policies regarding ocean security and conservation.
- Reserving funds for water conservation and plastic research.
- Promotion of sustainable biobased materials as plastic alternatives.

Fig. 3.1 Science and technology, community awareness, and effective policy making can help to ensure a sustainable environment by remediating water pollution caused by plastics

3.7 Scientific Solutions of Plastic Pollution in Water Reservoirs

Science and technology have a vital and active role in our daily lives. The modern development is all due to the science and its applicable form – technology. Plastics that were produced by the man using his scientific knowledge of chemistry and synthetic polyesters has now a strong demand to stop the same destroying our environment, therefore, the first strategy that we shall apply to degrade plastic pollutants in the environment most importantly in water bodies such as rivers, lakes, ponds, seas, and oceans should be the same—science and technology. A few methods that we can employ to tackle plastic pollution in water are discussed below.

3.7.1 Bioplastics Can Be a Replacement for Synthetic Plastics

Bioplastics are natural biopolymers obtained from biomass and are biodegradable. These can be produced from a number of biological sources such as plants, agricultural residues, and microorganisms. These sustainable plastics or bioplastics can therefore replace the synthetic versions of plastics that affect the seas and oceans and speaking on a broader term - the whole atmosphere (Bhat et al. 2017). Bioplastics are produced more easily using plant sources and using their biomass such as lignin from wood, starch from potatoes, and rice. There are a number of studies that are successful in creating different types of bioplastics from plant and microbial sources some of these studies along with their brief description are given in the tabular form in Table 3.2.

There are a number of feedstocks with a wide variety of methods that had been and are currently being investigated for the production of biopolymers used to form bioplastics. The reason that these polymers can extinguish the pollution caused by synthetic polymers or plastic is their closeness in properties however, with an advantageous difference that these are derived from biomass and are biodegradable unlike plastics which are the petrochemical derivatives and are nearly impossible to degrade. The plastics if incinerated or burnt to generate electricity, energy or other useful products they still create a huge problem in terms of their toxic gases; hence if we want to save our land, air, and most importantly water sources like seas and oceans, we need to replace synthetic plastics with bioplastics. This strategy can help us to reduce plastic litter in oceans as well as in land saving our planet and natural habitat.

A comparison between the properties of bioplastics and synthetic plastics (Table 3.3) gives us the knowledge on how we can replace these plastics with their natural alternatives such as bioplastic, so that we can replace the pollution-causing plastic but not the services it provides us.

Table 3.2 Production of bioplastics from different types of biomass that can reduce the use of fossil fuel-based synthetic plastics and help in water pollution reduction

Biomass	Brief summary of the study	Bioplastic Produced	Reference(s)
Switchgrass	Transgenic transformants of switchgrass were studied for the production of polyhydroxybutyrate. The plants produced 3.72% dry weight of polyhydroxybutyrate in leaf tissues while 1.23% dry weight of polyhydroxybutyrate was obtained from whole tillers.	Polyhydroxybutyrate	Somleva et al. (2008)
Starch	Starch from potatoes, rice, maize is rendered in granular form by blending it with moisture or gelatinizing it at 65 to 70 °C with 45% moisture it is then blended with a minute quantity of conventional plastic to get desired properties.	Polymeric film	Kumar and Thakur (2017)
Cassava starch	The potential of cassava starch waste water towards Polyhydroxyalkanoates production was determined. *Bacillus tequilensis* MSU 112 was seeded to the system which provided a great benefit in enhancing the production of Polyhydroxyalkanoates.	Polyhydroxybutyrate	Chaleomrum et al. (2014)
Soybean	Soy protein and oil are used to manufacture bioplastics with high stiffness thermoset polymers. These are replacement for urea formaldehyde.	Thermoset polymer with characteristics of synthetic plastics like urea formaldehyde and bio-based polyurethane.	Coles et al. (2010)
Agricultural wastes	Flax fibers and cotton linters are used to produce a biopolymer called cellulose acetate biofiber. The yield obtained was nearly 80% and 55% for flax fibers and cotton linters respectively.	Cellulose acetate biofiber	Mostafa et al. (2018)
Bacillus megaterium	Polyhydroxybutyrate is stored in the cytoplasm of the *Bacillus megaterium* under stressed conditions which was isolated and purified by different methods.	Poly (3-hydroxybutyrate)	Luengo et al. (2003)

Table 3.3 Similarities between bioplastics and synthetic plastics (Siracusa et al. 2008)

Bioplastic/Biopolymer	Synthetic plastic/ Synthetic polymer	Similar properties
Aliphatic polyesters	Polyethylene and polypropylene	Elasticity, decomposing temperatures, percent crystallinity
Polylactide aliphatic copolymer	Polystyrene and polypropylene	Hardness and flexibility
Polylactic acid	Polyethylene	Almost similar physiochemical properties like melting temperature, tensile strength.
Polyhydroxyalkanoates	Polypropylene and polyethylene	Similar melting temperatures, water vapor transmission rate, oxygen permeability rate.

Table 3.4 Common uses of biopolymers/bioplastics

Biopolymers/Bioplastics	Common use
Polyhydroxyalkanoates Polyhydroxybutyrate (from microorganisms)	Bioplastic production that is similar to polyethylene, polypropylene and can be used for purposes like packaging of food products (Haward 2018)
Polylactic acid (from microorganisms)	Bioplastic development (Benn and Zitomer 2018)
Cellulose (from plants mostly) Keratin (from animal wool, cotton, birds, feathers)	Antimicrobial packaging films. Bioplastics to make different products, (Reiniati et al. 2017; Bhagowati et al., 2017).
Poly(hydroxybutyrate-co-hydroxyvalerate)	For increasing the ductility and flexibility of different bioplastics (Wang et al. 2013).

It will be the best step towards the development of ecofriendly and sustainable products if we focus on natural polymers such as wool from Angora rabbit, Alpaca, and Mohair to produce keratin, which is a natural polymer and can be used to produce different types of plastics. Similarly, biomass feedstock from plant, fungi, algae, and other microbes can help us to accomplish sustainable goals. One such goal as proposed by United Nations is the use of sustainable materials such as biopolymers and biomass so that we can ensure a proper sanitation of water (Haward 2018). We can replace the synthetic plastics with bioplastics not just on the similarities between their physical properties but also for their common uses as mentioned in Table 3.4.

Hence, by using biotechnological knowledge to produce biopolymers for bioplastic synthesis we can effectively remove a large amount of plastics such as polyvinyl chloride, polyurethane, polystyrene, acrylonitrile butadiene styrene, polycarbonate, polyethylene terephthalate, polyethylene, and polypropylene from our daily use and hence save our cities and oceans becoming depositories of plastic dump sites and eventually saving our land and aquatic ecosystem (Arikan and Ozsoy 2015).

3.7.2 Microbial Degradation of Plastics or Biodegradation

Unfortunately, we cannot replace all the available plastics with bioplastics because of different prevailing limitations. Production of biomass can be a problem as huge amount of land is required if we use agropolymers that are produced by plants and this much of land is turning into a dream because of the population big bang and industrialization. If microorganisms are used to produce bioplastics using polyesters such as polyhydroxyalkonates and polylactic acid maintaining these cultures on large scale or on industrial level where bioplastic is to be produced is very difficult and expensive further more isolation and purification of these polyesters is not an easy job.

For what we have discussed briefly in the above paragraph we can say that bioplastics to replace the synthetic plastics is not a sufficient strategy to overcome plastic pollution in the environment, either on land or in oceans. Scientists have therefore adopted a more straightforward approach rather than swapping synthetic plastics with naturally available biopolymers; they are now trying to discover new sustainable methods to degrade plastics using enzymes present in microbes such as bacteria and algae. A large number of bacterial strains have been studied to degrade plastics so that these plastics don't turn into pollutants of the environment, saving land and water habitats and reversing its negative effects on the atmosphere.

Palm et al. 2019 has recently shown that polyethylene terephthalate debris that has been known as an environmental pollutant because of its extreme durability can now be degraded using a microbial strain *Ideonella sakaiensis* 201-F6. The polyethylene terephthalate (PET) degradation is a two-step simple process; during the first step the bacterial enzyme PETase converts polyethylene terephthalate to mono-(2-hydroxyethyl) terephthalate and in the second step another enzyme known as MHETase hydrolyzes mono-(2-hydroxyethyl) terephthalate to ethylene glycol and terephthalic acid both of which are nontoxic and can be used for other useful purposes. The simple enzymatic degradation reaction is shown in Fig. 3.2a and Fig. 3.2b.

Polyethylene terephthalate (PET) can be converted to its simple residual forms (ethylene glycol and terephthalic acid) which are nontoxic to the environment and have many useful applications (Palm et al. 2019). From this simple example of plastic degradation by the microorganisms we can now say that there are a lot of opportunities out there in environment to degrade plastics using different microbes or enzymes isolated from them for this purpose. In order to avoid extensive summary

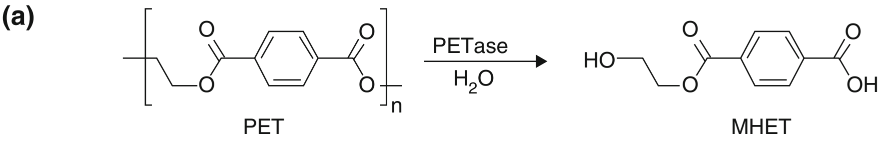


Fig. 3.2a PETase converts polyethylene terephthalate (PET) to mono-(2-hydroxyethyl) terephthalate (MHET)

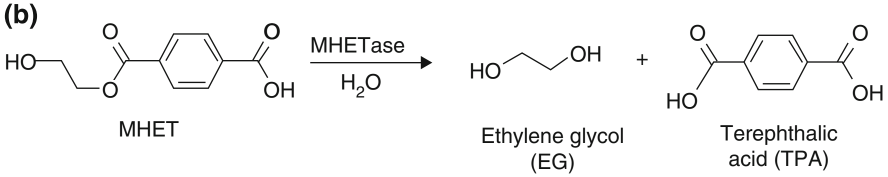


Fig. 3.2b MHETase hydrolyzes MHET to Terephthalic acid and ethylene glycol

Table 3.5 Microbial degradation of synthetic plastics

Microbial strain	Type of plastic degraded	Reference(s)
Pseudomonas sp.	Polyethylene, Polypropylene, Polyvinyl chloride.	Wilkes and Aristilde (2017)
Aspergillus flavus, *Mucor circinilloides,*	Low density polythene, Polyvinyl chloride films	Urbanek et al. (2018)
Alcaligenes faecalis *Clostridium botulinum*	Polycaprolactone	Caruso (2015)
Micrococcus sp.	Polyvinyl chloride	Patil and Bagde (2012)
Ideonella sakaiensis *Flavobacterium* sp. *Pseudomonas* sp.	Polyethylene terephthalate, Nylon	Ahmed et al. (2018) and Palm et al. (2019)
Thermophilic Bacillus	Low-density polyethylene, High density polyethylene	Dang et al. (2018)
Bacillus magaterium Strain B1	Polyvinyl chloride	Luengo et al. (2003)

Table 3.5 is given which gives the names of some important bacterial strains that are shown to degrade plastics (without concerning the fact that how efficient these strains are in the process of degradation).

The microbial strains mentioned in Table 3.5 are a few examples where we can use microbes to degrade plastics. One important thing to bear in mind that these microbial strains that has been studied until are not available on commercial scale to degrade large garbage dump sites in land, or to degrade plastic litter in oceans rather these studies are just a hope that in near future we might discover some strains or modify the existing strains using biotechnology, recombinant DNA technology or our knowledge of protein and enzyme engineering. Scientists are working to enhance the speed of catalytic activity of enzymes that degrade plastics so that these modified enzymes can break the strong bonds between the synthetic polymer chains of the plastics and convert them into simpler residues that might be less toxic or can be used in making a diverse range of other useful products. Hence we can say with confidence that in near future we can come up with new versions of plastic degrading enzymes that will help us to counter plastic pollution not only in land but also in ocean and other water bodies like rivers, lakes, and ponds.

3.7.3 Applying the Concept of Biorefinery: Converting Plastics to Fuel

We don’t know exactly when we will be able to replace plastics with bioplastic counterparts or to completely degrade synthetic plastics within a reasonable time, it means that we have to carry on with plastics for a while but what we can really do is to make them more useful by applying the concept of biorefinery which turns the plastics to a value added products. Synthetic polymers or plastics can be treated or recycled in such a way that they yield products that are economically beneficial (Owusua et al. 2017). One such concept that is in practice in some parts of the world is to convert used plastics to generate energy see Fig.3.3.

Millions of tons of plastics that are annually feed into the oceans we can set up instalments to gather plastic waste from our environment and take them to these industrial treatment plants where they can be treated to produce value-added products. One of the economically feasible and important solution for the plastic waste is the process of converting it into value-added products such as fuel. It is not only a beneficial recycling of plastics but also a technique for saving our cities and oceans to become loaded with tons of garbage and plastic pollutants that are a serious threat to the life of thousands of species in oceans and on land (Patil and Bagde 2012). Plastics can be converted into fuel that can be used for the purpose of electricity generation or other energy purposes. This not only help us to tackle the plastic waste but also help us to cope with electricity or energy generation problems and shortages.

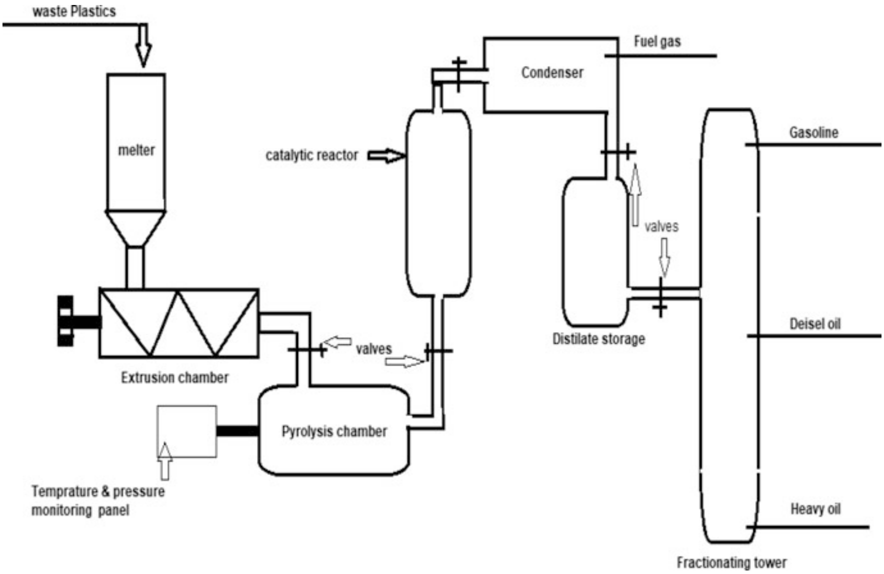


Fig. 3.3 Representation of a simple mechanism to generate energy by utilizing plastic wastes by converting them to industrially important products such as fuel

Thermochemical processes such as depolymerization, pyrolysis, catalytic cracking, and fractional distillation of plastic waste can be employed to obtain different value-added fuels which include petroleum products such as petrol, kerosene, diesel, lube oil, furnace oil, and coke. Different catalysts can be used for this purpose such as a zeolite, clay, alumina, and silicates. A simple schematic representation is shown in Fig. 3.3.

In the processes of fuel generation using thermal cracking of plastics, the plastic waste is first crushed into reasonable size and is added to a melter that melts the plastics. In next step in the pyrolysis chamber high temperature is given in an inert environment so that the plastic does not catchup fire the reaction than continues to flow in a chain of treatment finally reaching at a fractionating tower where different type of fuel is obtained. Steel reactors with temperature ranges between 100 to 400 °C are used for the thermal degradation of plastics. The normal yield of the process ranges between 80–90% which shows that almost the entire plastic is degraded in the process (Sarker et al. 2014). Fuel is produced from different types of plastics, for example, polyethylene whose global consumption is 33.5%, the highest among all other types of plastic and the main contributor of plastic waste pollution in ocean and water reservoirs so if we produce fuel from only this single type of plastic we are actually removing the same percent of this plastic from our environment and saving our seas and oceans (Cleetus et al. 2013).

Apart from the above discussed practical solutions to counter the side effects of plastic in oceans and on land, there are two other broader sections of the globe and society that can help us to save our beloved planet Earth. These two broader classes for the solution of plastic pollution are:

(i) Education, community awareness, and role of nongovernmental organizations.
(ii) Effect government policies regarding the production regulation, use, and disposal of plastics. These are briefly discussed in coming paragraphs.

3.7.4 Education and Community Awareness

Science and scientific discoveries alone cannot help us to tackle water pollution or environmental pollution caused by plastics. Community awareness and education are the two most important aspects to spread information of plastic pollution, talk about the problems, and seeking their solutions. Making people aware of the problem is the first step to solving it. Public awareness using social media platforms, advertisement, and local campaigns can spread out messages at a faster rate and with more efficiency so that a large number of people in different localities and geographical regions will become aware of the problem and can help and support those who are finding out the solutions for the problem (Ogunola et al. 2018).

It is the reason that educational institutes, research universities, and organizations can play a vital role in this regard. Universities and research institutes can organize seminars on the issue while experts of the field can talk with the community on such platforms to share their ideas about controlling plastic pollution in all of its localities either land or oceans. Community action can include initiatives that can effectively reduce and eliminate to a reasonable extent the amount of plastic entering the water bodies such as lakes and oceans. Recycling and reusing plastics is of the prime importance as it will diminish the production rate. Community awareness about the adverse effects of water pollution as a result of plastic debris can lead to the local use of practical mechanisms to stop water pollution caused by plastics such as litter traps (Haward 2018).

Nongovernmental organizations are playing a vital role in almost all of the aspects of this planet. There are nongovernmental organizations working for diverse agendas such as human rights to social justice and liberties. The role of such organizations is important because they speak, work, and campaign for a single or multiple closely related causes; therefore, such organizations can work more efficiently to create awareness in the community about the problems. Environmental organizations have diverse platforms; some work for forests or green revolution while others are related to anti-pollution works, some save whales in the ocean while other try to save the ocean itself; hence, we can use these platforms to spread our message everywhere in less time. Plastic pollution can therefore be stopped effectively by the services the nongovernmental organizations provide us.

3.7.5 Government Policies Regarding the Production, Regulation, Use, and Disposal of Plastics

New rules and regulations for plastic production can be formed in order to reduce or control plastic pollution. Policy making bodies can help the national and international organizations to draft new and effective laws to control plastic pollution (Thompson 2015). The government can ban the use of plastics at beachside and on cargo ships that may throw garbage in oceans. Similarly, government can impose tax on plastic products to discourage their use and the same money might be used as funds and research grants to create more ecofriendly plastics such as bioplastics. Similarly, new industrial setups that are producing sustainable goods like bioplastics and biopolymers might be given full or maximum tax exemptions to encourage more investors in the industry of sustainable products that do not pollute the environment. There are international protocols and conventions to stop and effectively clean our environment mostly oceans from plastic debris and pollution. For example, disposal of plastic-based products or goods by the cargo ships in the oceans is prohibited under the MARPOL (marine pollution) convention which ensures the prevention of pollution from ships in exclusive economic zones and the waters which are beyond national jurisdiction (Haward 2018). Similarly, "The Honolulu Strategy" is a policy and planning framework for the effective prevention and robust management of marine debris which include solid waste debris, plastics it furthers ensures to tackle the environmental problems, human health, and economic impacts of marine debris around the globe (Löhr et al. 2017). United Nations sustainable development goals were discussed during the oceans conference in New York, USA. The conference concluded its meeting agenda with the ideas and suggestions for the development of communities of ocean action that must be entitled to identify and sought out the possible solutions that change natural ocean environment as discussed in sustainable development goals of United Nations. All these steps have saved our water reservoirs and habitats (Haward 2018).

3.7.6 Role of International Forums and Agencies

There are international organizations, forums, and agencies that work for the natural conservation of our environment. These organizations are not just working to eliminate the environmental pollutants from our atmosphere but also closely working with the international community to effectively counter such challenges. A brief account of such international and national forums including other agencies that are working on a larger scale for the conservation of our natural environment is presented in Table 3.6.

3.8 Some Facts about Water Pollution

Given below are some of the most important facts on water pollution:

- Approximately 14 billion pounds of plastic is annually dumped into the oceans.
- Environmental Protection Agency estimates that each year 1.2 trillion gallons of industrial waste and untreated water is discarded into the oceans and waters surrounding U.S.A.
- Approximately 700 million people drink polluted water around the globe.
- The extinction rate of marine animals is five times higher than that of terrestrial animals.
- 30 billion tons of municipal and urban waste water or municipality waste water is released into fresh water and oceans each year.
- British Petroleum oil spill in 2010 resulted in the death of approximately 1000 animals.
- United Nations Children's Fund reports that each year more than 3000 children die due to the consumption of contaminated drinking water.
- Water pollution has affected over 100 million people in the world.
- Diseases like cholera, malaria, and diarrhea are all somehow waterborne.
- 300 million tons of new plastic is used every year.
- An estimated 4.8–12.7 million tons of plastic end up in the world's oceans and seas (Ocean Care. 2017).

Table 3.6 Role of different organizations to reduce plastic pollution

Organization	Description of Work	Online web address
United Nations Environment Assembly	Innovative solutions for environmental challenges and sustainable consumption and production	https://web.unep.org/environmentassembly/
Coastwatch Europe	Its goal is the protection and sustainable use of coastal resources. It ensures public participation in environmental planning and management. It is driven by public participation.	http://coastwatch.org/europe/
International Coastal CleanUp	Its work and aim are to ensure trash-free seas and ending the flow of trash into seas and oceans.	https://oceanconservancy.org/trash-free-seas/international-coastal-cleanup/
Marine Conservation Society	**It is a marine charity based in UK. It works to ensure plastic-free oceans.**	https://www.mcsuk.org/
The Ocean Cleanup	The Ocean Cleanup creates advanced technologies to rid world's oceans of plastics.	https://theoceancleanup.com/
Surfers Against Sewage	It works to inspire and empower communities to protect oceans, beaches, and wildlife to create sustainable oceans and biodiversity.	https://www.sas.org.uk/
World Ocean Council	Bring together the industry leaders to work for oceans' sustainable developments.	https://www.oceancouncil.org/
Coalition for plastic pollution	It is an alliance of different organizations and policymakers that cooperates to counter plastic pollution and its hazardous effects on humans, animals, waterways, oceans, and the environment.	https://www.plasticpollutioncoalition.org/
International ocean governance	It works for the sustainable management of oceans, coasts, transboundary, and marine ecosystems.	https://www.iucn.org/theme/marine-and-polar/our-work/international-ocean-governance
Parley for the Oceans	Parley is a platform where creators, inventors, philosophers, and leaders come together to raise awareness about the oceans, its beauty, fragility, and the raising concerns of its destruction such as pollution.	https://www.parley.tv/#fortheoceans
5 Gyres	It works to empower action against the global plastic pollution through science and technology.	https://www.5gyres.org/

3.9 Conclusion

Plastic pollution has serious environmental threats to planet earth. It is not just an alarming situation for human beings but also for the whole life in the biosphere. Increased production rate and continuous use of a wide range of plastic products is increasing the plastic pollution at precedent levels. Plastic has not just damaged our land but also our water resources like rivers, lakes, and oceans. Serious struggles are needed to control plastic pollution. Concluding in a nutshell we can say that to save our water resources such as oceans, seas, lakes, rivers, and ponds from plastic pollutions we need to adopt a three domains solution strategy system; First strategy or solution domain is science and technology which can enable us to create bioplastics that are naturally degradable and ecofriendly and can replace synthetic plastics which will diminish their production eventually decreasing their pollution effects on our environment on land or in oceans. The second strategy or solution domain is the effective education and community awareness because a more educated, informed, and aware community can support and help government, nongovernmental organizations, and other scientific organizations to effectively adopt methods, protocols rules of law that are made to counter plastic pollution. Moreover, a well-informed community will be more conscious of its actions that might affect their environment than a community lacking such knowledge and destroying the environment unknowingly. The last and the most important strategy or solution domain is effective government policies, rules, laws, protocols, and conventions that are developed by national or international bodies to conserve our environment. In one single statement we can say that in order to save our water resources from plastic pollution we have to work in all three solution domains being, science and technology, education, and community awareness and at last the national and international policies made in this regard.

References

Ahmed T, Shahid M, Azeem F, Rasul I, Shah AA, Noman M et al (2018) Biodegradation of plastics: current scenario and future prospects for environmental safety. Environ Sci Pollut Res 25(8):7287–7298. https://doi.org/10.1007/s11356-018-1234-9

Andrady AL (2011) Microplastics in the marine environment. Mar Pollut Bull 62(8):1596–1605. https://doi.org/10.1016/j.marpolbul.2011.05.030

Arikan EB, Ozsoy HD (2015) A review: investigation of bioplastics. Journal of Civil Engineering and Architecture 9(2):188–192. https://doi.org/10.17265/1934-7359/2015.02.007

Avio CG, Gorbi S, Regoli F (2017) Plastics and microplastics in the oceans: from emerging pollutants to emerged threat. Mar Environ Res 128:2–11. https://doi.org/10.1016/j.marenvres.2016.05.012

Barboza LGA, Dick Vethaak A, Lavorante BRBO, Lundebye AK, Guilhermino L (2018) Marine microplastic debris: an emerging issue for food security, food safety and human health. Mar Pollut Bull 133(January):336–348. https://doi.org/10.1016/j.marpolbul.2018.05.047

Beaumont NJ, Aanesen M, Austen MC, Börger T, Clark JR, Cole M et al (2019) Global ecological, social and economic impacts of marine plastic. Mar Pollut Bull 142(January):189–195. https://doi.org/10.1016/j.marpolbul.2019.03.022

Benn N, Zitomer D (2018) Pretreatment and anaerobic co-digestion of selected PHB and PLA bioplastics. Front Environ Sci 5(January):1–9. https://doi.org/10.3389/fenvs.2017.00093

Bhat, S., K R, Nichith., Y, Kiran., M, Nagendra., L, Pallavi., S, Shreya., . . . Dastidar., M. (2017). Production of bioplastics from microorganisms. Int J Adv Res, 5(2), 2710–2716. https://doi.org/10.21474/ijar01/3465

Eidsvoll DP, Halsband C, Almroth BC, Lusher A (2017) Micro- and macro-plastics in marine species from Nordic waters. https://doi.org/10.6027/TN2017-549

Caruso G (2015) Plastic degrading microorganisms as a tool for bioremediation of plastic contamination in aquatic environments. Journal of Pollution Effects & Control 03(03). https://doi.org/10.4172/2375-4397.1000e112

Chaleomrum N, Chookietwattana K, Dararat S (2014) Production of PHA from cassava starch wastewater in sequencing batch reactor treatment system. *APCBEE Procedia*, *8*(Caas 2013), 167–172. https://doi.org/10.1016/j.apcbee.2014.03.021

Cleetus C, Thomas S, Varghese S (2013) Synthesis of petroleum-based fuel from waste plastics and performance analysis in a CI engine. Journal of Energy 2013:1–10. https://doi.org/10.1155/2013/608797

Coles R, Kay M, Song J (2010) Bioplastics. Adv Biochem Eng Biotechnol 166(March 2011):427–468. https://doi.org/10.1007/10_2016_75

Dang, T. C. H., Nguyen, D. T., Thai, H., Nguyen, T. C., Tran, T. T. H., Le, V. H., . . . Thi Phuong Thao Pham, Truong Giang Nguyen, Q. T. N. (2018). Plastic degradation by thermophilic Bacillus sp. BCBT21 isolated from composting agricultural residual in Vietnam. Adv Nat Sci Nanosci Nanotechnol 9(1): 015014. https://doi.org/10.1088/2043-6254/aaabaf

Eerkes-Medrano D, Thompson RC, Aldridge DC (2015) Microplastics in freshwater systems: A review of the emerging threats, identification of knowledge gaps and prioritisation of research needs. Water Res. https://doi.org/10.1016/j.watres.2015.02.012

Frias JPGL, Nash R (2019) Microplastics: finding a consensus on the definition. Mar Pollut Bull 138(September 2018):145–147. https://doi.org/10.1016/j.marpolbul.2018.11.022

Geyer R, Jambeck JR, Law KL (2017) Production, use, and fate of all plastics ever made. Sci Adv 3 (7):e1700782. https://doi.org/10.1126/sciadv.1700782

Godfrey L (2019) Waste plastic, the challenge facing developing countries—ban it, change it, collect it? Recycling 4(1):3. https://doi.org/10.3390/recycling4010003

Halden RU (2010) Plastics and health risks. Annu Rev Public Health 31(1):179–194. https://doi.org/10.1146/annurev.publhealth.012809.103714

Haward M (2018) Plastic pollution of the world's seas and oceans as a contemporary challenge in ocean governance. Nat Commun 9(1):9–11. https://doi.org/10.1038/s41467-018-03104-3

Ivanova L, Sokolov K, Kharitonova G (2018) Plastic pollution tendencies of the Barents Sea and adjacent waters under the climate change. Arctic and North 32(32):121–145. https://doi.org/10.17238/issn2221-2698.2018.32.121

Karbalaei S, Hanachi P, Walker TR, Cole M (2018) Occurrence, sources, human health impacts and mitigation of microplastic pollution. Environ Sci Pollut Res 25(36):36046–36063. https://doi.org/10.1007/s11356-018-3508-7

Kumar S, Thakur K (2017) Bioplastics - classification, production and their potential food applications. Journal of Hill Agriculture 8(2):118. https://doi.org/10.5958/2230-7338.2017.00024.6

Lamb JB, Willis BL, Fiorenza EA, Couch CS, Howard R, Rader DN et al (2018) Plastic waste associated with disease on coral reefs. Science 359(6374):460–462. https://doi.org/10.1126/science.aar3320

Law KL (2017) Plastics in the marine environment. Annu Rev Mar Sci 9(1):205–229. https://doi.org/10.1146/annurev-marine-010816-060409

Löhr A, Savelli H, Beunen R, Kalz M, Ragas A, Van Belleghem F (2017) Solutions for global marine litter pollution. Curr Opin Environ Sustain 28:90–99. https://doi.org/10.1016/j.cosust.2017.08.009

Luengo, José M., García, B., Sandoval, A., Naharro, G., & Olivera, E. R. (2003). Bioplastics from microorganisms. Curr Opin Microbiol, 6(3), 251–260. https://doi.org/10.1016/S1369-5274(03)00040-7

Mostafa NA, Farag AA, Abo-dief HM, Tayeb AM (2018) Production of biodegradable plastic from agricultural wastes. Arab J Chem 11(4):546–553. https://doi.org/10.1016/j.arabjc.2015.04.008

Mrowiec B (2017) Plastic pollutants in water environment. Environ Prot Nat Resour 28(4):51–55. https://doi.org/10.1515/OsZn-2017-0030

Ogunola OS, Onada OA, Falaye AE (2018) Mitigation measures to avert the impacts of plastics and microplastics in the marine environment (a review). Environ Sci Pollut Res 25(10):9293–9310. https://doi.org/10.1007/s11356-018-1499-z

Owusua PA, Banaddaa N, Zziwaa A, Seaya J, Kiggundu N (2017) Reverse engineering of plastic waste into useful fuel products. J Anal Appl Pyrolysis 49. https://doi.org/10.1016/j.jaap.2017.12.020

Palm GJ, Reisky L, Böttcher D, Müller H, Michels EAP, Walczak MC et al (2019) Structure of the plastic-degrading Ideonella sakaiensis MHETase bound to a substrate. Nat Commun 10 (1):1–10. https://doi.org/10.1038/s41467-019-09326-3

Patil R, Bagde US (2012) Isolation of polyvinyl chloride degrading bacterial strains from environmental samples using enrichment culture technique. Afr J Biotechnol 11(31):7947–7956. https://doi.org/10.5897/ajb11.3630

Pietrelli L, Pignatti S, Fossi MC (2018) Foreword—plastic pollution: a short and impressive story. Rendiconti Lincei 29(4):803–804. https://doi.org/10.1007/s12210-018-0752-1

Porta R (2019) The plastics sunset and the bio-plastics sunrise. Coatings 9(8):526. https://doi.org/10.3390/coatings9080526

Reiniati I, Hrymak AN, Margaritis A (2017) Recent developments in the production and applications of bacterial cellulose fibers and nanocrystals. Crit Rev Biotechnol 37(4):510–524. https://doi.org/10.1080/07388551.2016.1189871

Rhodes CJ (2018) Plastic pollution and potential solutions. Sci Prog 101(3):207–260. https://doi.org/10.3184/003685018x15294876706211

Rhodes CJ, Ivanova L, Sokolov K, Kharitonova G, Kondori B, Mahmudi R et al (2018) The ocean plastic pollution challenge: towards solutions in the UK. Nat Commun 103(1):1–4. https://doi.org/10.1038/s41467-018-03104-3

Sarker M, Rashid MM, Md. Sadikur Rahman MM (2014) Conversion of low density polyethylene (LDPE) and polypropylene (PP) waste plastics into liquid fuel using thermal cracking process. British J Environ Climate Change 2(1):1–11. https://doi.org/10.9734/bjecc/2012/994

Shah AA, Hasan F, Hameed A, Ahmed S (2008) Biological degradation of plastics: A comprehensive review. Biotechnol Adv. https://doi.org/10.1016/j.biotechadv.2007.12.005

Sharma S, Chatterjee S (2017) Microplastic pollution , a threat to marine ecosystem and human health : a short review. Environ Sci Pollut Res:21530–21547. https://doi.org/10.1007/s11356-017-9910-8

Sigler M (2014) The effects of plastic pollution on aquatic wildlife: current situations and future solutions. Water Air Soil Pollut 225(11). https://doi.org/10.1007/s11270-014-2184-6

Siracusa V, Rocculi P, Romani S, Rosa MD (2008) Biodegradable polymers for food packaging: a review. Trends Food Sci Technol 19(12):634–643. https://doi.org/10.1016/j.tifs.2008.07.003

Somleva MN, Snell KD, Beaulieu JJ, Peoples OP, Garrison BR, Patterson NA (2008) Production of polyhydroxybutyrate in switchgrass, a value-added co-product in an important lignocellulosic biomass crop. Plant Biotechnol J 6(7):663–678. https://doi.org/10.1111/j.1467-7652.2008.00350.x

Thevenon F, Carroll C (2015) Plastic debris in the ocean: the characterization of marine plastics and their environmental impacts, situation analysis report. IUCN. https://doi.org/10.2305/iucn.ch.2014.03.en

Thompson RC (2015) Microplastics in the marine environment: sources, consequences and solutions. *Marine Anthropogenic Litter*:9–14. https://doi.org/10.1007/978-3-319-16510-3

Urbanek AK, Rymowicz W, Mirończuk AM (2018) Degradation of plastics and plastic-degrading bacteria in cold marine habitats. Appl Microbiol Biotechnol 102(18):7669–7678. https://doi.org/10.1007/s00253-018-9195-y

Van Sebille DE, Spathi DC, Gilbert A (2016) The ocean plastic pollution challenge: towards solutions in the UK. European Research Studies Journal 19:1–16. https://doi.org/10.1162/108819803323059424

Vegter AC, Barletta M, Beck C, Borrero J, Burton H, Campbell ML et al (2014) Global research priorities to mitigate plastic pollution impacts on marine wildlife. Endanger Species Res 25 (3):225–247. https://doi.org/10.3354/esr00623

Villarrubia-Gómez P, Cornell SE, Fabres J (2018) Marine plastic pollution as a planetary boundary threat – the drifting piece in the sustainability puzzle. Mar Policy 96(August 2017):213–220. https://doi.org/10.1016/j.marpol.2017.11.035

Wang Y, Chen R, Cai JY, Liu Z, Zheng Y, Wang H et al (2013) Biosynthesis and thermal properties of PHBV produced from Levulinic acid by Ralstonia eutropha. PLoS One 8(4):4–11. https://doi.org/10.1371/journal.pone.0060318

Wang J, Zheng L, Li J (2018) A critical review on the sources and instruments of marine microplastics and prospects on the relevant management in China. Waste Management and Research 36(10):898–911. https://doi.org/10.1177/0734242X18793504

Wilkes RA, Aristilde L (2017) Degradation and metabolism of synthetic plastics and associated products by Pseudomonas sp.: capabilities and challenges. J Appl Microbiol 123(3):582–593. https://doi.org/10.1111/jam.13472

Yu Y, Zhou D, Li Z, Zhu C (2018) Advancement and challenges of microplastic pollution in the aquatic environment: A review. Water Air Soil Pollut 229(5):2–18. https://doi.org/10.1007/s11270-018-3788-z

Chapter 4
Plastics and e-Waste, a Threat to Water Systems

Bhawana Jain, Ajaya K. Singh, and Md. Abu Bin Hasan Susan

Contents

Abstract Plastics and e-waste are major emerging problems in developed and developing countries around the globe. Annual production of plastics is 300 million metric tonnes and that of electronics goods is 50 million tonnes in the world. As per latest survey, it is estimated that approximately 8.3 billion tonnes of plastic has been produced since the early 1950s. About 60% of that plastic has ended up in either a landfill or the natural environment. Accumulation of plastics and electronic plastics in environment generally occurs by release of small particles from our daily chores, that is, use of cosmetics, textile fabrics, carry bag, disposal utensils, bottled water, mobiles, electronic gazettes, television, refrigerator, etc. Every bit of plastics and e-waste ever made will always remain and pollute the environment. We reviewed the overall scenario, which comprises a multitude of components with valuable materials, some containing toxic substances that can have an adverse impact on human health. Pollutants of this kind can affect the land, water, and air. Microplastics and e-wastes are extensively distributed in both fresh and sea water system. Once mixed

---

B. Jain · A. K. Singh (✉)
Department of Chemistry, Government V. Y. T. PG. Autonomous, College, Durg, Chhattisgarh, India

M. A. B. H. Susan
Department of Chemistry, Dhaka University, Dhaka, Bangladesh

Inamuddin et al. (eds.), *Water Pollution and Remediation: Organic Pollutants*, Environmental Chemistry for a Sustainable World 54,
https://doi.org/10.1007/978-3-030-52395-4_4

in water, they leach toxic chemicals and ultimately change the quality of water. Plastic and e-waste debris from big to tiny size (micro) particles are continuously increasing in marine water system due to modern life style.

Complete removal of microplastics from water is a difficult task, but we can minimize it by our wise behavior. Knowing with precision where litter is generated is important to target priority areas for the implementation of mitigation policies. Even the growth in plastic and e-waste can be reduced if developing economies significantly invest in waste management infrastructures as their gross domestic product grows in the future and if efforts are made internationally to reduce the fraction of plastic and e-waste in municipal solid waste. In this chapter, we demonstrate how plastics and e-wastes contaminate our water system and point out their hazardous effect on our health and describe how we can resolve it.

Keywords Plastics debris · e-waste · Fresh and marine water system · Pollution

4.1 Introduction

In the last 50 years, plastics and electronic devices especially mobiles and computers have become unavoidable elements of our daily lives. Furniture, grocery bags, vehicle parts, toys, television, washing machines, microwave, and refrigerator are now very essential components of our lives, which involve the use and generation of plastics and e-wastes. Plastics and e-waste have already been a great threat due to their omnipresence and we need to take their destruction and recycling very seriously.

Accumulation of plastic waste on the earth including plastic bottles, chips wrappers, etc., is known as plastic pollution, while e-waste is an electronic product that turns into non-working and reaches the end of the useful life. The rapid development of technology offers new and modern devices with better options and choice. Consequently, after few times of uses, many electronic devices become "trash" (Kontrick 2018; Koelmans et al. 2015; Zhang et al. 2012). Plastics are classified into micro-, meso-, or macrodebris, based on size of the pollutants (Kammer et al. 2012). Plastics and e-waste are durable, and as a result, the amount of pollutants produced by man is very high. They exhibit resistance to many natural processes. The degradation process becomes very slow because of their unique chemical structure (Webb et al. 2013). The percentage of e-waste also experiences a sharp increase in the whole world through export from developed to developing countries (Breivik et al. 2014). Despite making up only 2% of the trash in landfills, e-waste contains nearly 70% of the toxic heavy metals in these landfills. Plastics and e-waste are nonbiodegradable in our lifetime, but break down into small particles that persist in the ocean and river, adsorb toxins, and enter the food chain through fish, sea birds, and other aquatic life. These together show a high visibility of pollution in the environment. It is calculated that 1.1–8.8 million metric tonnes of plastic waste enters the ocean every year (Wagner et al. 2014). About 380 million tonnes of plastics are produced worldwide in 2018. From 1950 to 2018, approximately 6.3 billion tonnes of plastics have been manufactured worldwide, of which only 9% has been recycled and 12% has been incinerated (Velzeboer et al. 2014). Notwithstanding the fact that water bodies are also greatly affected by heavy metals that are found in e-waste. Our main concern is that such exposures are limited and will affect the diversity of aquatic organisms. There have also been alterations in the abundance and biomass of surviving species and changes in food chains. In addition to the hazardous effects on marine life, cleanliness of our living environment has decreased and has been contributing to climate change. Water pollution is affected by the production, use, and disposal of these wastes (Andrady 2011; Bhattacharya et al. 2010).

Presence of microplastics is one of the biggest problems for plastic pollution. These micro-/nanoplastic particles are either fabricated by human being for the production of other useful products or some time nature creates it by breaking down larger plastics into small by erosion or heat obtained by sun. Pervasive form of the microplastic is microfiber, which is usually used in the production of synthetic fabrics: nylon, polyester, etc. It is made of tiny strands of plastics. A recent study confirms that in a single wash of these fabrics, approximately 250 thousand fibers can be released (Hidalgo-Ruz et al. 2012). Their worst effect is dependent on their size and efficiency to avoid most filters. These microfibers enter into the bloodstreams of various organisms through which they are consumed. A recent analysis reveals that 83% microplastics are present in tap water of big cities and 93% from world's top brand bottled water (Pico and Barcelo 2019). Many researchers have studied the effect of plastics on human health (Wright and Kelley 2017; Smith et al. 2018). The presence of plastic contamination in the environment has been inferred to affect the ecosystem, and it has been crucial to develop a perfect and focused way to remove it (Parrales et al. 2018).

E-waste contaminates water by two ways: (a) e-waste dumped into landfill without proper disposal management; and (b) unawareness of recycling and scrapping of e-waste. E-waste contains precious metals and polymers, which make it lucrative for recycle and reuse. Due to continuous advancement in electronic devices, the extraction requires shredding, burning, leaching, and other processing techniques that release toxic byproducts into air, water, and soil. Chemical processes used to extract precious metals like gold, platinum, and copper from electronic devices highly affect surface water. Various technologies and methods have been developed to reuse or reduce the effect of e-waste (Hsu et al. 2019).

4.2 Effects of e-Waste

A. *On ecosystem*

The greatest impact on ecosystems through water sources contaminated by e-waste is through acidification of surface waterways. It kills marine and freshwater organisms, disrupts biodiversity, enables some species to dominate over others, and disrupts ecosystems. China is highly affected by this: for instance, Guiyu, a city of China, where local water streams get polluted and become black due to acidification of e-waste. If allowed to persist, acidification conditions can damage ecosystems to the point that recovery is unlikely or even impossible.

B. *On animals*

By the improper recycling and disposal, heavy metals can also enter surface waters. Such as its ingestion in fish leads to neurological damage, permanent disabilities and damage to the immune system. Presence of heavy metals also leads to tissue and gill damage with erratic movement. Heavy metals can impact not only fish but all other aquatic organisms.

C. *On human beings*

Effect of heavy metals extends well beyond fish, above and beneath fish on the food chain, ultimately extending to human beings and public health. If e-waste contaminates surface water, those drinking such water and bathing and recreating in this water are impacted. In extreme worst cases, toxic heavy metals can enter into the earth and leave groundwater nondrinkable. Bioaccumulation of heavy metals in fish leads to contamination up the food chain, all the way to humans and is the primary route of exposure for many people to heavy metals. Heavy metals are also persistent in the environment and do not degrade upon exposure to sunlight or other environmental conditions. As a result, they persist in surface water and can make their way down into groundwater tables, creating exposure risks to many both close to and miles away from the original point of contamination. Toxic metals, such as mercury, lead, and cadmium, which are found in printed circuit boards and other electronics, affect the nervous and reproductive systems and other organs. These impacts are particularly pronounced in children and the elderly. Instead, it is the cumulative effect of heavy metals, which severely affects the human health. These adverse effects of e-waste on all phases of life in the world should be removed as we delete data in our computer system “alt+ctrl+delete” (Li et al. 2015).

4.3 Types of Plastics and Its Effect

Plastic is a synthetic and semisynthetic polymer with malleable property and therefore can be molded into different solid objects. The addition of different additives to plastic gives desirable properties to the end product (Chen and Patel 2012). Food and beverage packing is the single largest category among plastics. Plastics are classified into two classes on the basis of heat resistance: (A) thermoplastic: it softens on heating and can be remolded again, (B) thermosetting: it cannot soften on heating and cannot be remolded again due to cross-linking in the polymers. Even plastics can be classified based on their hazardous ranking (Table 4.1).

Plastics are also classified on the basis of their recycling. There are mainly 7 types of plastics on the basis of recycling ability:

Table 4.1 Plastics and their hazardous ranking (Zhang et al. 2019)

Plastics	Hazardous ranking
High-density polyethylene/low-density polyethylene	11
Polypropylene	1
Polystyrene	1628-30
Polyamide	63-50
Polyethylene terephthalate	4
Polyvinyl chloride	10551-5001

A. *Polyethylene terephthalate* – It is a recyclable plastic and marked by 1, soda bottles, comb, water bottles, rope, bean bags, etc., are made up of polyethylene terephthalate.
B. *High density polyethylene* – It is also recyclable and marked as 2. Most of the shampoo bottles, grocery bags, trash bags, toys, etc., are fabricated by high-density polyethylene material.
C. *Polyvinyl chloride* – Polyvinyl chloride is a chlorinated plastic. It can release toxic chemicals into nearby soil. It can leach into groundwater or other nearest water bodies and affect the ecosystem. Chlorinated water causes serious threat to the species, which drink such chlorinated water. Landfill areas have many kinds of plastics.
D. *Low-density polyethylene* – Frozen food bag, flexible container lid, cling rap, etc., are made up of low-density polyethylene. We can recycle it but need proper recycling route. We cannot recycle so many times and after repeated recycling at a stage, it will lose its properties. Its products are marked as "4."
E. *Polypropylene* – Polypropylene was discovered by J. Paul Hogan and Robert L. Banks of Phillips Petroleum Company in 1951 during conversion of propylene into gasoline; surprisingly, they prepared plastics. Only a very small portion of polypropylene is recycled. Its products are marked as "5."
F. *Polystyrene* – It is the most lightweight and simplest to make plastic materials. It can break very easily, making environment more harmful. All beaches are filled with small pieces of polystyrene, which put marine animals in danger. Examples include disposal coffee cups, glasses, plastic food packets, etc.
G. *Others* – Rest includes all other plastics: polylactide, polycarbonate, acrylonitrile butadiene, acrylic, nylon, styrene, and fiberglass. Medical storage containers, baby bottles, eyeglasses, etc., are included in it.

4.4 Plastics in Water System

A. *Plasticsin marine*

Just like on land, ocean area has also negative impact of plastic on marine life. Every year, nearly 12.7 million tonnes of plastic wastes flows into the ocean. Marine litter poses a big problem for our ocean (Rochman 2013). Approximately 51 trillion microplastics are already present in the ocean as estimated by the United Nations Environment Programme and oceans find more microplastics even reaching Arctic water than ever thought (Costa and Barletta 2015). Source of ocean contamination by plastics come from land and sometimes, due to mismanagement of waste disposal, as well as the ships and offshore oil and gas platforms leakage (Chin and Fung 2019). This tiny plastic in the ocean distort the complete bio-geo cycle, which creates harmful problems to the marine ecosystem (Ding et al. 2019). The water life from small fish to bigger mammals is greatly affected by these tiny plastics through different ways. Plastic ingestion kills millions of seabirds and 100,000 marine mammals every year. Unfortunately, consumption of these plastics by marine species forces them to the verge of extinction. It creates intense digestive issues, which are mainly untreated. Consumption of plastics by fishes is very high; sometimes it goes to tonnes for a year (Fig. 4.1). Additionally, intestinal injury and fish death spread the risk across the food chain to bigger fish and marine mammals (Wagner et al. 2017). Apart from fishes, amphipods are the other unlucky target of plastic contamination in water. Other marine animals also consume plastic waste and eventually succumb to it (Jamieson et al. 2019). Ocean ruination is also created by excess use of plastic bags, bottles, and the fishing net. These plastic wastes affect the

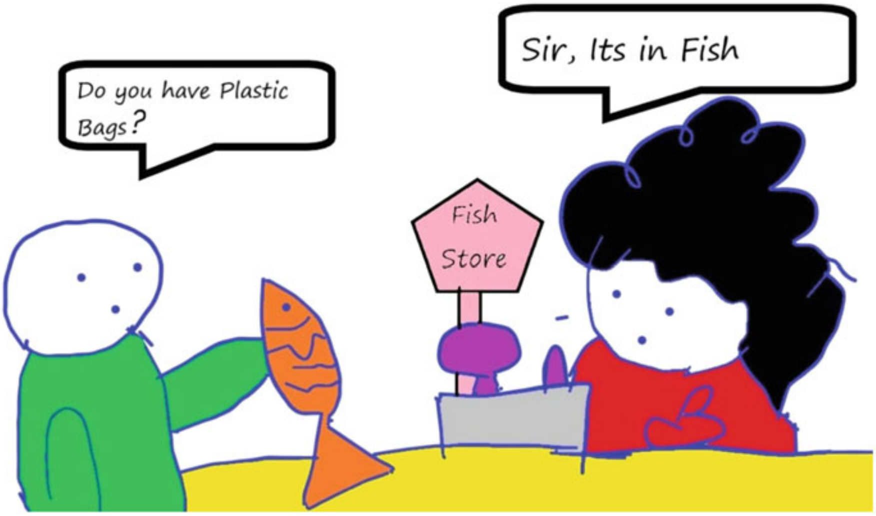


Fig. 4.1 Effect of improper disposal of plastic bags in fish

marine life by choking life forms and are called “Ghost Nets.” The process by which all kinds of marine creatures are being caught in them is known as “Ghost Fishing” (Stelfox et al. 2016). On the basis of food requirement, plastic waste in the oceans also terrorizes the life of birds, which depend on the oceanic life for their food need. These birds mostly suffer because of ingestion of plastic and suffocation. They are tricked by the beautiful colors of plastic debris. Sometimes they get caught in the debris and die due to suffocation: 44% of all sea bird species, sea turtle, and cetaceans have plastic junk inside or outside of their body. Plastic pollution in the marine also affects human life in other ways. Consumption of marine food, for example, fish, by people in turn affects their health, because ingestion of plastics by fish ultimately enters into the human body. During the fishing activities, there is high chance that fishes infected by such toxic matter might get their route into our daily chores to create health issues to the end consumers. A study reveals that toxic matter present in plastics creates severe health issues such as cancers, problem in immune system, and birth defects (Thompson and Napper 2019; Millet et al. 2018).

B. *Plasticsin fresh water*

Due to various environmental factors, plastics enter into the environment and persist with degradation and fragmentation to smaller particles. These microplastics and nanoplastics having larger surface area are likely to have a higher environmental risk. They are highly sensitive to adsorb organic pollutants and pathogens (Strungaru et al. 2019; Wang and Wang 2018; Blettler et al. 2018). Rivers receive important loads of litter by visitors and terrestrial runoff, but the particular sources of river in litter have not been identified. Presence of plasticcontaminants in fish of freshwater and its impacts on aquatic life and human beings are interlinked (Pinheiro et al. 2017). In ecosystems, plastics can have harmful effect for the local fauna. Nano- or microplastics are generally ingested by fish. It is believed that ingestion of plastics in fish is more often intentional, because they are attracted by their beautiful appearance in water. Sometimes accidently plastics may be ingested with their food (Peters and Bratton 2016; Lonnstedt and Eklov 2016). Even more concern is that microplastics are present in drinking water, in beer, food. Recent studies also reveal that water contamination by microplastics mainly comes from high consumption of bottled water (Ward et al. 2009; Oslon 1999; Raj 2005; Jain et al. 2019).

4.5 Impact of Plastics Present in Water

There is a noticeable correlation between the presence of plastic matter in the blood and certain health problems. These health problems incorporate reproductive abnormalities, cancer, early puberty, obesity, blood pressure, etc.

Our drinking water supply is highly contaminated with small particles of plastics. Those who are victims of plastic contamination have surely faced certain severe health problems. Nanoplastics highly affect the photosynthesis process of green algae. Ultimately, they affect the complete food chain. They harm aquatic life, plant, animals such as cow, buffalo, goat, and human beings by disturbing ecosystem.

4.6 Solution to Reduce Plastics and e-Waste Pollution

From the point of improving the quality of drinking water, we have to concentrate on three things:

A. *Prevention* – Controlling the concentration of plastic and electronic devices that reach any water body.
B. *Innovation* – Searching for new route to clean plastics and e-wastes that are already present in our water supply.
C. *Activism* – People should promote activities in reducing consumption of plastics by creating a culture where people actively think and create a path for this. Long-term use of electronic devices or manufacturing electronic devices with low toxicity metals may also help.

Several countries in Europe have stopped the use of certain plastics in food packaging that comes in contact with food and drink. Policies have been made to control the distribution and consumption of various single-use plastics, and disposal of e-waste. People should be aware of the potential risks of their drinking water and governments, national and local bodies, must come up with innovative solutions to overcome these problems. Microplastics and e-wastes are a compelling problem in water system. While systematic solutions are being developed, we can do few things to reduce our own contribution to the problem of drinking water contamination and to limit the risk of health issues:

A. *Proper disposal* – We should inhibit the fabrication of micro- and nanowastes by proper disposal of plastic and electronic products and be careful not to dispose these products around beaches, waterways, and in open places. Whenever we see wastes/garbage especially in ponds, streams, rivers, and beaches, if possible, we should bring up and dump or put in trash box. Around 90% of the plastic things in our daily life are used once and then dumped. For example, grocery bags, plastic wrap, disposable food plates, glasses, straws, cup, and electronic items are used for 6 months to 2 years with higher rate of consumption. We can make it a habit to carry our own bags to the store, and take our own mug/glass to coffee house.
B. *Campaigns*– Participate and organize clean-up activities as much as we can in our surroundings.
C. *Use brain* – Before purchasing, we may Google the product and gather the information. After that we may purchase products having fewer microbeads. We need to select products. which have natural exfoliates instead.

D. *Minimal use of synthetic clothes* – We should try to focus on changing the way we wash our clothes to reduce the release of microfibers. These include the following:

  - To wash less frequently synthetic clothes.
  - To use fiber filter during washing process of synthetic clothes.
  - Try to use more liquid laundry soap rather than powder soaps, since powder soap loosens more microfibers.
  - To use bags or other devices in washing machine to accumulate microfibers.
  - Not to wash floss from dryer down the drain. Throw it out into the bin.

E. *Shopping* – Always carry a cotton bag during shopping.
F. *Minimal use of bottled water* – Avoid use of bottled water, to stop single use of plastic and protect environment. Every year, around 20 billion polyethylene terephthalate bottles are disposed in the debris. This amount can be reduced by our little efforts. We can always bring usable bottle with us and avoid dumping used polyethylene terephthalate bottles anywhere in open land. If we are scared about the quality of our local tap water, we should use filter attached to our tap.
G. *Use of filter* – We search for a filter, which can eliminate or separate all microplastics from drinking water via simple filtration process.
H. *Recycling* – It looks obvious, although we are not doing a perfect job. We are confused about what can and can't go into the bin. We have lack of knowledge about different kinds of plastics and e-waste. In case of plastics, we can find out the number on the basis of the plastic canister and in case of e-waste, we need to categorize it to separate it for recycling.
I. *Organization fighting to save ocean fromplasticsande-wasteaccumulation* – A hazardous risk of plastics and e-waste in drinking bottled water was also reviewed by World Health Organization. It was reported that bottled water contains more than 90% tiny pieces of plastic. Even researchers also found high levels of microplastics in tap water. These e-plastics may be converted into energy to make them useful (Chandrasekaran et al. 2018).

4.7 Challenges During Detection of Microwaste and Nanowaste

A variety of issues may arise during the use of nanoparticles in aquatic tests or whole sediment toxicity tests in the presence or absence of cocontaminants. It is not possible to identify nanoparticles in the environment or to isolate adequate amounts from the environment for research. This reveals that manufactured nanoparticles need to be used and only commercially available types can be tested. Nanoparticles present in the environment include different polymers of varying sizes and shapes. Manufactured nanoparticles will thus show different behavior of environmental nanoparticles. Synthesized nanoparticles come with various additives, monomers, or oligomers of the plastics. Commercial nanoparticles are useless for toxicity test, because they are often provided with a biocide to stop bacterial growth during delivery and storage. Various dispersants such as sodium dodecyl sulfate are also used to stop agglomeration of nanoparticles. Concentration of the surfactant should be maintained very less to toxicity thresholds and should be included in the control. Nanoparticles can also be used for wastewater treatment to reduce the concentrations of unwanted chemicals. Efficiency of nanoparticles can be increased by modification/functionalization of surface; some other exposure conditions also affect the properties of nanoparticles. A free dispersion may lead to reduced particle size without agglomeration. Thus, aggregation should be monitored during the tests. Similar other challenges relating to the nanoparticles are similar to those for nonpolymer manufactured nanomaterials. Thus, detection test for nano- or macroplastics in environment is a major problem.

4.8 Conclusion

Plastic and electronic pollution are creating problems that place worst effect to the globe. Our water systems have severe impacts from such pollution on marine and river life, the increased uncleanness of our surrounding environment, and climate change, and the manufacturing, application, and expulsion of plastics and e-wastes containing lead, cadmium, beryllium, and other heavy metals. The lack of government policy action and unawareness of people in this realm are appalling. Government did not set any regulation for plastic leaching or presence of microplastic in bottled water ,which affects human health and e-waste in water stream. We need to place more emphasis on removing existing plastics and various forms of e-waste from water.

References

Andrady AL (2011) Microplastics in the marine environment. Mar Pollut Bull 62:1596–1605. https://doi.org/10.1016/j.marpolbul.2011.05.030

Bhattacharya P, Lin S, Turner JP, Ke PC (2010) Physical adsorption of charged plastic nanoparticles affects algal photosynthesis. J Phys Chem C 114:16556–16561. https://doi.org/10.1021/jp1054759

Blettler MCM, Abrial E, Khan FR, Sivri N, Espinola LA (2018) Freshwater plastic pollution: recognizing research biases and identifying knowledge gaps. Water Res 143:416–424. https://doi.org/10.1016/j.watres.2018.06.015

Breivik K, Armitage JM, Wania F, Jones KC (2014) Tracking the global generation and exports of e-waste. do existing estimates add up? Environ Sci Technol 48:8735–8743. https://doi.org/10.1021/es5021313

Chandrasekaran SR, Avasarala S, Murali D, Rajagopalan N (2018) Materials and energy recovery from e-waste plastics. ACS Sustain Chem Eng 6:4594–4602. https://doi.org/10.1021/acssuschemeng.7b03282

Chen GQ, Patel MK (2012) Plastics derived from biological resources: present and future: a technical and environmental review. Chem Rev 112:2082–2099. https://doi.org/10.1021/cr200162d

Chin LW, Fung TH (2019) Plastics in marine litter. Plast Environ, Royal Soc Chem:1–39. https://doi.org/10.1039/9781788013314-00021

Costa MF, Barletta M (2015) Microplastics in coastal and marine environments of the western tropical and subtropical Atlantic Ocean. Environ Sci: Processes Impacts 17:1868–1879. https://doi.org/10.1039/C5EM00158G

Ding J, Li J, Sun C, Jiang F, Ju P, Qu L, Zheng Y, He C (2019) Detection of microplastics in local marine organism using a multi-technology system. Anal Method 11:78–87. https://doi.org/10.1039/C8AY01974F

Hidalgo-Ruz V, Gutow L, Thompson RC, Thiel M (2012) Microplastics in the marine environment: a review of the methods used for identification and quantification. Environ Sci Technol 46:3060–3075. https://doi.org/10.1021/es2031505

Hsu E, Barmak K, West AC, Park AHA (2019) Advancement in the treatment and processing of electronic waste with sustainability: a review of metal extraction and recovery technologies. Green Chem 21:919–936. https://doi.org/10.1039/C8GC03688H

Jain B, Singh AK, Susan Md ABH (2019) Bottled and packaged water, 1st edn, pp 562–601. https://www.elsevier.com/books/bottled-and-packaged-water/grumezescu/978-0-12-815272-0

Jamieson AJ, Brooks LSR, Reid WDK, Piertney SB, Narayanaswamy BE, Linley TD (2019) Microplastics and synthetic particles ingested by deep sea amphipods in six of the deepest marine ecosystem on earth. Royal Soc 6. https://doi.org/10.1098/rsos.180667

Koelmans AA, Besseling E, Shim WJ (2015) Nanoplastics in the aquatic environment. Critical review. Mar Anthropol Lit:325–340. https://doi.org/10.1007/978-3-319-16510-3_12

Kontrick AV (2018) Microplastics and human health: our great future to think about now. J Med Toxicol 14(2):117–119. https://doi.org/10.1007/s13181-018-0661-9

Li J, Zeng X, Chen M, Ogunseitan OA, Stevels A (2015) 'Control alt delete' rebooting solution for the e-waste problem. Environ Sci Technol 49:7095–7108. https://doi.org/10.1021/acs.est.5b00449

Lonnstedt OM, Eklov P (2016) Environmentally relevant concentrations of microplastics particles influence larval fish ecology. Science 352:1213–1216. https://doi.org/10.1126/science.aad8828

Millet H, Vangheuwe P, Block C, Sevenster A, Garcia L, Antonopoulos R (2018) The nature of plastics and their societal usage. Plast Environ:1–20. https://doi.org/10.1039/9781788013314

Oslon E (1999) Bottled water, pure drink or pure hype? Natural Resources Defense Council, New York. http://www.nrdc.org/water/drinking/bw/bwinx.asp

Parrales AR, Sibaja TO, Redondo-Gomez C, Vega-Baudrit J (2018) Biological degradation of plastics: polyethylene biodegradation by aspergillius and Streptomyces species-a review. Integr Sustain Environ Remed 3:69–79. https://doi.org/10.1021/bk-2018-1302.ch003

Peters CA, Bratton SP (2016) Urbanization is a major influence on microplastic ingestion by sunfish in the Brazos River Basin, Central Texas, USA. Environ Pollut 210:380–387. https://doi.org/10.1016/j.envpol.2016.01.018

Pico Y, Barcelo D (2019) Analysis and prevention of microplastics pollution in water: current perspectives and future directions. ACS Omega 4:6709–6719. https://doi.org/10.1021/acsomega.9b00222

Pinheiro C, Oliveira U, Vieira NR (2017) Occurrence and impact of microplstics in freshwater fish. J Aquac Mar Biol 5. https://doi.org/10.15406/jamb.2017.05.00138

Raj SD (2005) Bottled water how safe is it? Water Environ Res 77:3013–3018. https://doi.org/10.2175/106143005X73893

Rochman CM (2013) Plastics and priority pollutants: a multiple stressor in aquatic habitats. Environ Sci Technol 47:2439–2440. https://doi.org/10.1021/es400748b

Smith M, Love DC, Rochman CM, Neff RA (2018) Microplastics in seafood and the implication for human health. Curr Environ Health Rep 5:375–386. https://doi.org/10.1007/s40572-018-0206-z

Stelfox M, Hudgins J, Sweet M (2016) A review of ghost gear entanglement amongst marine mammals, reptiles and elasmobranchs. Mar Pollut Bull 111:6–17. https://doi.org/10.1016/j.marpolbul.2016.06.034

Strungaru SA, Jijie R, Nicoara M, Plavan G, Faggio C (2019) Micro-(nano) plastics in freshwater ecosystems: abundance, toxicological impact and quantification methodology. TrAC Trends Anal Chem 110:116–128. https://doi.org/10.1016/j.trac.2018.10.025

Thompson RC, Napper IE (2019) Microplastics in the environment. Plast Environ, Royal Soc Chem. https://doi.org/10.1039/9781788013314-00060

Velzeboer I, Quik JTK, Van de Meent D, Koelmans AA (2014) Rapid settling of nanomaterials due to hetero-aggregation with suspended sediment. Environ Toxicol Chem 33:1766–1773. https://doi.org/10.1002/etc.2611

Von der Kammer F, Ferguson PL, Holden P, Masion A, Rogers K, Klaine SJ (2012) Analysis of nanomaterials in complex matrices (environment and biota): general considerations and conceptual case studies. Environ Toxicol Chem 31:32–49. https://doi.org/10.1002/etc.723

Wagner M, Scherer C, Alvarez-Muñoz D, Brennholt N, Bourrain X, Buchinger S, Fries E, Grosbois C, Klasmeier J, Marti T, Rodriguez-Moraz S, Urbatzka R, Vethaak AD, Winther-Nielsen M, Reifferscheid G (2014) Microplastics in freshwater ecosystems: what we know and what we need to know. Environ Sci Eur 26:1–9. https://doi.org/10.1186/s12302-014-0012-7

Wagner J, Wang ZM, Ghosal S, Rochman C, Gassel M, Wall S (2017) Novel method for the extraction and identification of microplastics in ocean trawl and fish gut matrices. Anal Method 9:1479–1490. https://doi.org/10.1039/C6AY02396G

Wang W, Wang J (2018) Investigation of microplastics in aquatic environments: an overview of the methods used, from sampling to laboratory analysis. TrAC Trends Anal Chem 108:195–202. https://doi.org/10.1016/j.trac.2018.08.026

Ward LA, Cain OL, Mullally RA, Holiday KS, Wernham AGH, Baillie PD, Greenfield SM (2009) Health beliefs about bottled water: a qualitative study. BMC Public Health 9:196. https://doi.org/10.1186/1471-2458-9-196

Webb HK, Arnott J, Crawford RJ, Ivanova EP (2013) Plastic degradation and its environmental implications with special reference to poly (ethylene terephthalate). Polymers 5:1–18. https://doi.org/10.3390/polym5010001

Wright SL, Kelley FJ (2017) Plastic and human health: A micro issue? Environ Sci Technol 51:6634–6647. https://doi.org/10.1021/acs.est.7b00423

Zhang K, Schnoor JL, Zeng EY (2012) e-waste recycling: where does it go from here? Environ Sci Technol 46:10861–10867. https://doi.org/10.1021/es303166s

Zhang S, Wang J, Liu X, Qu F, Wang X, Wang X, Li Y, Sun Y (2019) Microplastic in the environment: a review of analytical methods, distribution and biological effects. TrAC Trends Anal Chem 111:62–72. https://doi.org/10.1016/j.trac.2018.12.002

Chapter 5

Degradation of Polycyclic Aromatic Hydrocarbons by Functionalized Nanomaterials

Rachna, Manviri Rani, and Uma Shanker

Contents

Rachna · U. Shanker (✉)
Department of Chemistry, Dr B R Ambedkar National Institute of Technology, Jalandhar, Punjab, India
e-mail: shankeru@nitj.ac.in

M. Rani
Department of Chemistry, Malaviya National Institute of Technology, Jaipur, Rajasthan, India

Inamuddin et al. (eds.), *Water Pollution and Remediation: Organic Pollutants*, Environmental Chemistry for a Sustainable World 54,
https://doi.org/10.1007/978-3-030-52395-4_5

Abstract Polycyclic aromatic hydrocarbons, most commonly found organic contaminants in considerable amounts in various water bodies are persistent, cause severe health and environmental problems. Various strategies have been employed in the removal process of polycyclic aromatic hydrocarbons, but all have certain limitations associated along with them. In recent times, modification of basic materials through their coupling, pairing, or functionalization with other materials has been explored in order to get desired results. Degradation of polycyclic aromatic hydrocarbons has been also explored with these functionalized materials where it can be carbon nanotubes, graphene oxide, or metal-based materials.

Incorporated metal oxides have tendency of oxidizing as well as degrading the polycyclic aromatic hydrocarbons through the support of various reactive species (superoxide or hydroxyl radical). Most of the materials have shown good results, but the metal-based materials were explored vastly. Functionalization introduced additional energy levels in semiconducting phenomena and enhanced the surface activity of the catalysts. However, most of the studies were devoted to the three-ring membered polycyclic aromatic hydrocarbon degradation, namely, phenanthrene, anthracene, and naphthalene. This chapter will provide readers a good quality of information of recent trends of functionalization of nanocatalysts as well as various degradation strategies of polycyclic aromatic hydrocarbons.

Keywords Polycyclic aromatic hydrocarbons · Water · Pollution · Carcinogenic · Nanoparticles · Functionalization · Photodegradation

5.1 Introduction

A lot of environmental problems nowadays are found to be originated from polycyclic aromatic hydrocarbons owing to its carcinogenicity and potential ruinous effects on life. Polycyclic aromatic hydrocarbons belong to the class of the compounds containing two or more coupled benzene rings in different conformations (Chefetz et al. 2000). Polycyclic aromatic hydrocarbons generally originate from the unfinished burning of organic materials including coal, petroleum products, tobacco, and agricultural by-products. Anthropogenic activities leading to the formation of polycyclic aromatic hydrocarbons are military invention, household waste burnings, and seepage of petroleum from refineries and combustion of engines (Cerniglia 1984; Ravindra et al. 2008). Textile dye sludge was reported to contain a small amount of polycyclic aromatic hydrocarbons in it. In China, around ten dyeing factories were found to contain a significant polycyclic aromatic hydrocarbons level in its sludge (Ning et al. 2014). It has been reported that in most of the industrial areas of world, thousands of gallons of exploited motor oil including polycyclic aromatic hydrocarbons s are disposed untreated into soil (Irland et al. 1995). Most of the polycyclic aromatic hydrocarbons have high stability and lipid solubility causing its accumulation in organism including mankind above all. The US Environmental Protection Agency has included 16 polycyclic aromatic hydrocarbons into its most toxic organic pollutants (Callahan et al. 1979). In eastern Asia, the concentration of polycyclic aromatic hydrocarbons in soil ranges between 10 and 20 g kg^{-1} with highest proportion of 102 and 104 g kg^{-1} in critical areas. It was concluded through aerial examination of polycyclic aromatic hydrocarbon content in various cities of United States that highest level of polycyclic aromatic hydrocarbons occurs during the winter months (Sawicki et al. 1960).

Nitrogen- and oxygen-containing derivatives of polycyclic aromatic hydrocarbons are reportedly mutagenic, carcinogenic, and estrogenic (Lundstedt et al. 2007; Dipple 1985). Derivatives of polycyclic aromatic hydrocarbons are generally formed through homogeneous/heterogeneous photooxidation of parent polycyclic aromatic hydrocarbons with natural oxidants and photodecomposition along with heat exchange (Cochran et al. 2016). It is noteworthy that few of the derivatives of polycyclic aromatic hydrocarbons are more poisonous and possess greater danger to human health (EHC 2003).

In view of the above facts, a simple and economic strategy is needed to be developed for the removal of polycyclic aromatic hydrocarbons. One of the oldest effective methods of polycyclic aromatic hydrocarbons removal is bioremediation, where variety of microorganisms have been categorized and injected in affected soils (Kuppusamy et al. 2017). However, bioremediation is linked to certain limitations, such as lack of environmental support to microbial growth, little bioavailability of desired contaminants, involvement of various unwanted contaminants, and time consumption (Liu et al. 2017). Other well-known techniques include photo and chemical oxidation, adsorption, filtration, volatilization, discharge, and microorganism-based degradation (Wild and Jones 1995). Recently, heterogeneous catalysis has exhibited successful performance in wastewater treatment owing to its high activity and cheapness and use natural light source like sunlight (Saad Hassan et al. 2015). Semiconductor involved in photocatalysis causes the excitation of electron from lower energy level to higher energy level, creating a vacancy behind.

In the presence of a source of light, oxidation and reduction can take place resulting into degradation of contaminants in relatively short time (Zhang et al. 2008). Most of such nanomaterials exhibit outstanding properties such as mechanical strength along with chemical confrontation for a broad range of pH. However, their hydrophobic nature limits their use in water purification techniques. In recent times, modification of nanomaterials through their surface functionalization has gained a great attention worldwide owing to its simple fabrication, hydrophilicity, and better dispersion (Hebbar et al. 2016; Pereira et al. 2015).

5.2 Classification of Polycyclic Aromatic Hydrocarbons

Polycyclic aromatic hydrocarbons have been grouped in accordance to their toxicological potential (IARC 1998). However, most of the scientific literature is based upon the 16 Environmental Protection Agency's priority polycyclic aromatic hydrocarbons. Structure of such polycyclic aromatic hydrocarbons is as shown in Fig. 5.1. Detailed discussion of some of the widely studied polycyclic aromatic hydrocarbons is as below.

5.2.1 *Naphthalene*

Naphthalene having molecular formula $C_{10}H_{18}$ is the simplest of all the polycyclic aromatic hydrocarbons. The US Environmental Protection Agency has labeled it as a semi-volatile compound with International Agency for Research on Cancer and listing as almost carcinogenic to life (USEPA 1999; WHO 2002). Various studies have been focused upon the respiratory tract toxicity of naphthalene in rodents through tumor formation in mouse lungs and nasals (Van Winkle et al. 1995; National Toxicology Program 2000).

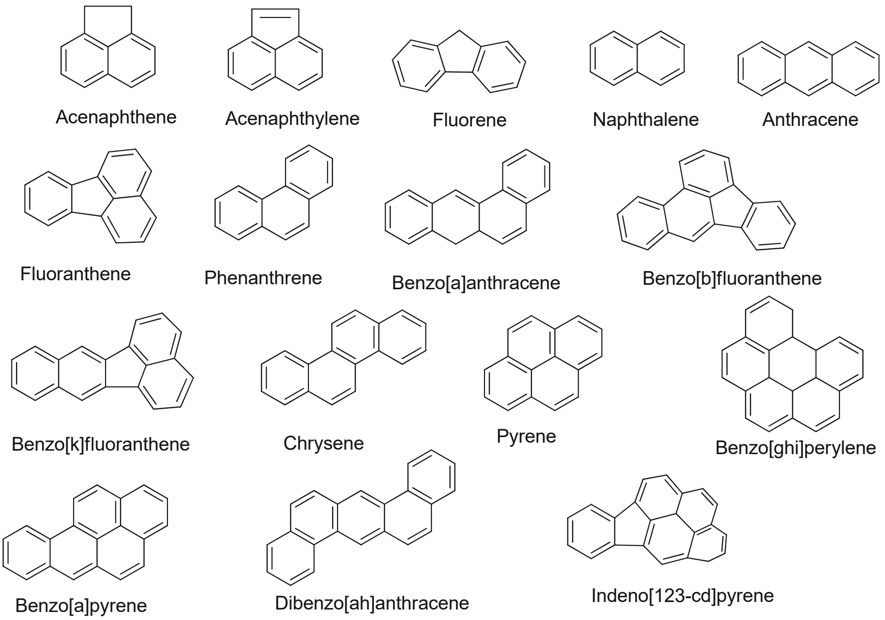


Fig. 5.1 Structures of 16 polycyclic aromatic hydrocarbons as listed by US Environmental Protection Agency. Popularly known for their hazardous effect on environment as well living species. (With permission through rightslink; Rani and Shanker 2018)

5.2.2 Acenaphthene

Acenaphthene is a crystalline white color compound that spreads into the environment via exhaust of fuels, gasper smoke, and metropolitan atmosphere (Severson et al. 1976; Grimmer et al. 1977; Cleary 1962). It has been found in residues of pesticides, plastics precursors, coloring agents, and oil refinery effluents and supposed to increase the risk of lung tumor deaths (Warshawsky 1999).

5.2.3 Fluorene

Fluorene is generally detected in environmental samples of soil, river sediments, and aquatic regions because of its involvement in most of the complex of polycyclic aromatic hydrocarbons. Structures similar to fluorine have been found in different mutagenic and or carcinogenic polyarenes such as 2-aminofluorene, 2-nitrofluorene, and 2-acetyl-aminofluorene (Garon et al. 2002). Fluorene has gained attention of environmentalist because of its xenobiotic behavior and its presence in oil spills, urbanization clear, and waste burns (Lu and Zhu 2007).

5.2.4 Phenanthrene

Phenanthrene having $C_{14}H_{10}$ molecular mass is a white/yellow tricyclic crystalline polycyclic aromatic hydrocarbons with the aromatic rings arranged in an angular manner. It lies in the low molecular weight class of polycyclic aromatic hydrocarbons and is isomeric with the anthracene (Young and Cerniglia 1995). Large proportion of coal and fossil fuels contain phenanthrene as a major component (Supaka et al. 2001).

5.2.5 Anthracene

Anthracene is one of the three ring-membered polycyclic aromatic hydrocarbons with serious toxicity and high pollution potential. It is a non-polar and hydrophobic compound and is found in other high molecular weight polycyclic aromatic hydrocarbons through repetition of its basic structure (Das et al. 2008). Anthracene is often present in organic polluted river remains, soils, and other scrap sites because of its utilization in bio-treatment studies (Jacques et al. 2005). Photooxidation of anthracene was reported to be toxic toward soil fungi with high threat to aquatic bodies (Larson and Berenbaum 1988; Bonnet et al. 2005).

5.2.6 Fluoranthene

Fluoranthene is a four-benzene ring containing high molecular weight compound. It has been classified as priority pollutant by Environmental Protection Agency (Abdel-Shafy and Mansour 2016). It is believed to be quite immiscible in water with solubility of 0.25 mg L^{-1} and, hence, is less bioavailable (Okere and Semple 2012). It has been used as a model complex, because of its presence in other high molecular weight carcinogenic polycyclic aromatic hydrocarbons (Pothuluri and Cerniglia 1994).

5.2.7 Pyrene

Pyrene is a four-ring-membered recalcitrant contaminant (Wang et al. 2012). It is less bio-available and highly opposing to biological attack (Dissanayake et al. 2010). Because of its wide distribution in water bodies, it creates threat to aquatic life and humans owing to its toxicity (Oliveira et al. 2012).

5.2.8 Benzo[a]anthracene

Benz[a]anthracene is a four-benzene ring containing high molecular weight polycyclic aromatic hydrocarbons classified priority pollutant by the Environmental Protection Agency. It has been called as carcinogenic owing to its high chemical stability (Agency for Toxic Substances and Disease Registry 1995). Due to its higher condensed form, it is relatively unmanageable.

5.2.9 Chrysene

The Environmental Protection Agency has included chrysene in to its priority pollutant record due to its mutagenic and carcinogenic effects (Agency for Toxic Substances and Disease Registry, Nwaichi et al. 2016). The prolonged being of chrysene in the atmosphere is due to its low water solubility lying between 1.6 and 2.2 mg L^{-1} and high molecular weight (May et al. 1978).

*5.2.10 Benzo[*a*]pyrene*

Out of all the polycyclic aromatic hydrocarbons, benzo[*a*]pyrene is the prime suspected carcinogen. Its presence in non-aqueous phase is because of its extremely small solubility of 3.8 μg L^{-1} with a large partition factor (Ko/w: 6.04) (Manoli and Samara 1999). It is considered as the most potent carcinogenic as well as genotoxic complex and has been widely studied until now (Kot-Wasik et al. 2004).

*5.2.11 Indeno(*1,2,3,c,d*)pyrene*

It is a six-benzene ring containing polycyclic aromatic hydrocarbons and defined as a main concern pollutant by the Environmental Protection Agency (Lawal 2017; Ping et al. 2017a). The World Health Organization has suggested its maximum value of 200 ng $L^{-1}$to be adopted as allowable concentration in drinking water (Ping et al. 2017b).

*5.2.12 Dibenzo[*a,h*]anthracene*

It is a white-yellow crystalline polycyclic aromatic hydrocarbon composed of five fused aromatic rings. It is commonly found in smoke and oil spills. It was not detected in humans, but its content in smoked meat was quite high with level of 0.0024 mg kg^{-1} day^{-1}. It was found to be most dosed polycyclic aromatic hydrocarbons in aquatic species (Taiwo et al. 2019).

*5.2.13 Benzo[*g,h,i*]perylene*

It has been found to be one of the most clustered benzene rings containing compound. There is very limited information about this polycyclic aromatic hydrocarbon, making its exploration even important to make the environment safe and free from it. Its content found in the sludge of China was less than 5000 ng g^{-1} (Sun et al. 2019a, b).

5.3 Sources

In environment polycyclic aromatic hydrocarbons are detected in all the regions through different ways such as via industrialization, farming, oil spilling, pollution, and burning of organics. Production of these is related with the partial burning of organic contents such as coal, woods, oil, and fuels. The combustion is incomplete because of the limited availability of oxygen and low temperature. This caused the production of neutral species which trigger fabrication of hydrocarbons. High molecular weight polycyclic aromatic hydrocarbons are formed through the free radicals of similar molecular weight. A few of these are released into the environment naturally via combustion of woods and volcanic eruption (Baek 1991; Harvey 1998). Anthropogenic supplies of polycyclic aromatic hydrocarbons consist of immobile and mobile sources. Immobile sources include housing smoke, industrial production, incineration, and power production. Ninety seven percentages of the polycyclic aromatic hydrocarbons emissions are occurred through stationary sources (Gaga 2004; Pikes 1992). Global annual polycyclic aromatic hydrocarbon atmospheric emission in year of 2007 was around 500 and 4 gigagram having 60% of suburban/industrial, while organic burning is 13.6% and fuel consumption through vehicles is 12.8%. The percentage of high molecular weight polycyclic aromatic hydrocarbons was 6.2% in these emissions (Shen et al. 2013). Cigarette butts are another wide source of polycyclic aromatic hydrocarbons. According to World Health Organization, one billion smokers had consumed over 5.4 trillion cigarettes worldwide (WHO 2017). These are found in every corner of an area including bus stops, roads, parking, streets, and in homes (Novotny et al. 2011). The total content of the carcinogenic polycyclic aromatic hydrocarbons in crude oils and coals ranged from less than 1–260 mg per kg (Wang et al. 2017). A few of the most common and widespread sources of polycyclic aromatic hydrocarbons is oil spilling. Polycyclic aromatic hydrocarbons are found to be most persistent in the oil spills. Some of the polycyclic aromatic hydrocarbon-related oil spilling incidents has been listed in the Table 5.1. Industrialization, particularly mining, has also contributed in spreading the polycyclic aromatic hydrocarbons in the environment. Coal gangue formed as a by-product of mining contains large content of polycyclic aromatic hydrocarbons in it depending on the rank of coal (Zhang and Zhao 2007). The residential areas around mines have been reported of soil contamination of polycyclic aromatic hydrocarbons. The Luling Coal Mine in China had maximum amount of polycyclic aromatic hydrocarbons, while the Zhangji coal mine had least concentration. In addition to this, the low molecular weight polycyclic aromatic hydrocarbons were found in greater amount (Wang et al. 2010a, b).

The particle-bound polycyclic aromatic hydrocarbons were also detected in the Angren industrial area of Uzbekistan from the coal combustion. However, it was found that places way from the point sources had lesser concentration of polycyclic aromatic hydrocarbons in the soil. Reports have suggested the convey space diminished with escalating weight as amount bound among the quick mending environmental elements raised (Musa Bandowe et al. 2010). Soil has been considered as

Table 5.1 Polycyclic aromatic hydrocarbon-related oil spilling incidents occurred around the world with their impact on environment

Site	Place	Year	Causes
Lakeview Gusher	California, United States	1910–1911	1200 tonnes of crude oil released
Kuwaiti oil lakes	Kuwait	1991	3409–6818 tonnes of crude oil released
Kuwaiti oil fires	Kuwait	1991	136,000 tonnes of crude oil released
Rhodamine Dye Spill	Boston	2007	2436$ lab cleaning cost
MT *Hebei Spirit* oil spill	South Korea	2007	10,800 tonnes of crude oil released
Deep WaterHorizon oil spill	United States	2010	11 deaths, instant killing of aquatic species, accumulation
Sundarbans oil spill	Bangladesh	2014	Captain of the ship died, 1,000,000,000 Bangladeshi taka (currency) was lost
Ennore oil spill	Chennai	2017	More than 70 tonnes of crude oil released

exceptional well arsenal along with transmit deposition drop for polycyclic aromatic hydrocarbons. These are spread in to the plane soil via dry as well as wet deposition. Such contamination also leads to the other contamination of vegetation and hence into the human beings (Wang et al. 2010a, b; Liu et al. 2012).

5.4 Concentration of Polycyclic Aromatic Hydrocarbons

Many studies suggest that the proportion of polycyclic aromatic hydrocarbons was found to be lowest during summer days than that of winter. This appearance is due to the fact that inversion days in winters decrease along with their resource and inhabited oil burning for heat (Hussain et al. 2016). Another observation was that the risk of individual's contact with polycyclic aromatic hydrocarbons is more in developed places because of the large inhabitants, traffic, and inadequate distribution of contaminants (Rockens et al. 2000). Amount of polycyclic aromatic hydrocarbons in water and river sediment of various countries as reported by the studies is shown in the Table 5.2.

5.5 Environmental Concern of Polycyclic Aromatic Hydrocarbons

Exposure of polycyclic aromatic hydrocarbons to the humans has raised increased risk of various tissues cancer such as stomach, skin, bladder, and lung. Moreover, to what extent the cancer is severe, it depends upon the mode of exposure and kind of the polycyclic aromatic hydrocarbons (Kim et al. 2013). Polycyclic aromatic

Table 5.2 Concentration of polycyclic aromatic hydrocarbons in river water and sediments worldwide

Place	Concentration	% of polycyclic aromatic hydrocarbons
Evoikos Gulf, Greece	0.0009–0.14 μgL^{-1}	68.6
Malliakos Gulf, Greece	0.002–0.05 μgL^{-1}	75.0
Surface water of northern Greece	0.001–0.68 μgL^{-1}	85.2
Kor River water, Iran	0.0003–0.24 μgL^{-1}	81.6
Water resources in Mahasarakham University, Thailand	0.001–0.009 μgL^{-1}	13.4
Reclaimed and surface water of Tianjin, China	1.80–35 μgL^{-1}	95.9
Suez Canal, Egypt	0.01–0.5 μgL^{-1}	16.2
Shallow Lake, Zeekoevlei, South Africa	0.00001–0.01 μgL^{-1}	95.0
Mvudi River water, South Africa	126–7510 μgL^{-1}	25.3
Lakes and rivers around Johannesburg/Pretoria in South Africa	0.021–0.62 μgL^{-1}	86.6
Petroleum produced water, Sergipe, Brazil	3.50–44.30 μgL^{-1}	52.4
West Mediterranean Sea (French Riviera, Corsica, Sardinia)	1.5–20,440 μgKg^{-1}	–
The Czech Republic (Industrial)	3500–61,700 μgKg^{-1}	–
Inshore coastal areas around Malta	0–14,990 μgKg^{-1}	–
Gulf and the Gulf of Oman, UAE	0.6–9.4 μgKg^{-1}	–
Coastal of Bushehr, Persian Gulf	41.7–227.5 μgKg^{-1}	–
Industrial Port Area of Southern Kaohsiung Harbour	4425–51,261 μgKg^{-1}	56.3
Mumbai Harbour Line, India	17–134,134 μgKg^{-1}	–
Gulf and the Gulf of Oman, Qatar	0.55–92 μgKg^{-1}	–
Khure-Musa Estuarine, Persian Gulf	703–3302 μgKg^{-1}	80.9
Gulf and the Gulf of Oman, Bahrain	13–6600 μgKg^{-1}	–
Marine Environment, Korea	8.80–18,500 μgKg^{-1}	–
Coastal and estuarine areas of the northern Bohai and Yellow Seas, China	52.3–1871 μgKg^{-1}	78.3
Gulf and the Gulf of Oman, Oman	1.6–30 μgKg^{-1}	–
Delhi, India	920–19,321 μgKg^{-1}	62.4
Kor River, Iran	167.4–530.3 μgKg^{-1}	82.5
Kyeonggi Bay, Korea	10–1400 μgKg^{-1}	–
Middle of Muggah Creek Estuary, Sydney (Australia)	142 μgKg^{-1}	–
South San Francisco Bay	~120–9560 μgKg^{-1}	–
Gulf of Naples and nearby Coastal Areas, US	0.34–31.77 μgKg^{-1}	–
Casco Bay, Maine, Texas	16–20,798 μgKg^{-1}	93.6
Kitimat Harbour, Canada	310–528,000 μgKg^{-1}	–
Fore River and Portland Harbor, Maine	2953–278,300 μgKg^{-1}	69

(continued)

Table 5.2 (continued)

Place	Concentration	% of polycyclic aromatic hydrocarbons
San Francisco Bay, California	36–6273 μgKg^{-1}	87.5
Todos Santos Bay, Mexico	7.6–813 μgKg^{-1}	–
Bagnoli Surface Sediment (industrial side of the Gulf of Naples)	0.1–2947 μgKg^{-1}	–
Tabasco state, Mexico	454–3120 μgKg^{-1}	–
Northwest Coast Mediterranean Sea	86.5–48,090 μgKg^{-1}	–
Suez Canal, Egypt	103.41–238.76 μgKg^{-1}	76.2
Central South Africa (industrial, residential, and agricultural)	44–39,000 μgKg^{-1}	–
Lakes and Rivers around Johannesburg/Pretoria in South Africa	61–45,281 μgKg^{-1}	52.3
Rivers in Thohoyandou, Limpopo Province, South Africa	111.6–61,764 μgKg^{-1}	–
Taylor Creek, Southern Nigeria (non-tidal freshwater – Bayelsa)	1.781×10^8–1.266×10^9 μgKg^{-1}	–
Mvudi River water, South Africa	266–21,600 μgKg^{-1}	55.3
Nzhelele River water, South Africa	206–13,710 μgKg^{-1}	87.4
Tema Harbour, Ghana	28,600–190,300 μgKg^{-1}	–

hydrocarbons can easily bind the endogenous receptors and are also called as endocrine disrupting compounds (Wattiau 2002). Other than this, polycyclic aromatic hydrocarbons can cause genetic alterations, effect growth and tissue alterations, and harm the immune system (Delistraty 1997). Polycyclic aromatic hydrocarbons can create distortions in the chromosomal deoxyribonucleic acid, and even a 0.002 mg Kg^{-1} amount present in mice can cause liver tumors (Jung et al. 2013; Tongo et al. 2017). Some of the polycyclic aromatic hydrocarbons have similar structure with that of steroid hormones can induce estrogenic activity (Yin et al. 2017a, b). Polycyclic aromatic hydrocarbons are activated by the microsomal cytochrome P450 monooxygenases and can form biologically dynamic products (Peltonen and Dipple 1995). Daily intake of acenaphthene by humans has been reported in recent study indicating its presence in the diet (Taiwo et al. 2019). The ozonated product of some of the polycyclic aromatic hydrocarbons such as phenanthrene has been found to be more hepatotoxic, and nephrotoxicity is one of the apparent effects (Kasumba and Holmen 2018). Cooking of meat with some of the style such as grilling, roasting, and frying can lead into the formation of polycyclic aromatic hydrocarbons. Moreover, it is found in content in meat having higher fat content, thus directly affecting the humans consuming these (Rogge et al. 1991). A lot of people, residing near coastal areas, consume seafood as their main daily diet source. However, regardless of its profits toward human health, daily ingestion of water species can raise the risk of contaminant exposure (Moon et al. 2010). The

European Food Safety Authority concluded that the in general food disclosure of polycyclic aromatic hydrocarbons by a person of 60 kg is around 235 nanogram per day (benzo[a]pyrene), 641 nanogram per day (benzo[a]pyrene + chrysene), around 1100 nanogram per day (benzo[a]pyrene + chrysene + benz[a]anthracene), and approximately 1700 nanogram per day (benzo[a]pyrene + chrysene + benz[a]anthracene + indeno(*1,2,3,c,d)*pyrene) (EFSA 2008). Polycyclic aromatic hydrocarbons are able to cause mutagenic cancerous activities as well as noncancerous health effects like cardiovascular illness, lung failure, liver damage, and pulmonary disease (Lakhani 2012). Polycyclic aromatic hydrocarbons are known to be soluble in non-polar solvents and, hence, are easily captivated through the alimentary canal of mammals. Once entered inside the human, polycyclic aromatic hydrocarbons can quickly disperse in various tissues with a striking capacity of localizing in internal hydrocarbon molecules (Abdel-Shafy and Mansour 2016). Persistency of polycyclic aromatic hydrocarbons in the environment is well known along with their bioaccumulation. Studies have shown that the content of polycyclic aromatic hydrocarbons observed in fish as well as in shellfish was surprisingly higher than their amount in their environmental source (Tudoran and Putz 2012). The cell damage caused by the polycyclic aromatic hydrocarbons can cause mutations, tumors, and developmental malformations. The immune-potentiating produces higher secretion of cytokines through immune cells that results into inflammation (Burchiel and Luster 2001). All the above facts clearly indicate that the irregular use of polycyclic aromatic hydrocarbons is harmful to human life as well as environment.

5.6 Functionalized Nanomaterials

Environmental cleanup is one of the most challenging tasks to be done to make the resources of water safe for use. Till date, numerous conventional wastewater treatment processes have been employed, like coagulation (Lin et al. 2017), photocatalytic oxidation (Berberidou et al. 2017), Fenton oxidation (Cristóvão et al. 2014), filtration (Noor et al. 2017), and adsorption (Caprariis et al. 2017). Among the different removal technologies, adsorption is known to be most popular owing to its effectiveness and easiness (Xiao et al. 2019). Besides this advanced oxidation is another kind of technology that can show advanced removal performance. The advanced oxidation is associated with high level of security, better oxidation tendency, and minimum toxicity. It is based upon consumption of hydroxyl radicals generated in situ by the electrochemical process. Studies based upon adsorption and oxidation have shown higher degradation and mineralization of the contaminants (Shanker et al. 2017a, b).

Nowadays, the term heterogeneous catalysis based upon solar light or artificial light source has been quite famous for environmental applications; wastewater treatment, contaminantremediation, and water disinfection are some of it (Priya et al. 2016; Sudhaik et al. 2018). Various transition metal oxides, polymers, carbon nanotubes, graphene-based nanostructures, and other metal-based nanomaterials have been used for the waste treatment (Raizada et al. 2017a, b; Raizada et al. 2019; Jun et al. 2018; Mahto et al. 2015). Despite of their high activity, majority of nanomaterials have certain limitations restricting utilization of 100% of their tendency. Firstly, recombination of the charge carriers has a negative impact on photodegradation; secondly, potential effect on human health, reusability, and restricted selectivity of nanocatalysts; and lastly, their reliability upon environmental circumstances (Rani and Shanker 2018a, b).

So as to overcome these limitations, surface modification is believed to have an important role in improving the overall activity of nanocatalysts (Yin et al. 2017a, b). In recent times surface functionalization has drawn attention of researchers owing to its potential benefits such as enhanced chemical reactivity, improved adsorption capacity, low charge recombination, and better semiconducting properties (Rachna and Shanker 2018, 2019a, b). List of some of the reported functionalized nanomaterials is listed in Table 5.3.

Degradation of polycyclic aromatic hydrocarbons using some of the commonly used functionalized nanomaterials is as described below.

5.6.1 Degradation Using Functionalized Carbon-Based Nanomaterials

Carbon-based materials have some fascinating electronic and mechanical properties like surface area and semiconducting behavior. Functionalization of these with other acidic or basic groups can increase their activity in treatment of polluted water. The decoration of carbon nanotubes with tungsten oxide significantly improved the number of surface active sites and lowered the combination of charges. Consequently, the nanocomposite degraded the naphthalene into smaller and safer products by the attack of reactive species on the first and second position of naphthalene (Rani and Shanker 2018). Overall degradation strategy has been given in Fig. 5.2.

Hybrid of carbon dots and fatty acid coated with magnetite nanoparticles were successfully utilized for the photocatalytic mineralization of benzo[a]pyrene. The nanocomposite was able to remove 93.9% of the benzo[a]pyrene from the environmental sample. The hydrophilic behavior of carbon dots enhanced the dispersibility of the catalyst, and the hydrophobic interactions increased the removal benzo[a] pyrene (Yang et al. 2019). Bai et al. 2017studied the photodegradation of some polycyclic aromatic hydrocarbons using titanium dioxide-based graphene oxide polymer. The nanocomposite possessed large surface area as well as high surface energy sites including various defects, edges, and grooves. The contact of the polycyclic aromatic hydrocarbons molecules with the nanocomposite was through the pi-pi interaction. Structural similarity between the grapheme oxide and polycyclic aromatic hydrocarbons molecules caused their quick adsorption. Moreover, the photogenerated holes, $O_2^{\bullet-}$ and •OH, formed the oxygenated and hydroxylated

Table 5.3 Fabricated functionalized nanomaterials with their enhanced activity results

Nanomaterial type	Functionalization	Improved properties	Reference
Carbon nanotubes	Graphene oxide Ammonia Heteroatoms (N, B,P,O) Polymers Silicon Ni-Co alloy α -Fe_2O_3/Amino Tetraethylene pentamine Cu nanoparticles Cu(II) triazole Schiff base	Surface areas rise to 1900m^2g^{-1} Enhanced the adsorption of organicspecies from water Introduces electrocatalytic active sites and increasessurface hydrophilicity and electrical conductivity Enhance the chemicalcompatibility, mechanical strength, and conductivity and adsorption properties Quickly responding were photodetectors formed Fast-reacting hybrid having co-existence of radical oxidation and non-radical pathway Good adsorption capacity, easy separation from water, and simple regeneration procedures 45.5 mg/g bisphenol A was adsorbed at pH 6.5, 30 °C, and 40 min Practically well-applicable filter for drinking water was formed Endothermic and spontaneous removal of azo dyes from water	Srinivas et al. (2012) Mangun et al. (2001) Xue et al. (2012) Choi and Ryoo (2003) Salvato et al. (2019) Kang et al. (2019) Wu et al. (2019) Naeemullah and Tuzen, (2019) Luan et al. (2019) El-Sharkawy and El-Ghamry, (2019)
Graphene and derivatives	Ag nanoparticles Zero-valent iron Polydopamine Nitrogen doped, palladium decorated Polyamine Nitrogen-sulfur Glutaraldehyde Chitosan/nitrogen Cu_2O Fe_3O_4 Biochar	Enhanced electromagnetic field and strengthened charge transfer Self-regenerating prolonged catalyst with total removal capacity up to 660 mg/g Spontaneous and endothermic removal of methylene blue Doping enhanced both adsorption and activationprocesses Hybrid of high surface area of 226 $m^2\ g^{-1}$ was formed Better results under less dosage of the catalyst 90% monolayer adsorption of chromate ions from wastewater Good ability to remove dyes and stability in supercapacitors Excellent removal of As (V) and Rhodamine B Better π-π electron-donor-acceptor interaction	Alatalo et al. (2019) He et al. (2019) Li et al. (2016) Abdi et al. (2019) Sun et al. (2019a, b) Moghaddam et al. (2019) Li et al. (2011) Ding et al. (2015) Huang et al. (2017a, b)

(continued)

Table 5.3 (continued)

Nanomaterial type	Functionalization	Improved properties	Reference
Polymers	Ti(IV)oxide Carbon dot/ZnO Al_2O_3 Cobalt ferrite Zirconium silicate CdS Iron/zirconium Copper ferrite $Ni(OH)_2$ ZnO-Fe_3O_4	Great potential for phosphate removal from the water Efficient solarenergy-assisted recyclable photocatalyst Showed higher water flux Cost-effective, biocompatible, and potential adsorbent Excellent recovery of nitrocompounds from tap (95.4%), industrial (97.67%), and sea water (95.77%) Enhanced photocatalyticactivity in dye degradation Simultaneous removal of ammonium, phosphate, Cd (II) Easily separable magnetic nanocomposite Reduction of Cr(VI) to less poisonous Cr (III) species Nanocomposite still retains 95% of the original adsorption	Nie et al. (2019) Duarah and Karak (2019) Ghaemi and Daraei (2016) Mahmoud et al. (2019) Alipour and Lakouarj (2019) Zhou et al. (2018) Kharazi et al. (2019) Bhaumik et al. (2018) Rakati et al. (2019)
Metal and metal based	ZnHCF/Fe_2O_3 ZnHCF/ZnO FeHCF/ZnO CdO/ZnO Fe_2O_3/MnO_2 MoS_2/TiO_2 BiOBr/Ti_3C_2 MgO/SiO_2 Fe/MgO Fe_3O_4/Ag/C	Highly surface active, semiconducting hybrid Quick degradation of bisphenol a from water Biocompatible, better adsorbent, and photocatalytic agent Incorporation of CdO into ZnOreduces the band gap Excellent degradation toward Rhodamine B Photoactive, active catalyst, and environment friendly Cr(VI) completely removed with 80 min Nanocomposite exhibited highsurface area 356.02 $m^2\ g^{-1}$ Simultaneously remove Pb(II) and dye from water Highly surface active 744.7 $m^2\ g^{-1}$ and ferromagnetic	Rachna and Shanker (2018) Rani and Shanker (2018) Rachna et al. (2019) Mahendiran et al. (2019) Li et al. (2019a, b) Kumar et al. (2019) Huang et al. (2019) Yue et al. (2019) Ge et al. (2018) Muntean et al. (2019)
Silica based	TiO_2 Fe (0)	•OH radicals rise fast with the intrawall pore size	Dong et al. (2019a, b)

(continued)

Table 5.3 (continued)

Nanomaterial type	Functionalization	Improved properties	Reference
	Cobalt ferrite Guar gum Bi_2MO_6/graphene Fe(0)/magnetite	Easilyseparablemagnetic nanocomposite Adsorbed75.5 ± 1.21 mg g^{-1} of malachite green Quick adsorption of both cationic dyes and metal ions Mesoporous highly surface active (334.65 m^2 g^{-1}) hybrid 0.1 g of adsorbent adsorbed the 11.1 mg g^{-1} of Cr(VI)	Shukla et al. (2018) Amiri et al. (2017) Patra et al. (2017) Nguyen et al. (2018) Kumari et al. (2018)

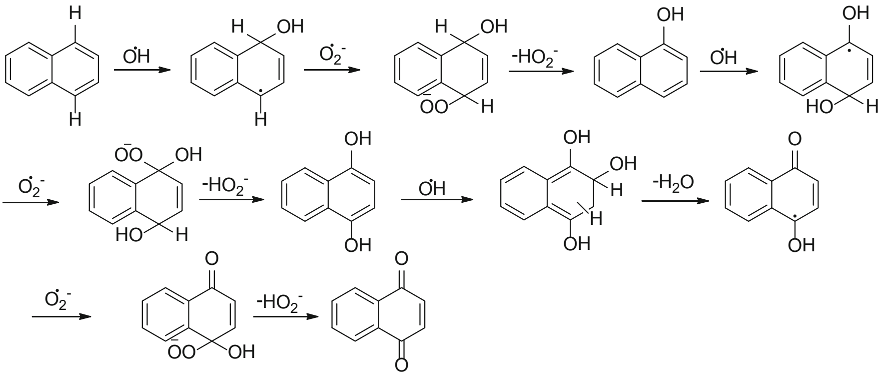


Fig. 5.2 Degradation pathway of naphthalene using carbon nanotubes coupled with oxide of tungsten nanomaterial having involvement of free radicals in formation of various products generated through light source. (With permission through marketplace Royal society of Chemistry)

derivatives under the ultraviolet irradiation (Bai et al. 2017). The complete degradation pathway of the polycyclic aromatic hydrocarbons is shown in Fig. 5.3.

Under sunlight irradiation degradation of phenanthrene was reported using nanocomposite of graphene oxide coupled with titanium dioxide and strontium hydroxide and carbonate. The synergistic interaction between the three parent materials of the nanocomposite facilitated the use of both ultraviolet as well as visible light energy from the sunlight. The overall degradation mechanism includes the shifting of absorption toward higher wavelength by the coupling of two semiconductors (titanium dioxide and strontium hydroxide and carbonate) and push the transfer of photo excited charge carriers (Fu et al. 2018). Graphene oxide/silver phosphate fabricated through a simple precipitation method was thriving in visible light induced degradation of two, three, and four ring-membered polycyclic aromatic

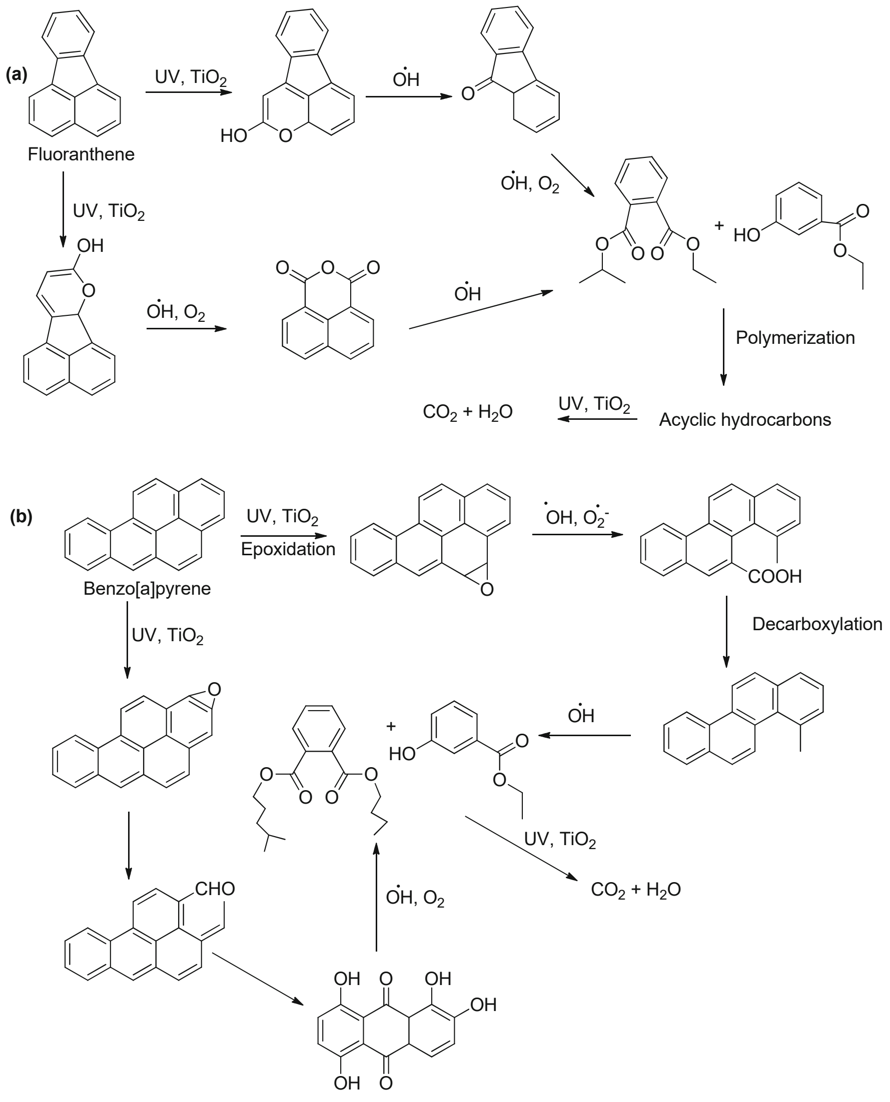


Fig. 5.3 Degradation pathway of polycyclic aromatic hydrocarbons; fluoranthene and benzo[a] pyrene with the titanium dioxide-modified graphene oxide nanomaterial under ultraviolet light, formation of different reaction products, and their ultimate mineralization ()

hydrocarbons. Upon addition of 3 wt% graphene oxide/silver phosphate, complete phenanthrene degradation was achieved within 7 minutes. Possibly, the cross-linked bridge formed between the silver phosphate semiconductors and graphene oxide sheets could initiate the separation and transfer of photogenerated electron-hole pair. Moreover graphene oxide acted as an electron reservoir that can restrain the charge carriers merge. Consequently, the accumulated electrons can confine the oxygen present in solution and make different charged oxygen species to support the polycyclic aromatic hydrocarbon removal (Yang et al. 2018). Composite of reduced graphene oxide and iron oxides was used to remove naphthalene as well as contrasted with the multi-walled carbon nanotubes/iron oxide composite. Higher catalytic activity of graphene oxide/iron oxide composites was based upon its higher electron donor-acceptor interaction. On the other hand, aggregation in cylindrical multi-walled carbon nanotubes upon all random orientations resulted into congested interstitial spaces, which resisted the entrance of aromatic compound (Yang and Xing 2007; Yang et al. 2013a).

5.6.2 Degradation Using Functionalized Polymers

In recent times, coupling of semiconducting nanoparticles with the polymers are fabricated in a lot worldwide due to its plenty functions. In a recent study, naphthalene was degraded under light source with the iron-doped zinc oxide and polyvinyl alcohol nanofibers. Under ultraviolet light, 40 ppm of polycyclic aromatic hydrocarbons was kept for 4 h at neutral pH. Consequently, 96% degradation of naphthalene was achieved owing to the better semiconducting nature achieved upon doping of Fe as well as formation of oxygen vacancies that can trap electrons and holes in interstitial sites to prevent their recombination (Li et al. 2015a, b; Sekar et al. 2018). Recently, the degradation of phenanthrene was utilized with the polydopamine functionalized upon zero-valent iron and reduced graphene oxide. It successfully degraded the 98.7% of phenanthrene at 7.74 pH via formation of $SO_4^{\bullet -}$ and $HO^{\bullet}$ radicals within the reaction mixture (Gu et al. 2018). A hybrid of zirconium oxide-acetylacetonate derived from a gel was studied for the oxidative degradation of phenanthrene in dark. The polymeric hybrid acted like a heterogeneous catalyst in the absence of light, as the free radicals were generated via charge transfer between metal and polymer. Moreover, the limitation of charge carriers' recombination found in various studies was overpowered here by the oxygen molecule scavenging the electrons in conduction band. The presence of various radicals such as superoxide, hydrogen peroxide, and hydroxyl initiated the oxidation and hence mineralization of organic carbons. The identified end products here were alkanoic acids, alkanols, and alkanes (Sannino et al. 2014).

5.6.3 Degradation Using Functionalized Metal and Metal-Based Nanomaterials

Most of the work associated with polycyclic aromatic hydrocarbons degradation is based upon the metals and metal-based nanomaterials. This is attributed to the vast amount of data available on these as it makes the further exploration a bit easy. Recently, metal oxides of iron, zinc, and titanium-based nanomaterials have been explored vastly for the degradation of polycyclic aromatic hydrocarbons (Wang et al. 2016; Gupta and Gupta 2015; Liu et al. 2009a, b). Anthracene degradation was reported with the zinc oxide and manganese oxide-coupled nanocatalyst under ultraviolet irradiation. The nanocatalyst degraded the polycyclic aromatic hydrocarbons into anthraquinone based upon the high transient time constant at n-zinc oxide and p-manganese oxide junction (Martínez-Vargas et al. 2019). Coupling of cobalt oxide with bismuth oxycarbonate was achieved to study visible light-irradiated degradation of naphthalene. Within 150 min of reaction, 91.02% degradation was achieved owing to the excellent interaction between the constituents through the formation of heterojunction and suppressed merging of active species (Guo et al. 2018). As such, heterojunction can affect the charge migration as well as the separation through the interface (Fig. 5.4). The synergistic effect of titanium dioxide and titanate nanotubes was thriving in degrading 93.2% of phenanthrene within 4 h under ultraviolet light (Fig. 5.5).

Otherwise well-known factor of charge carriers recombination of titanate nanotubes was overcome by the excellent photons absorber titanium dioxide (anatase phase) (Cheng et al. 2019). Naphthalene removal was studied with the nickel-doped titaniumnanocomposite under visible light. The nanocomposite exhibited almost double removal efficiency in comparison to titanium dioxide alone. Generally in the heterogeneous catalysis, energy more than the gap between energy levels is required, here the nanocomposite generated e^{-}-h^{+} pairs via irradiation of visible light. The oxygen molecules present in the reaction mixture scavenged the electrons trapped by nickel, which in turn generated the superoxide radicals. Other than superoxide radicals, the presence of hydroxyl radicals through localized holes caused the degradation/mineralization of naphthalene (Sharma and Lee 2015). The coupled silicon dioxide and titanium dioxide were demonstrated for the degradation and mineralization of naphthalene and anthracene. The coupling raised the surface area to 235 m^2g^{-1}, after 240 min of ultraviolet light exposure mineralization of both the polycyclic aromatic hydrocarbons was achieved. The highest photocatalytic

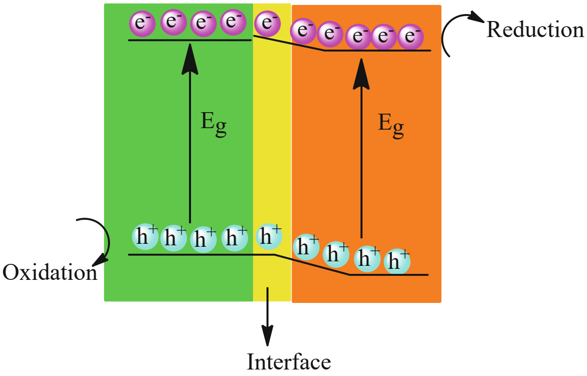


Fig. 5.4 Representation of interface between the two coupling materials with migration and separation of charge carriers at interface of heterojunction. Formation of this interface has a significant role to play in the activity of nanomaterials

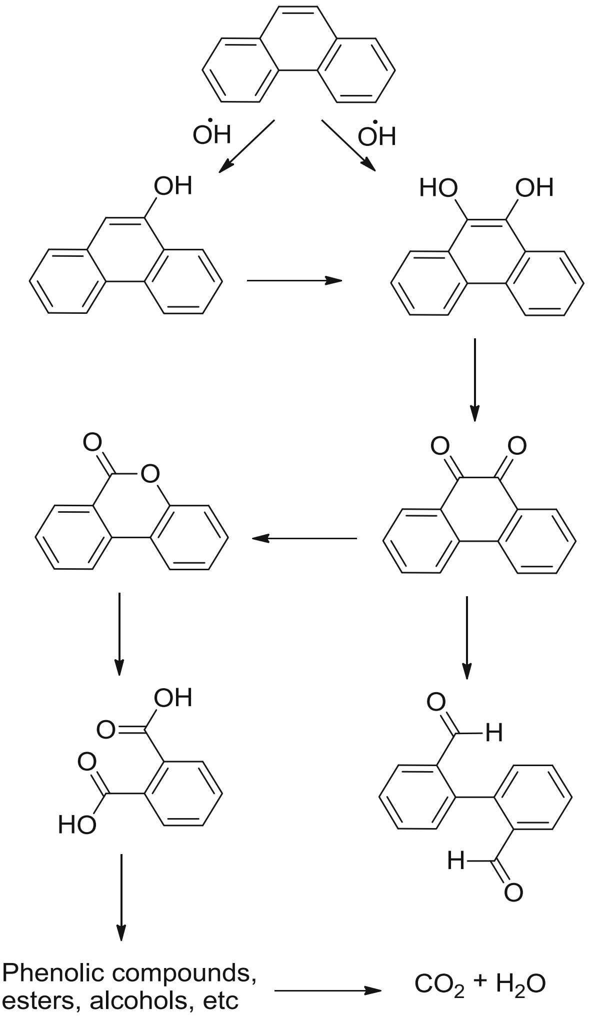


Fig. 5.5 Degradation of phenanthrene using titanium dioxide/titanate nanotube under ultraviolet light and involvement of hydroxyl radicals in the ring cleavage with overall reaction process showing degradation, formation of by-products, and mineralization

activity of the nanocomposite was attributed to superior mass transfer mechanism along with the diffusion of contaminants upon TiO_2 (Grover et al. 2017). Mukwevho and his co-workers synthesized multi-metal oxide nanocomposite (gadolinium, zinc, and copper) via co-precipitation method and utilized it for degradation of phenanthrene under ultraviolet light. Within 180 min of exposure, 99.6% phenanthrene removal was achieved. The photocatalytic mechanism can be explained by the equation below.

$$h\nu + Gd_2O_2CO_3 \rightarrow Gd_2O_2CO_3\ (\text{hole} + \text{electron})$$

$$h\nu + CuO - ZnO \rightarrow CuO - ZnO\ (\text{hole} + \text{electron})$$

$$CuO - ZnO(\text{hole} + \text{electron}) \rightarrow CuO(\text{hole}) + ZnO(\text{electron})$$

$$ZnO(\text{electron}) + \text{Oxygen} \rightarrow \cdot O^{-}{}_{2}$$

$$CuO(\text{hole}) + H_2O \rightarrow \cdot OH + H^{+}$$

$$\cdot O^{-}{}_{2} + H_2O \rightarrow \cdot OH + HO^{-} + O_2$$

$$\cdot OH + \text{Phenanthrene} \rightarrow \text{Degraded products}$$

Sediment-based polycyclic aromatic hydrocarbons were also degraded with the magnetic wood biochar incorporated Fe_3O_4 to catalyze sodium persulfate. Six, five, and four ring-membered polycyclic aromatic hydrocarbons were successfully degraded to 90%, 84%, and 87%, respectively. Its mechanism is based upon involvement of huge amount of O_2-based groups. This in turn forms Fe^{2+} ions, which initiate electron transfer and generate $SO_4{}^{-\bullet}$ radicals. Biochar helps in rising the porosity plus aromatic character, hence, generating large negative surface energy (Dong et al. 2018). Three polycyclic aromatic hydrocarbons, namely, anthracene, phenanthrene, and naphthalene, were degraded using copper@zinc oxide brush-like nanostructures. It converted almost 90%, 50% along with 10% of anthracene, phenanthrene, and naphthalene, respectively. Other than the effective transport of electron, coupled copper has great tendency to activate oxygen causing the collection of negative charge on the surface that results in high catalytic efficiency of nanocomposite (Chen et al. 2013). It was observed that it is difficult to degrade multiple ring polycyclic aromatic hydrocarbons in the presence of bare ultraviolet light. Coupling of titanium dioxide with various metal atoms such as iron, manganese, and chromium can shift the light activity toward naturally available light range (Khan et al. 2008). Doping of Fe(III) on titanium dioxide resulted in large number of photogenerated electron-hole pair; Fe(III) also laid the trap for carriers to delay the charge recombination. Consequently, phenanthrene was degraded into quinone and phthalic and finally into 9-octadecanoic acid under visible light (Theerakarunwong and Phanichphant 2018). From the past few decades, metal hexacyanoferrates are gaining attention worldwide due to its ability to exhibit supreme catalytic property in remediation of contaminants as well as for their semiconducting properties. Functionalization of metal hexacyanoferrates with the transition metal oxides can further enhance these properties and play an essential role in the wastewater treatment. Recently, various nanocomposites of metal hexacyanoferrates with zinc oxide and iron oxide have been reported to degrade the polycyclic aromatic hydrocarbons essentially. Zinc hexacyanoferrates encapsulated with the zinc oxide nanoparticles degraded the high molecular weight containing polycyclic aromatic hydrocarbons, benz[a]anthracene, and benzo[a]pyrene up to 93% and 90%, respectively, within 24 h of sunlight irradiation at neutral pH. The benz[a]anthracene degradation followed formation of (E)-2-hydroxy-3-(2-hydroxyanthracen-1-yl)acrylic acid intermediate, which through oxidation and attack of huge amount of hydroxyl radicals degraded into naphthalene-2,3-dicarboxylic acid. The oxidation of terminal rings formed various smaller by-products such as but-3-ene-1,1,2-triol, acrylic acid, and prop-2-en-1-ol (4c; m/z = 59). On the other hand, benzo[a]pyrene being comparatively stable formed intermediates of m/z values 246 and 273. However, since functionalized nanomaterials had better semiconducting properties, large number of hydroxyl radicals was fabricated. The presence of these radicals helped in degradation of huge rings into smaller products such propionic acid. The doping enhanced the photocatalytic activity through the charge transfer mechanism and suppression of charge recombination process (Rachna et al. 2019). Chrysene known as persistent carcinogenic polycyclic aromatic hydrocarbon was degraded under sunlight with the iron oxide@zinc hexacyanoferrate nanocomposite up to 92% owing to the remarkably enhanced surface area (around 350 m^2g^{-1}) as well as semiconducting nature (2.18 eV) (Rachna and Shanker 2018). The formation of charge carriers and other reactive species in the nanocomposites are as shown in Fig. 5.6.

The complete degradation pathways of these three polycyclic aromatic hydrocarbons have been shown in Figs. 5.7 and 5.8. Nanocomposite functionalized with zinc, chromium, and titanium was fabricated to degrade naphthalene under visible light.

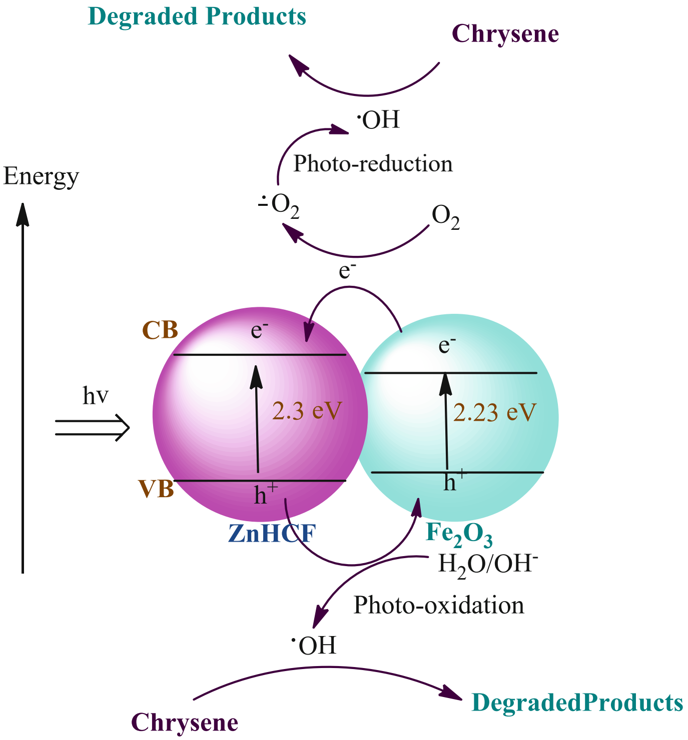


Fig. 5.6 Degradation of chrysene with the iron oxide-coupled zinc hexacyanoferrate nanocomposite and mechanism of flow of electrons and holes to form charge carriers that eventually help in the final degradation process

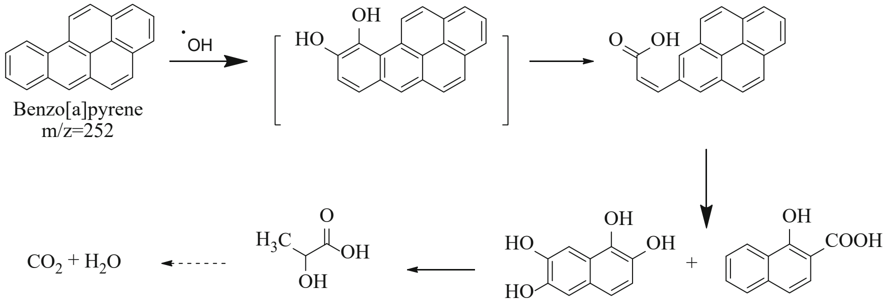


Fig. 5.7 Degradation pathway of benzo[a]pyrene with the zinc oxide encapsulated zinc hexacyanoferrate nanocomposite involving formation of an intermediate which upon attack of hydroxyl radicals ends up into mineralization

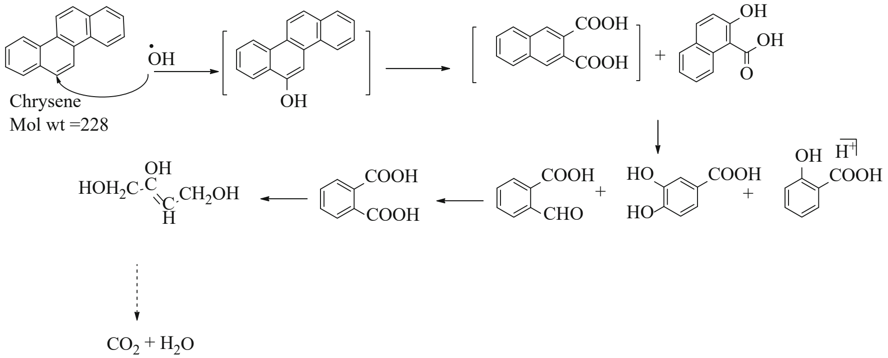


Fig. 5.8 Involvement of hydroxyl radicals formed through excitation of iron oxide-coupled zinc hexacyanoferrate nanocomposite into the degradation of chrysene to form smaller products

Nanocomposite having higher specific area and narrower band gap degraded 90.2% within 240 min (Xia et al. 2015). The mineralization of polycyclic aromatic hydrocarbons was also confirmed in various studies through total organic carbon analysis. Rachna et al. (2019) showed around 60% of total organic carbon loss of high molecular weight polycyclic aromatic hydrocarbons within 24 h of reaction under sunlight. Whereas, one of the four ring-membered polycyclic aromatic hydrocarbons lost around 60% and 40% of organic content in reaction mixture after 5 and 24 h (Rachna and Shanker 2019b). Degradation of polycyclic aromatic hydrocarbons with various nanomaterials has been listed in Table 5.4.

5.6.4 Mechanism of Degradation

Functionalized nanomaterials have various tempting properties that benefit the degradation of polycyclic aromatic hydrocarbons. Herein, extensive investigation

Table 5.4 Degradation of polycyclic aromatic hydrocarbons with various nanomaterials

Polycyclic aromatic hydrocarbon	Nanomaterial	Process details and result	Reference
Anthracene	ZnO/MnO	Under ultraviolet irradiation anthracene was converted into anthraquinone	Martínez-Vargas et al. (2019)
Naphthalene	$Co_3O_4/Bi_2O_2CO_3$	Within 150 min of reaction, 91.02% naphthalene was degraded	Guo et al. (2018)
Phenanthrene	TiO_2/titanate	93.2% of degradation within 4 h under ultraviolet light	Cheng et al. (2019)
Napthalene	Ni/TiO_2	Composite showed double removaltendency than TiO_2	Sharma and Lee, (2015)
Napthalene	SiO_2/TiO_2	Complete mineralization	Grover et al. (2017)
Anthracene	SiO_2/TiO_2	Mineralization after 240 min of reaction under ultraviolet light	Grover et al. (2017)
Phenanthrene	$Gd_2O_2CO_3 \cdot ZnO \cdot CuO$	Under ultraviolet exposure 99.6% phenanthrene was degraded within 180 min	Mukwevho et al. (2019)
Six, five and four ring membered	Biochar/Fe_3O_4/ sodium persulfate	Degraded to 90%, 84%, and 87%	Dong et al. (2018)
Anthracene	Cu@ZnO	90% of anthracene degradation	Chen et al. (2013)
Phenanthrene	Cu@ZnO	50% of phenanthrene degradation	Chen et al. (2013)
Naphthalene	Cu@ZnO	10% naphthalene degradation	Chen et al. (2013)
Phenanthrene	Fe(III)/TiO_2	Under visible light phenanthrenedegraded into quinone and phthalic	Theerakarunwong and Phanichphant, (2018)
Chrysene	Fe_2O_3@zinc hexacyanoferrate	Under sunlight 92% degradation was obtained after 24 h	Rachna and Shanker (2018)
Benzo[a] anthracene	ZnO@ zinc hexacyanoferrate	Under sunlight 93% degradation was obtained after 24 h	Rachna and Shanker (2019a)
Benzo[a] pyrene	ZnO@ zinc hexacyanoferrate	Under sunlight 90% degradation was obtained after 24 h	Rachna and Shanker et al. (2019a)
Naphthalene	Ti/ZnO–Cr_2O_3	Under visible light 90.2% degradation obtained within 240 min	Xia et al. (2015)
Naphthalene	Carbon nanotubes/ WO_3	Higher surface area and activity degraded naphthalene into smaller and safer products	Farhadian et al. (2016)
Benzo[a] pyrene	Carbon dots/fatty acid/ Fe_3O_4	93.9% of the targeted pollutant was removed	Yang et al. (2019)
Phenanthrene	Graphene oxide-TiO_2-$Sr(OH)_2/SrCO_3$	Nanocomposite facilitated the use of both ultraviolet as well as visible light energy from the sunlight	Fu et al. (2018)

(continued)

Table 5.4 (continued)

Polycyclic aromatic hydrocarbon	Nanomaterial	Process details and result	Reference
Naphthalene	Graphene oxide/ Ag_3PO_4	Accumulated electrons captured the dissolved O_2 and degraded the naphthalene	Yang et al. (2018)
Phenanthrene	Graphene oxide/ Ag_3PO_4	Under 7 min impressive degradation ability of the catalyst was noticed	Yang et al. (2018)
Pyrene	Graphene oxide/ Ag_3PO_4	Photogenerated e- h + caused the degradation of polycyclic aromatic hydrocarbons	Yang et al. (2018)
Napthalene	Fe doped ZnO/polyvinyl alcohol	Under ultraviolet light 96% degradation was obtained	Sekar et al. (2018)
Phenanthrene	Polydopamine/Fe (0)/ reduced graphene oxide	98.7% of phenanthrene at 7.74 pH	Gu et al. (2018)
Phenanthrene	Co/TiO_2	Pseudo-first-order rate constant was 0.39 h^{-1}, under sunlight	Zhao et al. (2016)
Benzo[a] anthracene	Fe^{3+}-modified montmorillonite	17% in 6 h	Zhao et al. (2017)

was done to understand the mechanism behind the good results found with the functionalized nanocatalysts. In the presence of light source (ultraviolet or visible), the electron from the lower energy level gets promoted to the higher level with the formation of holes of same number. Electron and hole generated in this way migrate upon the surface of the catalyst, where these participate in the redox reactions to form various radicals (superoxide, hydroxyl) (Huang et al. 2017a, b). These radicals are ultimately responsible for the direct oxidation, degradation, and mineralization of organic pollutants. Upon coupling or functionalization, the photogenerated e^- is transferred to the other materials higher level, causing efficient separation of charge carriers and, hence, lower recombination rate.

The reactive species facilitate the degradation of polycyclic aromatic hydrocarbons by attacking their most active site and disturb the arrangement of electron cloud of aromatic rings. This disturbance generates various intermediate products of polycyclic aromatic hydrocarbons; these further get converted into stable/less harmful products (carbon dioxide and water) (Mukwevho et al. 2019). According to energy band theory, when one material absorbs quanta of energy more than difference between energy levels, the transfer of electrons takes place to generate holes. The functionalization helps in shifting the optical properties toward the visible region that is responsible for the better activity of nanocatalyst for polycyclic aromatic hydrocarbons degradation (Xia et al. 2015).

Subramanian et al. suggested that nanocomposite of $BiFeO_3$–$GdFeO_3$ showed reasonably better catalytic activity owing to the various factors. Firstly, $BiFeO_3$ being not completely covered with $GdFeO_3$ makes it available for photo absorption and promotes the development of depletion layer between both semiconductors in sunlight. Secondly, the greater electronic diffusion between these two forms a distinct junction. This heterojunction facilitates the transportation of charge carriers. Further, the tuning between the band gap energies resulted into the overall low difference between valence and conduction gap of the nanocomposite. In addition to the functionalization widen the visible light absorption area and enhance the redox reaction on surface of the catalyst (Subramanian et al. 2019). Involvement of metal-based nanocatalysts has been seen to be more in these degradation processes as described above. This is due to the unique nature of semiconductors oxides. The outermost electrons are mostly in the d orbitals, which are partially filled and permit the alteration of electronic properties to enable these in visible/solar light (Bouzid et al. 2015). Generation of defects in the semiconductors, through their functionalization, results into the trapping of electrons and holes, which result into the generation of superoxide and hydroxyl radical (Ani et al. 2018).

5.7 Other Factors Affecting Degradation

5.7.1 Concentration

The initial concentration of polycyclic aromatic hydrocarbons has high effect on the degradation ability of the functionalized catalyst. Rise in concentration results into the blocking of the active sites on the catalyst surface for further adsorption as well as lowers the contact between polycyclic aromatic hydrocarbon molecules and the catalyst owing to the restricted active sites. Moreover, the fall in the path length of photons lowers the photocatalytic activity of the catalyst (Shanker et al. 2017a, b). The influence of initial number of molecules of chrysene upon iron oxide@zinc hexacyanoferrate was studied by Rachna and Shanker (2018) under sunlight. The polycyclic aromatic hydrocarbon molecules also interacted with the absorbed photons and, hence, reduced the access of photons for the catalyst that initiates the reactive radicals (Rachna and Shanker 2018).

5.7.2 Catalyst Loading

Economical aspect of a degradation technology is one of the important factors to be focused on. Dosage of a photocatalyst plays a vital role in the removal of polycyclic aromatic hydrocarbons owing to the interaction between its number of molecules and the number of active sites. Generally it has been noticed that the activity of functionalized nanocatalysts rises with the rise in its dosage (Rani and Shanker 2018a), but after a particular mount, the activity decreases (Rani and Shanker 2018b). This is because as the catalyst amount increases, the photon energy is interrupted by the excess catalyst, thus declining in overall activity. After a certain amount, agglomeration between catalyst particles reduces the available surface area, so becoming unfavorable to the system (Rachna et al. 2019).

5.7.3 pH

In the degradation of polycyclic aromatic hydrocarbons, pH of the reaction mixture can affect the various phenomena occurring in between the system. Some of the studies have shown that under acidic pH, highest degradation of polycyclic aromatic hydrocarbons was obtained, while some showed it to be at basic or neutral pH (Rachna and Shanker 2018, 2019b; Dong et al. 2019a, b). It was suggested that under low pH, generation of $SO_4^{-\bullet}$ radicals was facilitated in soil. Since in soilthe chemical oxidation is based upon both the sulfate and hydroxyl radicals (Matzek and Carter 2016). In a soil degradation study of polycyclic aromatic hydrocarbons by $Fe_3O_4 - CM/PS$, $SO_4^{-\bullet}$ radicals were found as the chief dynamic species formed though the activation of PS, and it had greater tendency of oxidizing than bare •OH radicals (Peluffo et al. 2018). On the other hand, under basic conditions, magnetite showed its property and catalytic stabilities (Li et al. 2019a, b). Under neutral condition, zinc hexacyanoferrate@zinc oxide was able to degrade some five ring-membered polycyclic aromatic hydrocarbons owing to their stability in these conditions. The π-electron cloud of the polycyclic aromatic hydrocarbons formed complexes ("cation-π") with the nanocatalyst through surface interaction (Rachna and Shanker 2019b).

5.7.4 Time

Time is another factor playing critical role in degradation of polycyclic aromatic hydrocarbons. Increase in irradiation time enhances the degradation of polycyclic aromatic hydrocarbons mainly in water. In real samples there are other contaminants present along with the polycyclic aromatic hydrocarbons, and those are difficult to degrade due to competitiveness between them. Moreover, concentration also inhibits the catalytic activity of the catalysts. Hence, much time is needed to achieve reasonable degradation of polycyclic aromatic hydrocarbons in wastewater (Khan et al. 2015).

5.7.5 Temperature

Various studies have suggested that the removal tendency of functionalized nanocatalysts is affected by the temperature of reaction mixture (Shahrezaei et al. 2012). As the temperature increases up to 45 °C, the degradation is generally favored. These trends are attributed to the enhanced kinetic energy of contaminants molecule that increases the overall collisions and hence electron transfer. Thus the development of reactive charge carriers increases, which fasten up the overall process (Shahrezaei et al. 2012). However, further rise in heat can lower the reaction rate because of the evaporation of water; since the volume of the medium decreases, concentration of pollutant increases. Certain reports also suggest that the temperature has negligible effect upon the degradation mechanism as the activation of photons occurs between the temperature 20 and 80 °C (Diya'Uddeen et al. 2011). All in all normal conditions of reaction variables are most satisfactory in degradation.

5.7.6 Light Intensity

At a particular range of wavelength, light intensity can predict the amount of light absorbed by the functionalized material. Light intensity plays an important role in the excitation of electrons. Inadequate amount of light source surely cannot generate large number of photo-electrons and photo-holes. Intense beam of light can generate enough amounts of electrons and holes that could enhance the pace of the experiment. Guozheng et al. (2010) realized that for a carbon fiber-activated titanium dioxide upon increasing the light intensity of ultraviolet source from ~0.9 to ~3.0 W/L, overall deprivation percentage of an organic pollutant increases. However, further rise in intensity had no noteworthy impact on degradation. Generally, this happens for the reason that at low intensity collision, the amount of overall reactive species is low, while at higher intensity, these can be generated in sufficient amount. Thus there are more chances that the mobile charge carriers could penetrate the surface of nanomaterial to eradicate and release the energy via emission that can enhance the removal rate and lower the combination of charge carriers (Diya'Uddeen et al. 2011).

5.8 Synergistic Effect

Synergistic effect arises when a common effect exists between two or more components of a material resulting into higher overall activity. In nanocatalysis, synergistic effect has been found to create more active agent having interaction between its catalyst and a co-catalyst (Ding 2008; Singh and Xu 2013). The close contact between constituents of a catalyst changes the surface energy, semiconducting properties, and electronic structure (Chen et al. 2016). Coupling of titanium dioxide with two or more materials has been observed to gain synergism than single dopant owing to suitably matched constituents effecting charge carrier transfer and lowering the recombination of charge carriers. Moreover, enhanced activities help in shifting the light absorption toward visible region of light (Qui et al. 2018). Better findings with the carbon or chromium-titanium dioxide-incorporated material than titanium dioxide were also due to better synergistic effect. Synergistic effects helped in effective separation of $e^{-}$and h^{+} for better sonocatalytic activity (Shujuan Zhang 2012). The synergism in metals such as iron and palladium enhanced the pollutant degradation (Li et al. 2015a, b).

5.9 Photocatalysis

In the twenty-first century, involvement of natural processes has been the major focus of researchers in all the fields. Photocatalysis is one such field that can easily work on solar energy depending upon the kind of the material used in catalysis (Kudo and Miseki 2009). Photocatalysis has faced a lot of limitations of thin spectral responses, low quantum effectiveness, pitiable constancy, and difficulty in reusability (Hernández-Alonso et al. 2009; Liu et al. 2009a, b). Functionalization has helped in overcoming all these limitations of photocatalysis. Transition metal oxides upon functionalized having all ranges of band gap energy can rely entirely upon ultraviolet region or visible region of sunlight.

Visible light absorption has been improved in nanocomposites through surface modification. Generally, formation of the heterophase and homophase junction in these coupled materials helps in enhancing the degradation activity. Two reasons are held responsible for better activity; first is wide range of photo-response and second better activity of photogenerated charge carriers. One such nanocomposite of silver carbonate@silver oxide with better junction of different phases showed enhanced photocatalytic degradation activity for organic pollutants. Under sunlight, complete degradation as well as mineralization of organic material was possible (Yi et al. 2010).

5.10 Conclusions and Future Scopes

In the present review, the main focus was given to the polycyclic aromatic hydrocarbons, their degradation through the functionalized nanomaterials, and factors affecting the degradation. Even though many attempts have been made to investigate the polycyclic aromatic hydrocarbons and their degradation, there is still demand thriving more light on the degradation of higher polycyclic aromatic hydrocarbons and its mechanism. Various final points could be concluded drawn from this review:

- Functionalization not only enhances the overall properties of the materials but also increases its role in the degradation of toxic polycyclic aromatic hydrocarbons into safer by-products.

- A lot of functionalized materials (carbon nanotubes, graphene oxide, metal oxides, etc.) were able to degrade polycyclic aromatic hydrocarbons mainly anthracene, phenanthrene, naphthalene, benzo[a]pyrene, chrysene, and benz[a] anthracene.
- Coupling between different materials lowered the band gap energy, charge recombination, and enhanced the overall surface active sites and radical species.
- Radical species such as superoxide along with the hydroxyl radicals are the main agents causing the degradation of polycyclic aromatic hydrocarbons.
- Coupling also shifted the overall light response of nanomaterials toward the naturally available light region (visible), hence increased its application under natural scenario such as sunlight.
- A very few reports were available on the degradation of higher molecular weight polycyclic aromatic hydrocarbons removal; this needs further attention.
- Functionalization of carbon-based materials has been done exhaustively, yet their application in polycyclic aromatic hydrocarbons degradation is very limited.
- Although attempts have been done to explore the role of functionalization in the degradation ability of catalyst, there is still a need to put more light on the degradation mechanism.
- In-depth detail of the synthesized materials such as size, shape, porosity, and surface activity should be further explored. Complete knowledge of the materials properties can help in designing a well active strategy to remove organic contaminants.
- To achieve desired targets of environmental cleanup, better understanding of functionalization is needed. Stability of functionalized materials under different conditions of solvent, pH, and temperature should be known. Other than these, the biocompatibility of the nanocatalysts should be adequately checked before practical involvement.
- All in all a great deal of information was gathered for the degradation of polycyclic aromatic hydrocarbons with functionalized materials. It was seen that most of the work was based on the lab results, yet the practical applicability of the nanocatalysts through field study is needed.
- Involvement of noble metals for the coupling should be explored since even in past inventions introduction of noble metals has shown tremendous results.
- Development of more facile, simple, one-step, and cheap processes for engineering application is highly recommended.

Acknowledgments One of the author Dr. Manviri Rani is grateful for the financial assistance from DST-SERB, New Delhi (Sanction order no. SRG/2019/000114), and TEQIP-III MNIT Jaipur. Authors also wish to thank TEQIP-III, NIT Jalandhar, and Ministry of Human Resource and Development, New Delhi, India.

References

Abdel-Shafy HI, Mansour MS (2016) A review on polycyclic aromatic hydrocarbons: source, environmental impact, effect on human health and remediation. Egypt J Pet 25:107–123. https://doi.org/10.1016/j.ejpe.2015.03.011

Abdi G, Alizadeh A, Amirian J, Rezaei S, Sharma G (2019) Polyamine-modified magnetic graphene oxide surface: feasible adsorbent for removal of dyes. J Mol Liq 289:111118. https://doi.org/10.1016/j.molliq.2019.111118

Agency for Toxic Substances, Disease Registry. Toxicological profile for polycyclic aromatic hydrocarbons. US Department of Health and Human Services 1995. US Government Printing Office: 1995-639-298

Alatalo S-M, Daneshvar E, Kinnunen N, Meščeriakovas A, Thangaraj SK, Janis J, Tsang DCW, Bhatnagar A, Lahde A (2019) Mechanistic insight into efficient removal of tetracycline from water by Fe/graphene. Chem Eng J 373:821–830. https://doi.org/10.1016/j.cej.2019.05.118

Alipour A, Lakouarj MM (2019) Photocatalytic degradation of RB dye by CdS-decorated nanocomposites based on polyaniline and hydrolyzed pectin: isotherm and kinetic. J Environ Chem Eng 7:10287. https://doi.org/10.1016/j.jece.2018.102837

Amiri M, Salavati-Niasari M, Akbari A, Gholami T (2017) Removal of malachite green (a toxic dye) from water by cobalt ferrite silica magnetic nanocomposite: herbal and green sol-gel autocombustion synthesis. Int J Hydrog Energy 42:24846–24860. https://doi.org/10.1016/j.ijhydene.2017.08.077

Ani IJ, Akpan UG, Olutoye MA, Hameed BH (2018) Photocatalytic degradation of pollutants in petroleum refinery wastewater by TiO2- and ZnO-based photocatalysts: recent development. J Clean Prod 205:930–954. https://doi.org/10.1016/j.jclepro.2018.08.189

Baek SO (1991) A review of atmospheric polycyclic aromatic hydrocarbons: sources, fates and behaviour. Water Air Soil Pollut 60:279–300. https://doi.org/10.1007/BF00282628

Bai H, Zhou J, Zhang H, Tang G (2017) Enhanced adsorbability and photocatalytic activity of TiO2-graphenecomposite for polycyclic aromatic hydrocarbons removal in aqueous phase. Colloids Surf B: Biointerfaces 150:68–77. https://doi.org/10.1016/j.colsurfb.2016.11.017

Berberidou C, Kitsiou V, Lambropoulou DA, Antoniadis A, Ntonou E, Zalidis GC, Poulios I (2017) Evaluation of an alternative method for wastewater treatment containing pesticides using solar photocatalytic oxidation and constructed wetlands. J Environ Manag 195:133–139. https://doi.org/10.1016/j.jenvman.2016.06.010

Bhaumik M, Gupta VK, Maity A (2018) Synergetic enhancement of Cr(VI) removal from aqueous solutions using polyaniline@$Ni(OH)_2$ nanocomposites adsorbent. J Environ Chem Eng 6:2514–2527. https://doi.org/10.1016/j.jece.2018.03.047

Bonnet JL, Guiraud P, Dusser M, Kadri M, Laffosse J, Steiman R, Bohatier J (2005) Assessment of anthracene toxicity towards environmental eukaryotic microorganism *Tetrahymena pyriformis* and selected micromycetes. Ecotoxicol Environ Saf 60:87–100. https://doi.org/10.1016/j.ecoenv.2003.10.001

Bouzid H, Faisal M, Harraz FA, Al-Sayari SA, Ismail AA (2015) Synthesis of mesoporous Ag/ZnO nanocrystals with enhanced photocatalytic activity. Catal Today 252:20–26. https://doi.org/10.1016/j.cattod.2014.10.011

Burchiel SW, Luster MI (2001) Signaling by environmental polycyclic aromatic hydrocarbons in human lymphocytes. Clin Immunol 98:2–10. https://doi.org/10.1006/clim.2000.4934

Callahan MA, Slimak MW, Gabelc NW, May IP, Fowler CF, Freed JR, Jennings P, Durfee RL, Whitmore FC, Maestri B, Mabey WR, Holt BR, Gould C (1979) Water-related environmental fate of 129 priority pollutants, EPA-440/4–79-029. Office of Water Planning and Standards, Office of Water and Waste Management, Washington, DC

Cerniglia CE (1984) Microbial transformation of aromatic hydrocarbons. In: Atlas RM (ed) Petroleum Microbiology. Macmillian Publishers, New York

Chefetz F, Deshmukh AP, Hatcher PG (2000) Pyrene sorption by natural organic matter. Environ Sci Technol 34:2925–2930. https://doi.org/10.1021/es9912877

Chen H, Wen M, Huang Z, Wu Q, Liu J, Tu T (2013) Construction of Cu@ZnO Nanobrushes based on Cu nanowires and their high-performance selectivity degradation for polycyclic aromatic hydrocarbons. J Mater Chem A 00:1–3. https://doi.org/10.1039/C4TA05204H

Chen Z, Liang Y, Hao J, Cui Z-M (2016) Noncontact synergistic effect between Au nanoparticles and the Fe2O3 spindle inside a Mesoporous silica Shell as studied by the Fenton-like reaction. Langmuir 32:12774–12780. https://doi.org/10.1021/acs.langmuir.6b03235

Cheng K, Cai Z, Fu J, Sun X, Sun W, Chen L, Zhang D, Liu W (2019) Synergistic adsorption of Cu (II) and photocatalytic degradation of phenanthrene by a Jaboticaba-like TiO_2/titanate nanotube composite: an experimental and theoretical study. Chem Eng J 358:1155–1165. https://doi.org/10.1016/j.cej.2018.10.114

Choi M, Ryoo R (2003) Ordered nanoporous polymer–carbon composites. Nat Mater 2:473–476. https://doi.org/10.1038/nmat923

Cleary GJ (1962) Discreet separation of polycyclic hydrocarbons in air borne particulates using very long alumina columns. Journal of Chromatography A 9:204–215

Cochran RE, Jeong H, Haddadi S, Derseh RF, Gowan A, Beránek J, Kubátová A (2016) Identification of products formed during the heterogeneous nitration and ozonation of polycyclic aromatic hydrocarbons. Atmos Environ 128:92–103. https://doi.org/10.1016/j.atmosenv.2015.12.036

Cristóvão RO, Gonçalves C, Botelho CM, Martins RJE, Boaventura RAR (2014) Chemical oxidation of fish canning wastewater by Fenton's reagent. J Environ Chem Eng 2:2372–2376. https://doi.org/10.1016/j.jece.2013.12.023

Das P, Mukherjee S, Sen R (2008) Improved bioavailability and biodegradation of a model polyaromatic hydrocarbon by a biosurfactant producing bacterium of marine origin. Chemosphere 72:1229–1234. https://doi.org/10.1016/j.chemosphere.2008.05.015

de Caprariis B, De Filippis P, Hernandez AD, Petrucci E, Petrullo A, Scarsella M, Turchi M (2017) Pyrolysis wastewater treatment by adsorption on biochars produced by poplar biomass. J Environ Manag 197:231–238. https://doi.org/10.1016/j.jenvman.2017.04.007

Delistraty D (1997) A critical review of the application of toxic equivalency factors to carcinogenic effects of polycyclic aromatic hydrocarbons in mammals. Handbook Environ Chem 3:311

Ding KL (2008) Synergistic effect of binary component ligands in chiral catalyst library engineering for enantioselective reactions. Chem Commun 2008:909–921. https://doi.org/10.1039/B710668H

Ding J, Li B, Liu Y, Yan X, Zeng S, Zhang X, Hou L, Cai Q, Zhang J (2015) Fabrication of Fe_3O_4@reduced graphene oxide composite *via* novel colloid electrostatic self-assembly process for removal of contaminants from water. J Mater Chem A 3:832–839. https://doi.org/10.1039/C4TA04297B

Dipple A (1985) Polycyclic aromatic hydrocarbon carcinogenesis: an introduction. In: Harvey RG (ed) Polycyclic hydrocarbons and carcinogenesis, vol 283. American Chemical Society, Washington, DC, pp 1–17. https://doi.org/10.1021/bk-1985-0283

Dissanayake A, Piggott C, Baldwin C, Sloman KA (2010) Elucidating cellular and behavioural effects of contaminant impact (Polycyclic aromatic hydrocarbons) in both laboratory-exposed and field-collected shore crabs, Carcinus maenas (Crustacea; Decapoda). Mar Environ Res 70:368–373. https://doi.org/10.1016/j.marenvres.2010.07.004

Diya'Uddeen BH, Daud WMAW, Abdul Aziz AR (2011) Treatment technologies for petroleum refinery effluents: a review. Process Saf Environ Protect 89:95e105. https://doi.org/10.1016/j.psep.2010.11.003

Dong C, Chen C, Kao C, Chien C, Hung C (2018) Wood-biochar-supported magnetite nanoparticles for remediation of PAH-contaminated estuary sediment. Catalysts 8:73. https://doi.org/10.3390/catal8020073

Dong C-D, Lu Y-C, Chang J-H, Wang T-H, Chen C-W, Hung C-M (2019a) Enhanced persulfate degradation of PAH-contaminated sediments using magnetic carbon microspheres as the catalyst substrate. Process Saf Environ Prot 125:219–227. https://doi.org/10.1016/j.psep.2019.03.011

Dong W, Li L, Chen X, Yao Y, Ru Y, Sun Y, Hua W, Zhuang G, Zhao D, Yan S, Song W (2019b) Mesoporous anatase crystal-silica nanocomposites with large intrawall mesopores presenting quite excellent photocatalytic performances. Appl Catal B Environ 246:284–295. https://doi.org/10.1016/j.apcatb.2019.01.055

Duarah R, Karak DN (2019) Hyperbranched polyurethane/reduced carbon dot-zinc oxide nanocomposite-mediated solar-assisted photocatalytic degradation of organic contaminant: an approach towards environmental remediation. Chem Eng J 370:716–728. https://doi.org/10.1016/j.cej.2019.03.248

EHC (2003) Selected Nitro– and Nitro–Oxy–Polycyclic Aromatic Hydrocarbons. Hanover, Germany

El-Sharkawy R, El-Ghamry HA (2019) Multi-walled carbon nanotubes decorated with Cu (II) triazole Schiff base complex for adsorptive removal of synthetic dyes. J Mol Liq 282:515–526. https://doi.org/10.1016/j.molliq.2019.02.137

European Food Safety Authority, Food Consumption, Database (2008) http://www.efsa.europa.eu/EFSA/ScientificPanels/efsa_locale-1178620753812_DATEX.htm

Farhadian M, Sangpour P, Hosseinzadeh G (2016) Preparation and photocatalytic activity of WO3-MWCNT nanocomposite for degradation of naphthalene under visible light irradiation. RSC Adv 00:1–11. https://doi.org/10.1039/C6RA04642H

Fu J, Kyzas GZ, Cai Z, Deliyanni EA, Liu W, Zhao D (2018) Photocatalytic degradation of phenanthrene by graphite oxide-TiO_2-$Sr(OH)_2$/$SrCO_3$nanocomposite under solar irradiation: effects of water quality parameters and predictive modelling. Chem Eng J 335:290–300. https://doi.org/10.1016/j.cej.2017.10.163

Gaga EO (2004) Investigation of polycyclic aromatic hydrocarbon (PAH) deposition in Ankara. PhD, The Middle East of Technical University

Garon D, Krivobok S, Wouessidjewe D, Seigle-Murandi F (2002) Influence of surfactants on solubilization and fungal degradation of fluorene. Chemosphere 47(3):303–309

Ge L, Wang W, Peng Z, Tan F, Wang X, Chen J, Qiao X (2018) Facile fabrication of Fe@MgO magnetic nanocomposites for efficient removal of heavy metal ion and dye from water. Powder Technol 326:393–401. https://doi.org/10.1016/j.powtec.2017.12.003

Ghaemi N, Daraei P (2016) Enhancement in copper ion removal by PPy@Al_2O_3 polymeric nanocomposite membrane. J Ind Eng Chem 40:26–33. https://doi.org/10.1016/j.jiec.2016.05.027

Grimmer G, Böhnke H, Glaser A, (1977) Investigation on the carcinogenic burden by air pollution in man. XV. Polycyclic aromatic hydrocarbons in automobile exhuast gas-aninventory 164:218. https://europepmc.org/article/med/70130

Grover IS, Prajapat RC, Singh S, Pal B (2017) SiO_2-coated pure anatase TiO_2 catalysts for enhanced photo-oxidation of naphthalene and anthracene. Particuology 34:156–161. https://doi.org/10.1016/j.partic.2017.03.001

Gu M, Sui Q, Farooq U, Zhang X, Qui Z, Lyu S (2018) Degradation of phenanthrene in sulfate radical based oxidative environment by nZVI-PDA functionalized rGO catalyst. Chem Eng J 534:541–552. https://doi.org/10.1016/j.cej.2018.08.039

Guo Y, Dai Y, Zhao W, Li H, Xu B, Sun C (2018) Highly efficient photocatalytic degradation of naphthalene by Co_3O_4/$Bi_2O_2CO_3$ under visible light: a novel p–n heterojunction nanocomposite with nanocrystals/lotus-leaf-like nanosheets structure. Appl Catal B Environ 237:273–287. https://doi.org/10.1016/j.apcatb.2018.05.089

Guozheng J, Guoxiang W, Yong Z, Linsheng Z (2010) Effects of light intensity and H2O2 on photocatalytic degradation of phenol in wastewater using TiO2/ACF. 1. 623–626. https://doi.org/10.1109/ICDMA.2010.431

Gupta H, Gupta B (2015) Photocatalytic degradation of polycyclic aromatic hydrocarbon benzo[a] pyrene by iron oxides and identification of degradation products. Chemosphere 138:924–931. https://doi.org/10.1016/j.chemosphere.2014.12.028

Harvey GR (1998) In: Neilson AH (ed) The handbook of environmental chemistry. Springer, Berlin

He K, Zeng G, Chen A, Huang Z, Peng M, Huang T, Chen G (2019) Graphene hybridized polydopamine-kaolin composite as effective adsorbent for methylene blue removal. Compos Part B Eng 161:141–149. https://doi.org/10.1016/j.compositesb.2018.10.063

Hebbar RS, Isloor AM, Ananda K, Ismail AF (2016) Fabrication of polydopamine functionalized halloysite nanotube/polyetherimide membranes for heavy metal removal. J Mater Chem A 4:764–774. https://doi.org/10.1039/C5TA09281G

Hernández-Alonso MD, Fresno F, Suárez S, Coronado JM (2009) Development of alternative photocatalysts to TiO_2: challenges and opportunities. Energy Environ Sci 2:1231–1257. https://doi.org/10.1039/B907933E

Huang D, Hu C, Zeng G, Cheng M, Xu P, Gong X, Wang R, Xue W (2017a) Combination of Fenton processes and biotreatment for wastewater treatment and soil remediation. Sci Total Environ 574:1599–1610. https://doi.org/10.1016/j.scitotenv.2016.08.199

Huang D, Wang X, Zhang C, Zeng G, Peng Z, Zhou J, Cheng M, Wang R, Hu Z, Qin X (2017b) Sorptive removal of ionizable antibiotic sulfamethazine from aqueous solution by graphene oxide-coated biochar nanocomposites: influencing factors and mechanism. Chemosphere 186:414–421. https://doi.org/10.1016/j.chemosphere.2017.07.154

Huang Q, Liu Y, Cai T, Xia X (2019) Simultaneous removal of heavy metal ions and organic pollutant by BiOBr/Ti_3C_2nanocomposite. J Photochem Photobiol A Chem 375:201–208. https://doi.org/10.1016/j.jphotochem.2019.02.026

Hussain K, Rahman M, Prakash A, Sarma KP, Hoque RR (2016) Atmospheric bulk deposition of polycyclic aromatic hydrocarbons over Brahmaputra valley: characteristics and influence of meteorology. Aerosol Air Qual Res 16:1675–1689. https://doi.org/10.4209/aaqr.2016.02.0060

IARC (1998) IARC monographs on the evaluation of carcinogenic risks to humans, volume 32. In: Polynuclear aromatic compounds, part I, chemical, environmental and experimental data. IARC, Lyon

Irland JC, D'avila B, Moreno H, Fink SK, Tassos S (1995) Heterogeneous photocatalytic decomposition of polyaromatic hydrocarbons over titanium dioxide. Chemosphere 30:965–984. https://doi.org/10.1016/0045-6535(94)00452-Z

Jacques RJS, Santos EC, Bento FM, Peralba MCR, Selbach PA, Enilson LSSF, Camargo AO (2005) Anthracene biodegradation by *Pseudomonas* sp. isolated from a petrochemical sludge land farming site. Int Biodeter Biodegrad 56:143–150. https://doi.org/10.1016/j.ibiod.2005.06.005

Jun LY, Mubarak NM, Yee MJ, Yon LS, Bing CH (2018) An overview of functionalized carbon nanomaterial for organic pollutant removal. J Ind Eng Chem 67:175–186. https://doi.org/10.1016/j.jiec.2018.06.028

Jung KH, Kim JK, Noh JH, Eun JW, Bae HJ, Kim MG (2013) Characteristic molecular signature for the early detection and prediction of polycyclic aromatic hydrocarbons in rat liver. Toxicol Lett 216:1–8. https://doi.org/10.1016/j.toxlet.2012.11.001

Kang J, Zhang H, Duan X, Sun H, Tan X, Liu S, Wang S (2019) Magnetic Ni-Co alloy encapsulated N-doped carbon nanotubes for catalytic membrane degradation of emerging contaminants. Chem Eng J 362:251–261. https://doi.org/10.1016/j.cej.2019.01.035

Kasumba J, Holmen B (2018) Heterogeneous ozonation reactions of polycyclic aromatic hydrocarbons and fatty acid methyl esters in biodiesel particulate matter. Atmos Environ 175:15–24. https://doi.org/10.1016/j.atmosenv.2017.11.051

Khan MA, Woo SI, Yang OB (2008) Hydrothermal stability Fe (III) doped titania active under visible light splitting reaction. Int J Hydrog Energy 33:5345–5351. https://doi.org/10.1016/j.ijhydene.2008.07.119

Khan WZ, Najeeb I, Tuiyebayeva M, Makhtayeva Z (2015) Refinery wastewater degradation with titanium dioxide, zinc oxide, and hydrogen peroxide in a photocatalytic reactor. Process Saf Environ Prot 94:479–486. https://doi.org/10.1016/j.psep.2014.10.007

Kharazi P, Rahimi R, Rabbani M (2019) Copper ferrite-polyaniline nanocomposite: structural, thermal, magnetic and dye adsorption properties. Solid State Sci 93:95–100. https://doi.org/10.1016/j.solidstatesciences.2019.05.007

Kim KH, Jahan SA, Kabir E, Brown RJ (2013) A review of airborne polycyclic aromatic hydrocarbons (Polycyclic aromatic hydrocarbons) and their human health effects. Environ Int 60:71–80. https://doi.org/10.1016/j.envint.2013.07.019

Kot-Wasik A, Dąbrowska D, Namieśnik J (2004) Photodegradation and biodegradation study of benzo(a)pyrene in different liquid media. Journal of Photochemistry and Photobiology A: Chemistry 168(1-2):109–115

Rakati Kavosi K, Mirzaei M, Maghsoodi S, Shahbazi A (2019) Preparation and characterization of poly aniline modified chitosan embedded with ZnOFe3O4 for Cu(II) removal from aqueous solution. International Journal of Biological Macromolecules 130:1025–1045

Kudo A, Miseki Y (2009) Heterogeneous photocatalyst materials for watersplitting. Chem Soc Rev 38:253–278. https://doi.org/10.1039/B800489G

Kumar N, Badwal AS, Mizaikoff B, Singh S, Kranz C (2019) Electrochemical detection and photocatalytic performance of MoS_2/TiO_2 nanocomposite against pharmaceutical contaminant: Paracetamol. Sens Bio-Sens Res 24:100288. https://doi.org/10.1016/j.sbsr.2019.100288

Kumari D, Goswami R, Kumar M, Payalmazumder, Kataki R, Shim J (2018) Removal of Cr (VI) ions from the aqueous solution through nanoscale zero-valent iron (nZVI) Magnetite Corn Cob Silica (MCCS): a bio-waste based water purification perspective. Groundw Sustain Dev 7:470–476. https://doi.org/10.1016/j.gsd.2017.12.007

Kuppusamy S, Thavamani P, Venkateswarlu K, Lee YB, Naidu R, Megharaj M (2017) Remediation approaches for polycyclic aromatic hydrocarbons contaminated soils: technological constraints, emerging trends and future directions. Chemosphere 168:944–968. https://doi.org/10.1016/j.chemosphere.2016.10.115

Lakhani A (2012) Source apportionment of particle bound polycyclic aromatic hydrocarbons at an industrial location in Agra, India. Sci World J 2012. https://doi.org/10.1100/2012/781291

Larson RA, Berenbaum MR (1988) Environmental phototoxicity – solar ultraviolet-radiation affects the toxicity of natural and man-made chemicals. Environ Sci Technol 22:354–360. https://doi.org/10.1021/es00169a001

Lawal AT (2017) Polycyclic aromatic hydrocarbons. A review. Cogent Environ Sci 3:1339841. https://doi.org/10.1080/23311843.2017.1339841

Li B, Cao H, Yin G, Lua Y, Yin J (2011) Cu_2O@reduced graphene oxide composite for removal of contaminants from water and supercapacitors. J Mater Chem 21:10645. https://doi.org/10.1039/C1JM12135A

Li J, Zhao F, Zhang L, Zhang M, Jiang H, Li S, Li J (2015a) Electrospun hollow ZnO/NiO heterostructures with enhanced photocatalytic activity. RSC Adv 5:67610–67616. https://doi.org/10.1039/C5RA08903D

Li X, Liu X, Xu L, Wen Y, Mac J, Wu Z (2015b) Highly dispersed Pd/PdO/Fe2O3 nanoparticles in SBA-15 for Fenton-like processes: confinement and synergistic effects. Appl Catal B Environ 165:79–86. https://doi.org/10.1016/j.apcatb.2014.09.071

Li L, Gong L, Wang Y, Liu Q, Zhang J, Mu Y, Yu H-Q (2016) Removal of halogenated emerging contaminants from water by nitrogen-doped graphene decorated with palladium nanoparticles: experimental investigation and theoretical analysis. Water Res 98:235–241. https://doi.org/10.1016/j.watres.2016.04.024

Li J, Guo R, Ma Q, Nengzi L, Cheng X (2019a) Efficient removal of organic contaminant via activation of potassium persulfate by γ-Fe_2O_3/α-MnO_2 nanocomposite. Sep Purif Technol 227:115669. https://doi.org/10.1016/j.seppur.2019.06.007

Li Y, Liao X, Huling S, Xue T, Liu Q, Cao H, Lin Q (2019b) The combined effects of surfactant solubilization and chemical oxidation on the removal of polycyclic aromatic hydrocarbon from soil. Sci Total Environ 647:1106–1112. https://doi.org/10.1016/j.scitotenv.2018.07.420

Lin C-Y, Chiang C-C, Thi Nguyen M-L, Lay C-H (2017) Enhancement of fermentative biohydrogen production from textile desizing wastewater via coagulation-pretreatment. Int J Hydrog Energy 42:12153–12158. https://doi.org/10.1016/j.ijhydene.2017.03.184

Lu H, Zhu L (2007) Pollution patterns of polycyclic aromatic hydrocarbons in tobacco smoke. Journal of Hazardous Materials 139(2):193–198

Liu G, Sun C, Cheng L, Jin Y, Lu H, Wang L, Smith SC, Lu GQ, Cheng HM (2009a) Efficient promotion of anatase TiO_2 photocatalysis via bifunctional surface-terminating Ti−O−B−N structures. J Phys Chem C 113:12317–12324. https://doi.org/10.1021/jp900511u

Liu L, Kou JH, Guo DM, Yang J, Liu HL, Yu HX, Chu S, Jiang KR, Wang Y, Zou ZG (2009b) Synthesis of thiol-functionalized TiO_2 nanocomposite and photocatalytic degradation for PAH under visible light irradiation. Chin Chem Lett 20:1366–1370. https://doi.org/10.1016/j.cclet.2009.06.026

Liu J, Liu G, Zhang J, Yin H, Wang R (2012) Occurrence and risk assessment of polycyclic aromatic hydrocarbons in soil from the Tiefa coal mine district, Liaoning, China. J Environ Monit 14:2634. https://doi.org/10.1039/c2em30433c

Liu SH, Zeng GM, Niu QY, Liu Y, Zhou L, Jiang LH, Tan XF, Xu P, Zhang C, Cheng M (2017) Bioremediation mechanisms of combined pollution of polycyclic aromatic hydrocarbons and heavy metals by bacteria and fungi: a mini review. Bioresour Technol 224:25–33. https://doi.org/10.1016/j.biortech.2016.11.095

Luan H, Teychene B, Huang H (2019) Efficient removal of As(III) by Cu nanoparticles intercalated in carbon nanotube membranes for drinking water treatment. Chem Eng J 355:341–350. https://doi.org/10.1016/j.cej.2018.08.104

Lundstedt S, White PA, Lemieux CL, Lynes KD, Lambert IB, Oberg L, Haglund P, Tysklind M (2007) Sources, fate, and toxic hazards of oxygenated polycyclic aromatic hydrocarbons (Polycyclic aromatic hydrocarbons) at PAH contaminated sites. Natl Libr Med 36:475–485. https://doi.org/10.1579/0044-7447(2007)36[475:sfatho]2.0.co;2

Mahendiran M, Mathen JJ, Mohamed R, Madhavan J, Raj MVA (2019) Investigation of structural, optical and electrical properties of transition metal oxide semiconductor CdO-ZnO nanocomposite and its effective role in the removal of water contaminants. J Phys Chem Solids 126:322–334. https://doi.org/10.1016/j.jpcs.2018.11.012

Mahmoud ME, Amira MF, Seleim SM (2019) Solvent free microwave synthesis of nano polyaniline-zirconium silicate nanocomposite for removal of nitro derivatives. J Ind Eng Chem 77:371–384. https://doi.org/10.1016/j.jiec.2019.05.001

Mahto TK, Chandra S, Haldar C, Sahu SK (2015) Kinetic and thermodynamic study of polyaniline functionalized magnetic mesoporous silica for magnetic field guided dye adsorption. RSC Adv 5:47909–47919. https://doi.org/10.1039/C5RA08284F

Mangun CL, Benak KR, Economy J, Foster KL (2001) Surface chemistry pore sizes and adsorption properties of activated carbon fibers and precursors treated with ammonia. Carbon 39:1809–1820. https://doi.org/10.1016/S0008-6223(00)00319-5

Manoli E, Samara C (1999) Polycyclic aromatic hydrocarbons in natural waters: sources, occurrence and analysis. Trends Anal Chem 18:417–428

Martínez-Vargas BL, Cruz-Ramíreza M, Díaz-Reala JA, Rodríguez-Lópezb JL, Bacame-Valenzuelaa FJ, Ortega-Borgesa R, Reyes-Vidala Y, Ortiz- Fradea L (2019) Synthesis and characterization of n-ZnO/p-MnO nanocomposites for the photocatalytic degradation of anthracene. J Photochem Photobiol A Chem 369:85–96. https://doi.org/10.1016/j.jphotochem.2018.10.010

Matzek LW, Carter KE (2016) Activated persulfate for organic chemical degradation: a review. Chemosphere 151:178–188. https://doi.org/10.1016/j.chemosphere.2016.02.055

May WE, Wasik SP, Freeman DH (1978) Determination of the solubility behavior of some polycyclic aromatic hydrocarbons in water 50:997–1000. https://doi.org/10.1021/ac50029a042

Moghaddam AZ, Esmaeilkhanian E, Shakourian-Fard M (2019) Immobilizing magnetic glutaraldehyde cross-linked chitosan on graphene oxide and nitrogen-doped graphene oxide as well-dispersible adsorbents for chromate removal from aqueous solutions. Int J Biol Macromol 128:61–73. https://doi.org/10.1016/j.ijbiomac.2019.01.086

Moon HB, Kim HS, Choi M, Choi HG (2010) Intake and potential health risk of polycyclic aromatic hydrocarbons associated with seafood consumption in Korea from 2005 to 2007. Arch Environ Contam Toxicol 58:214–221. https://doi.org/10.1007/s00244-009-9328-5

Mukwevho N, Fosso-Kankeu E, Waanders F, Kumar N, Ray SS, Mbianda XY (2019) Photocatalytic activity of $Gd_2O_2CO_3{\cdot}ZnO{\cdot}CuO$ nanocomposite used for the degradation of phenanthrene. https://link.springer.com/article/10.1007/s42452-018-0012-0

Muntean SG, Nistow MA, Ianos R, Pacurariu C, Capraru A, Surdu V (2019) Combustion synthesis of Fe_3O_4/Ag/C nanocomposite and application for dyes removal from multicomponent systems. Appl Surf Sci 481:825–837. https://doi.org/10.1016/j.apsusc.2019.03.161

Musa Bandowe A, Nosir S, Kersten M, Wilcke W (2010) Polycyclic aromatic hydrocarbons (Polycyclic aromatic hydrocarbons) and their oxygen-containing derivatives (OPolycyclic aromatic hydrocarbons) in soils from the Angren industrial area, Uzbekistan, Benjamin. Environ Pollut 158:2888–2899. https://doi.org/10.1016/j.envpol.2010.06.012

National Toxicology Program (2000) Toxicology and carcinogenesis studies of naphthalene (CAS no 91-20-3) in F344/N rats (inhalation studies). Natl Toxicol Program Tech Rep Ser 500:1–173

Nguyen DCT, Cho KY, Jung C, Oh W (2018) Photocatalytic activities of contaminants by Bi_2WO_6-graphene composites decorated with mesoporous silica. J Alloys Compd 766:477–487. https://doi.org/10.1016/j.jallcom.2018.06.379

Nie G, Wu L, Du Y, Wang H, Xu Y, Ding Z, Liu Z (2019) Efficient removal of phosphate by a millimeter-sized nanocomposite of titanium oxides encapsulated in positively charged polymer. Chem Eng J 360:1128–1136. https://doi.org/10.1016/j.cej.2018.10.184

Ning XA, Lin MQ, Shen LZ, Zhang JH, Wang JY, Yang ZY, Liu YJ (2014) Levels, composition profiles and risk assessment of polycyclic aromatic in sludge from ten textile dyeing plants. Environ Res 132:112–118. https://doi.org/10.1016/j.envres.2014.03.041

Noor SFM, Ahmad N, Khattak MA, Khan MS, Mukhtar A, Kazi S, Badshah S, Khan R (2017) Application of Sayong ball clay membrane filtration for Ni (II) removal from industrial wastewater. J Taibah Univ Sci 11:949–954. https://doi.org/10.1016/j.jtusci.2016.11.005

Novotny TE, Hardin SN, Hovda LR, Novotny DJ, McLean MK, Khan S (2011) Tobacco and cigarette butt consumption in humans and animals. Tob Control 20:17–20. https://doi.org/10.1136/tc.2011.043489

Nwaichi EO, Chuku LC, Ighoavwogan E, (2016) Polycyclic Aromatic Hydrocarbons and Selected Heavy Metals in Some Oil Polluted Sites in Delta State Nigeria 7:1389–1410. https://doi.org/10.4236/jep.2016.710120

Okere U, Semple K (2012) Biodegradation of polycyclic aromatic hydrocarbons in 'pristine'soils from different climatic regions. J Bioremed Biodegr 1(2). https://doi.org/10.4172/2155-6199.S1-006

Oliveira M, Gravato C, Guilhermino L (2012) Acute toxic effects of pyrene on Pomatoschistus microps (Teleostei, Gobiidae): mortality, biomarkers and swimming performance. Ecol Indic 19:206–214. https://doi.org/10.1016/j.ecolind.2011.08.006

Peltonen K, Dipple A (1995) Polycyclic Aromatic Hydrocarbons: Chemistry of DNA Adduct Formation. Journal of Occupational and Environmental Medicine 37(1):52–58

Patra AS, Ghorai S, Sarkar D, Das R, Sarkar S, Pal S (2017) Anionically functionalized guar gum embedded with silica nanoparticles: an efficient nanocomposite adsorbent for rapid adsorptive removal of toxic cationic dyes and metal ions. Bioresour Technol 225:367–376. https://doi.org/10.1016/j.biortech.2016.11.093

Peluffo M, Rosso JA, Morelli IS, Mora VC (2018) Strategies for oxidation of polycyclic aromatic hydrocarbons in aged contaminated soil by batch reactors. Ecotoxicol Environ Saf 151:76–82. https://doi.org/10.1016/j.ecoenv.2017.12.067

Pereira VR, Isloor AM, Bhat UK, Ismail AF, Obaid A, Fun H-K (2015) Preparation and performance studies of polysulfone-sulfated nano-titania (S-TiO_2) nanofiltration membranes for dye removal. RSC Adv 5:53874–53885. https://doi.org/10.1039/C5RA07994B

Pikes S (1992) Polycyclic aromatic hydrocarbons. In: Sullivan JB, Krieger GR (eds) Hazardous materials toxicology: clinical priciples of environmental medicine. Williams and Wilkins, Baltimore 1151–1154

Ping L, Zhang C, Cui H, Yuan X, Cui J, Shan S (2017a) Characterization and application of a newly isolated pyrene-degrading bacterium, Pseudomonas monteilii. 3 Biotech 7:309. https://doi.org/10.1007/s13205-017-0945-9

Ping L, Guo Q, Chen X, Yuan X, Zhang C, Zhao H (2017b) Biodegradation of pyrene and benzo [a] pyrene in the liquid matrix and soil by a newly identified Raoultella planticola strain. 3 Biotech 7:56. https://doi.org/10.1007/s13205-017-0704-y

Pothuluri JV, Cerniglia CE (1994) Microbial metabolism of polycyclic aromatic hydrocarbons:92–124. https://doi.org/10.1016/S0065-2164(08)70052-2

Priya B, Shandilya P, Raizada P, Thakur P, Singh N, Singh P (2016) Photocatalytic mineralization and degradation kinetics of ampicillin and oxytetracycline antibiotics using graphene sand composite and chitosan supported BiOCl. J Mol Catal A Chem 423:400–413. https://doi.org/10.1016/j.molcata.2016.07.043

Qui P, Park B, Choi J, Thokchom B, Pandit AB, Khim J (2018) A review on heterogeneous sonocatalyst for treatment of organic pollutants in aqueous phase based on catalytic mechanism. Ultrason Sonochem 45:29–49. https://doi.org/10.1016/j.ultsonch.2018.03.003

Rachna RM, Shanker U (2018) Enhanced photocatalytic degradation of chrysene by Fe_2O_3@ZnHCF nanocubes. Chem Eng J 348:754–764. https://doi.org/10.1016/j.cej.2018.04.185

Rachna RM, Shanker U (2019a) Sunlight active ZnO@FeHCF nanocomposite for the degradation of bisphenol A and nonylphenol. J Environ Chem Eng 7:103153. https://doi.org/10.1016/j.jece.2019.103153

Rachna RM, Shanker U (2019b) Sunlight mediated improved photocatalytic degradation of carcinogenic benz[*a*]anthracene and benzo[*a*]pyrene by zinc oxide encapsulated hexacyanoferrate nanocomposite. J Photochem Photobiol A Chem 381:111861. https://doi.org/10.1016/j.jphotochem.2019.111861

Rachna, Rani M, Shanker U (2019) Degradation of tricyclicpolyaromatic hydrocarbons in water, soil and river sediment with a novel TiO2 based heterogeneous nanocomposite. J Environ Manag 248:109340. https://doi.org/10.1016/j.jenvman.2019.109340

Raizada P, Shandilya P, Singh P, Thakur P (2017a) Solar light-facilitated oxytetracycline removal from the aqueous phase utilizing a H2O2/ZnWO4/CaO catalytic system. J Taibah Univ Sci 11:689–699. https://doi.org/10.1016/j.jtusci.2016.06.004

Raizada P, Kumari J, Shandilya P, Dhiman R, Singh VP, Singh P (2017b) Magnetically retrievable Bi2WO6/Fe3O4 immobilized on graphene sand composite for investigation of photocatalytic mineralization of oxytetracycline and ampicillin. Process Saf Environ Prot 106:104–116. https://doi.org/10.1016/j.psep.2016.12.012

Raizada P, Sudhaik A, Singh P (2019) Photocatalytic water decontamination using graphene and ZnO coupled photocatalysts: a review. Mater Sci Energy Technol 2:509–525. https://doi.org/10.1016/j.mset.2019.04.007

Rani M, Shanker U (2018) Insight in to the degradation of bisphenol A by doped ZnO@ZnHCF nanocubes: high photocatalytic performance. J Colloid Interface Sci 530:16–28. https://doi.org/10.1016/j.jcis.2018.06.070

Rani M, Shanker U (2018a) Effective adsorption and enhanced degradation of various pesticides from aqueous solution by Prussian blue Nanorods. J Environ Chem Eng 6:1512–1521. https://doi.org/10.1016/j.jece.2018.01.060

Rani M, Shanker U (2018b) Removal of chlorpyrifos, thiamethoxam, and tebuconazole from water using green synthesized metal hexacyanoferrate nanoparticles. Environ Sci Pollut Res 25:10878–10893. https://doi.org/10.1007/s11356-018-1346-2

Ravindra K, Sokhi R, Vangrieken R (2008) Atmospheric polycyclic aromatic hydrocarbons: source attribution, emission factors and regulation. TrAC Trends Anal Chem 42:2895–2921. https://doi.org/10.1016/S0165-9936(99)00111-9

Rockens E, Dumolin J, Matheeussen C (2000) PM10 dust and chemical characterisation of aerosols in Flanders, Belgium. In: Longhurst JWS, Brebbia CA, Power H (eds) Air pollution VIII. WIT Press, Ashurst, pp 699–707

Rogge WF, Hildemann LM, Mazurek MA, Cass GR (1991) Sources of fine organic aerosol. 1. Charbroilers and meat cooking operations. Environ Sci Technol 2:1112–1125. https://doi.org/10.1021/es00018a015

Saad Hassan SM, Waleed Azab IMEL, Hager Ali R, Mona Mansour SM (2015) Green synthesis and characterization of ZnO nanoparticles for photocatalytic degradation of anthracene. Adv Nat Sci Nanosci Nanotechnol 6:045012. (11pp)

Salvato M, Scagliotti M, Crescenzi MD, Bpscardin M, Attanasio C, Avallone G, Cirillo C, Prosposito P, Matteis FD, Messi R, Castrucci P (2019) Time response in carbon nanotube/Si based photodetectors. Sensors Actuators A Phys 292:71–76. https://doi.org/10.1016/j.sna.2019.04.004

Sannino F, Pirozzi D, Vitiello G, Derrico G, Aronne A, Fanelli E, Pernice P (2014) Oxidative degradation of phenanthrene in the absence of light irradiation by hybrid ZrO_2-acetylacetonate gel-derived catalyst. Appl Catal B Environ 156–157:101–107. https://doi.org/10.1016/j.apcatb.2014.03.006

Sawicki E, Elbert WC, Hauser TR, Fox FT, Stanley TW (1960) Benzo(a)pyrene content of the air of American communities. Am Ind Hyg Assoc J 21:443–451. https://doi.org/10.1080/00028896009344103

Severson RF, Snook ME, Arrendale RF, Chortyk OT (1976) Gas chromatographic quantitation of polynuclear aromatic hydrocarbons in tobacco smoke. Analytical Chemistry 48(13):1866–1872

Sekar AD, Muthukumar H, Chandrasekaran NI, Matheswaran M (2018) Photocatalytic degradation of naphthalene using calcined Fe-ZnO/PVA nanofibers. Chemosphere 205:610–617. https://doi.org/10.1016/j.chemosphere.2018.04.131

Shahrezaei F, Akhbari A, Rostami A (2012) Photodegradation and removal of phenol and phenolic derivatives from petroleum refinery wastewater using nanoparticles of TiO_2. Energy Environ 3:267–274, ISSN 2076-2895, ISSN 2076-2909

Shanker U, Jassal V, Rani M (2017a) Degradation of toxic polycyclic aromatic hydrocarbons in water and soil using potassium zinc hexacyanoferratenanocubes. J Environ Manag 204:337–348. https://doi.org/10.1016/j.jenvman.2017.09.015

Shanker U, Jassal V, Rani M (2017b) Green synthesis of iron hexacyanoferrate nanoparticles: potential candidate for the degradation of toxic polycyclic aromatic hydrocarbons. J Environ Chem Eng 5:4108–4120. https://doi.org/10.1016/j.jece.2017.07.042

Sharma A, Lee B (2015) Adsorptive/photo-catalytic process for naphthalene removal from aqueous media using in-situ nickel doped titanium nanocomposite. J Environ Manag 155:114–122. https://doi.org/10.1016/j.jenvman.2015.03.008

Shen H, Huang Y, Wang R, Zhu D, Li W, Shen G, Wang B, Zhang Y, Chen Y, Lu Y, Chen H, Li T, Sun K, Li B, Liu W, Liu J, Tao S (2013) Global atmospheric emissions of polycyclic aromatic hydrocarbons from 1960 to 2008 and future predictions. Environ Sci Technol 47:6415–6424. https://doi.org/10.1021/es400857z

Shujuan Zhang (2012) Synergistic effects of C–Cr codoping in TiO2 and enhanced sonocatalytic activi under ultrasonic irradiation 19:767–771. https://doi.org/10.1016/j.ultsonch.2011.12.016ty

Shukla N, Gupta V, Rawat AS, Gahlot VK, Shrivastava S, Rai PK (2018) 2, 4-Dinitrotoluene (DNT) and 2, 4, 6-Trinitrotoluene (TNT) removal kinetics and degradation mechanism using zero valent iron-silica nanocomposite. J Environ Chem Eng 6:5196–5203. https://doi.org/10.1016/j.jece.2018.08.018

Singh AK, Xu Q (2013) Synergistic catalysis over bimetallic alloy nanoparticles. ChemCatChem 5:652–676. https://doi.org/10.1002/cctc.201200591

Srinivas G, Burress J, Yildirim T (2012) Graphene oxide derived carbons (GODCs): synthesis and gas adsorption properties. Energy Environ Sci 5:6453–6459. https://doi.org/10.1039/C2EE21100A

Subramanian Y, Ramasamy V, Karthikeyan RJ, Srinivasan GR, Arulmozhi D, Gubendiran RK, Sriramalu M (2019) Investigations on the enhanced dye degradation activity of heterogeneous BiFeO3–GdFeO3 nanocomposite photocatalyst. Heliyon 5:e01831. https://doi.org/10.1016/j.heliyon.2019.e01831

Sudhaik A, Raizada P, Shandilya P, Jeong DY, Lim JH, Singh P (2018) Review on fabrication of graphitic carbon nitride based efficient nanocomposites for photodegradation of aqueous phase organic pollutants. J Ind Eng Chem 67:28–51. https://doi.org/10.1016/j.jiec.2018.07.007

Sun P, Liu H, Feng M, Guo L, Zhai Z, Fang Y, Zhang X, Sharma VK (2019a) Nitrogen-sulfur co-doped industrial graphene as an efficient peroxymonosulfate activator: singlet oxygen-dominated catalytic degradation of organic contaminants. Appl Catal B Environ 251:335–345. https://doi.org/10.1016/j.apcatb.2019.03.085

Sun S-J, Zhao Z-B, Li B, Ma L-X, Fu D-L, Sun X-Z, Thapa S, Shen J-M, Qi H, Wu Y-N (2019b) Occurrence, composition profiles and risk assessment of polycyclic aromatic hydrocarbons in municipal sewage sludge in China. Environ Pollut 249:764–770. https://doi.org/10.1016/j.envpol.2018.11.067

Supaka N, Pinphanichakarn P, Pattaragulwanit K, Thaniyavarn S, Omori T, Juntongjin K (2001) Isolation and characterization of a phenanthrene-degrading Sphingomonas sp. strain P2 and its ability to degrade fluoranthene and pyrene via cometabolism, 27:21–28. https://doi.org/10.2306/scienceasia1513-1874.2001.27.021

Taiwo AM, Ihedioha EC, Nwosu SC, Oyelakin OA, Efubesi PC, Shitta JS, Osinubi TO (2019) Levels and health risk assessment of polycyclic aromatic hydrocarbons in protein foods from Lagos and Abeokuta, Southwestern Nigeria. J Food Compos Anal 79:28–38. https://doi.org/10.1016/j.jfca.2019.03.001

Theerakarunwong CD, Phanichphant S (2018) Visible-light-induced Photocatalytic degradation of PAH-contaminated soil and their pathways by Fe-doped TiO_2 Nanocatalyst. Water Air Soil Pollut 229:291. https://doi.org/10.1007/s11270-018-3951-6

Tongo I, Ogbeide O, Ezemonye L (2017) Human health risk assessment of polycyclic aromatic hydrocarbons in smoked fish species from markets in Southern Nigeria. Toxicol Rep 4:55–61. https://doi.org/10.1016/j.toxrep.2016.12.006

Tudoran MA, Putz MV (2012) Polycyclic aromatic hydrocarbons: from in Cerebro to in Silico eco-toxicity fate. Chem Bull 57:1

Tuzen NM (2019) Development of tetraethylene pentamine functionalized multi-wall carbon nanotubes as a new adsorbent in a syringe system for removal of bisphenol A by using multivariate optimization techniques. Microchem J 147:1147–1154. https://doi.org/10.1016/j.microc.2019.04.040

USEPA (1999) Compendium of methods for determination of toxic organic compounds in ambient air, 2nd edn. Center for Environmental Research Information; Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati

Van Winkle LS, Buckpitt AR, Nishio SJ, Isaac JM, Plopper CG (1995) Cellular response in naphthalene-induced Clara cell injury and bronchiolar epithelial repair in mice. Am J Phys Lung Cell Mol Phys 269:800–818. https://doi.org/10.1152/ajplung.1995.269.6.L800

Wang R, Liu G, Chou C-l, Liu J, Zhang J (2010a) Environmental assessment of polycyclic aromatic hydrocarbons in soils around the Anhui Coal District, China. Arch Environ Contam Toxicol 59:62–70. https://doi.org/10.1007/s00244-009-9440-6

Wang WT, Staci L, Simonich M, Xue M, Zhao JY, Zhang N, Wang R, Cao J, Tao S (2010b) Concentrations, sources and spatial distribution of polycyclic aromatic hydrocarbons in soils from Beijing, Tianjin and surrounding areas, North China. Environ Pollut 158:1245–1251. https://doi.org/10.1016/j.envpol.2010.01.021

Wang MC, Chen YT, Chen SH, Chien SWC, Sunkara SV (2012) Phytoremediation of pyrene contaminated soils amended with compost and planted with *ryegrass* and *alfalfa*. Chemosphere 87:217–225. https://doi.org/10.1016/j.chemosphere.2011.12.063

Wang Y, Yang Y, Xi L, Zhang X, Jia M, Xu H, Wu H (2016) A simple hydrothermal synthesis of flower-like ZnO microspheres and their improved photocatalytic activity. Mater Lett 180:55–58. https://doi.org/10.1016/j.matlet.2016.05.107

Wang R, Sun R, Liu G, Yousaf B, Wu D, Chen J, Zhang H (2017) A review of the biogeochemical controls on the occurrence and distribution of polycyclic aromatic compounds (PACs) in coals. Earth Sci Rev 171:400–418. https://doi.org/10.1016/J.EARSCIREV.2017.06.011

Warshawsky D (1999) Polycyclic aromatic hydrocarbons in carcinogenesis. Environ Health Perspect 107:317–319

Wattiau P (2002) Microbial aspects in bioremediation of soils polluted by polyaromatic hydrocarbons. In: Biotechnology for the environment: strategy and fundamentals. Springer, Dordrecht, pp 69–89. https://doi.org/10.1007/978-94-010-0357-5_5

WHO (2002) IARC monographs on the evaluation of carcinogenic risks to humans – some traditional herbal medicines, some mycotoxins, naphthalene and styrene, vol 82. IARC Press, Lyon

WHO Report on the Global Tobacco Epidemic (2017) Monitoring tobacco use and prevention policies. World Health Organization, Geneva

Wild SR, Jones KC (1995) Polynuclear aromatic hydrocarbons in the United Kingdom environment: a preliminary source inventory and budget. Environ Pollut 88:91–108. https://doi.org/10.1016/0269-7491(95)91052-M

Wu Y, Wang Y, Lin Z, Wang Y, Li Y, Liu S, Gui X, Yang X (2019) Three-dimensional α-Fe_2O_3/amino-functionalization carbon nanotube sponge for adsorption and oxidative removal of tetrabromobisphenol A. Sep Purif Technol 211:359–367. https://doi.org/10.1016/j.seppur.2018.10.002

Xia S, Zhang L, Zhou X, Shao M, Pan G, Ni Z (2015) Fabrication of highly dispersed Ti/ZnO–Cr2O3 composite as highly efficient photocatalyst for naphthalene degradation. Appl Catal B Environ 176–177:266–277

Xiao F, Guo X, Li J, Sun H, Zhang H, Wang W (2019) Electrospinning preparation and dye adsorption capacity of TiO_2@Carbon flexible fiber. Ceram Int 45:11856–11860. https://doi.org/10.1016/j.ceramint.2019.03.067

Xue Y, Liu J, Chen H, Wang R, Li D, Qu J, Dai L (2012) Nitrogen-doped graphene foams as metal-free counter electrodes in high-performance dye-sensitized solar cells. Angew Chem Int Ed 51:12124–12127. https://doi.org/10.1002/anie.201207277

Yang K, Xing B (2007) Desorption of polycyclic aromatic hydrocarbons from carbon nanomaterials in water. Environ Pollut 145:529–537. https://doi.org/10.1016/j.envpol.2006.04.020

Yang X, Li J, Wen T, Ren X, Huang Y, Wang X (2013a) Adsorption of naphthalene and its derivatives on magnetic graphene composites and the mechanism investigation. Colloids Surf A Physicochem Eng Asp 422:118–125. https://doi.org/10.1016/j.colsurfa.2012.11.063

Yang D, Tammin SK, Li X, Yang Y (2019) Enhanced removal and detection of benzo[a]pyrene in environmental water samples using carbon dots-modified magnetic nanocomposites. Ecotoxicol Environ Saf 170:383–390. https://doi.org/10.1016/j.ecoenv.2018.11.138

Yang X, Li J, Wen T, Ren X, Huang Y, Wang X (2013b) Adsorption of naphthalene and its derivatives on magnetic graphene composites and the mechanism investigation. Colloids Surf A Physicochem Eng Asp 422:118–125. https://doi.org/10.1016/j.colsurfa.2012.11.063

Yang X, Cai H, Bao M, Yu J, Lu J, Li Y (2018) Insight into the highly efficient degradation of PAHs in water over graphene oxide/Ag3PO4 composites under visible light irradiation. Chemical Engineering Journal 334:355–376

Yi Z, Ye J, Kikugawa N, Kako T, Ouyang S, Williams HS, Yang H, Cao J, Luo W, Li Z, Liu Y, Withers RL (2010) An orthophosphate semiconductor with photooxidation properties under visible-light irradiation. Nat Mater 9:559–564. https://doi.org/10.1038/nmat2780

Yin F, Gu B, Lin Y, Pawar N, Tjin SC, Qu J, Lau SP, Yong K-T (2017a) Functionalized 2D nanomaterials for gene delivery applications. Coord Chem Rev 347:77–97. https://doi.org/10.1016/j.ccr.2017.06.024

Yin S, Tang M, Chen F, Li T, Liu W (2017b) Environmental exposure to polycyclic aromatic hydrocarbons: the correlation with and impact on reproductive hormones in umbilical cord serum. Environ Pollut 220:1429–1437. https://doi.org/10.1016/j.envpol.2016.10.090

Young LY, Cerniglia CE (1995) Microbial transformation and degradation of toxic organic chemicals. Wiley-Liss Inc., New York, 654 pages, ISBN No.: 0–471–52109–4

Yue Y, Peng Z, Wang W, Cai Y, Tan F, Wang X, Qiao X (2019) Facile preparation of MgO-loaded SiO_2nanocomposites for tetracycline removal from aqueous solution. Powder Technol 347:1–9. https://doi.org/10.1016/j.powtec.2019.02.034

Zhang L, Li P, Gong Z, Li X (2008) Photocatalytic degradation of polycyclic aromatic hydrocarbons on soil surfaces using TiO_2 under UV light. J Hazard Mater 158:478–484. https://doi.org/10.1016/j.jhazmat.2008.01.119

Zhang Y, Zhao B (2007) Simulation and health risk assessment of residential particle pollution by coal combustion in China. Build Environ 42:614–622. https://doi.org/10.1016/j.buildenv.2005.10.006

Zhao S, Jia H, Nulaji G, Gao H, Wang F, Wang C (2017) Photolysis of polycyclic aromatic hydrocarbons on Fe^{3+}- montmorillonite surface under visible light: degradation kinetics, mechanism, and toxicity assessments. Chemosphere 184:1346–1354. https://doi.org/10.1016/j.chemosphere.2017.06.106

Zhao X, Cai Z, Wang T, O'Reilly SE, Liu W, Zhao D (2016) A new type of cobalt-deposited titanate nanotubes for enhanced photocatalytic degradation of phenanthrene. Appl Catal B Environ 187:134–143. https://doi.org/10.1016/j.apcatb.2016.01.010

Zhou K, Wu B, Dai X, Chai X (2018) Development of polymeric iron/zirconium-pillared clinoptilolite for simultaneous removal of multiple inorganic contaminants from wastewater. Chem Eng J 347:819–827. https://doi.org/10.1016/j.cej.2018.04.104

Chapter 6
Aerobic Granulation in Hydrocarbon-Rich Wastewater Treatment

Sayanti Ghosh and Saswati Chakraborty

Contents

S. Ghosh (✉)
Centre for the Environment, Indian Institute of Technology Guwahati, Guwahati, Assam, India
e-mail: g.sayanti@iitg.ac.in

S. Chakraborty
Centre for the Environment, Indian Institute of Technology Guwahati, Guwahati, Assam, India

Department of Civil Engineering, Indian Institute of Technology Guwahati, Guwahati, Assam, India
e-mail: saswati@iitg.ac.in

Inamuddin et al. (eds.), *Water Pollution and Remediation: Organic Pollutants*, Environmental Chemistry for a Sustainable World 54,
https://doi.org/10.1007/978-3-030-52395-4_6

Abstract Petroleum industry alone is regulating a major part of the world economy. Everyday million litres of hydrocarbon-rich wastewater is generated from oil refineries, which is one of the major drawbacks of oil industries. Oily wastewater is carcinogenic for humans and animals, and oils can cause ground seepage and can reduce oxygen solubility in water which further affects the marine ecosystems. Among the treatment processes, biological techniques are more suitable to provide eco-friendly results.

The current research trends in hydrocarbon-rich wastewater treatment suggest aerobic granulation as one of the modern biological remedies for oily wastewater. Aerobic granules are densely packed microbial aggregates containing millions of different bacteria. They offer cost-effective and simultaneous degradation of carbon, nitrogen, phosphorus and hydrocarbons in a single reactor system. This technology has been successfully employed in treating petrochemical, coal gasification and palm oil meal effluents. About 1–3.5 mm-sized aerobic granules containing extracellular polymeric substances of 200–300 mg/g volatile suspended solids with 30–70 m/h settling velocity provided almost 90% chemical oxygen demand and 70–90% oil removal while treating 5.6–320 mg/L of hydrocarbon containing wastewater. Above 5 g/L of granule biomass and below 50 mL/g sludge volume index indicated granule stability and compactness throughout oil removal process. This chapter focuses on the mechanisms, effecting factors, characteristics and characterization techniques of aerobic granulation with its detailed application in hydrocarbon-rich wastewater treatment.

Keywords Hydrocarbon-rich wastewater · Poor biodegradability · Aerobic granular reactor · Granulation mechanism · Characterization · Parameters · Factors · Oil degradation

6.1 Introduction

Hydrocarbon-rich wastewater is generated from crude oil reservoirs, palm oil meals, petroleum refineries and fuel manufacturing companies. Oily wastewater can impose hazardous effects on water bodies, aquatic lives, crop production and also on animal and human health (Biswal et al. 2009). Residual crude oil can cause groundwater pollution (Novaković et al. 2012) and ecotoxicity of polyaromatic hydrocarbons were also investigated by researchers (Manzetti 2012). According to the standards for Effluent Discharge Regulations of Environment Protection Act 2002, the permissible limit of oil and grease in effluent is 10 mg/L and according to the Indian

Table 6.1 Hydrocarbon wastes generated in petroleum refineries (Alva-Argáez et al. 2007)

Unit name	Hydrocarbon wastes
Crude desalting	Free floating oil
Crude oil distillation	Oil
Catalytic cracking	Oil
Alkylation	Oil

drinking water standards, in drinking water it is 0.2 mg/L. Petrochemical wastewater is produced in large volume which has poor biodegradability due to the recalcitrant nature of oil (Zhang et al. 2011). Table 6.1 summarizes different units of a petroleum refinery which are the main sources of hydrocarbon waste generation reported by Alva-Argáez et al. (2007).

Several physical and chemical processes, like adsorption, ultrafiltration, membrane separation and chemical oxidation have been employed for oil remediations. But due to their environmental and economical limitations, biological methods are considered to be more feasible in oily wastewater treatment (Mondal et al. 2010). Biological treatments are classified into aerobic and anaerobic processes. However, anaerobic processes mostly produce secondary pollutants during wastewater treatment which make aerobic processes more attractive to the environmentalists (Beun et al. 2002). Aerobic granulation technology is considered as one of the latest techniques in hydrocarbon-rich wastewater treatment (Adav et al. 2008). Granulation is an immobilization phenomenon of different sludge bacteria which is controlled by organic loading and reactor parameters (Show et al. 2012; Tay et al. 2001a; Liu and Tay 2004; Adav et al. 2007). Aerobic granulation is more advantageous than conventional sludge process for the following characteristics (Adav et al. 2008):

(i) Smooth and round granular shape, (ii) high settleability, (iii) high biomass retention, (iv) granule compactness, (v) ability to bear high organic loading rate and (vi) high tolerance to shock loading and toxicity.

All these characteristics are found in a single compact aerobic granule which requires very less settling time and hydraulic retention time. Aerobic granular reactors can approximately reduce 20% of the wastewater treatment running cost and can further reduce 75% space requirement (De Kreuk et al. 2005) than conventional activated sludge process. Figure 6.1 describes the application of aerobic granulation subsequently in laboratory scale, pilot scale and in full scale for treating pulp and paper mill wastewater (Sengar et al. 2018).

Aerobic granulation technology has dealt with a large variety of industrial wastewater treatments (Zhang et al. 2016; Gobi et al. 2011; Franca et al. 2015; Vashi et al. 2019). Among the hydrocarbon-rich wastewaters, aerobic granular treatment of petroleum, coal gasification and palm oil meal effluent treatments have been reported so far.

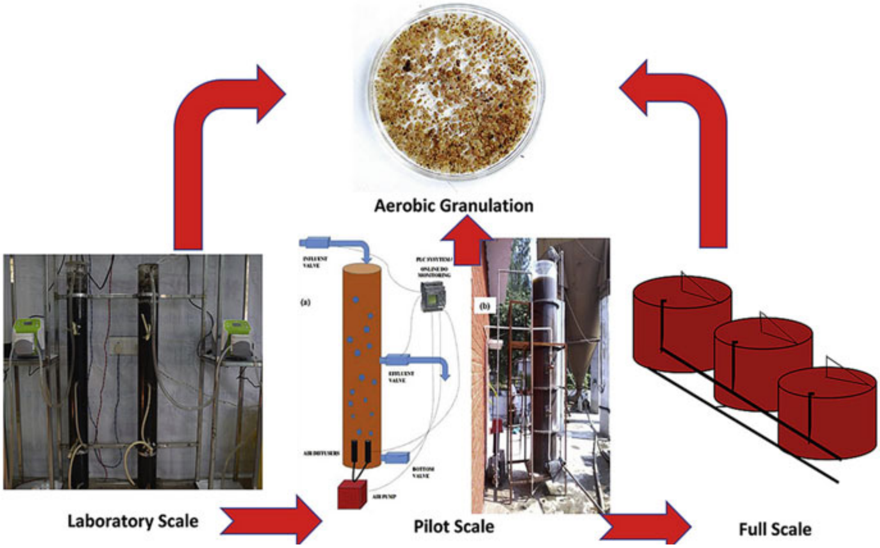


Fig. 6.1 Aerobic granulation technology is given in a nutshell. Granule formation and its subsequent scale-up implementation are described in laboratory scale, pilot scale and in full scale for treating pulp and paper mill wastewater (Sengar et al. 2018)

6.2 Mechanism of Granulation

Granulation mechanisms have been hypothesized by many researchers. But the process is not well defined so far. Some of the proposed mechanisms are described below.

6.2.1 Triggering Forces in Aerobic Granules

Liu and Tay (2002) proposed that granulation takes place in four steps:

- Bacterium to bacterium interaction mediated by physical processes such as diffusion, gravity, and hydrodynamic and/or thermodynamic forces;
- Bacterial aggregation by either physical forces like thermodynamic forces and Van der Waals or by chemical forces like inter-particulate bridging, ionic bonding or by biochemical forces such as cell surface dehydration, fusion of the cell membranes, cell to receptor attraction and so on;
- Cell aggregation by cellular forces like cell clustering or extracellular polymeric substances production;
- Granule structure stabilization by hydrodynamic shear force. This shear force was found to be responsible to provide a final three-dimensional granular structure to the microbial community.

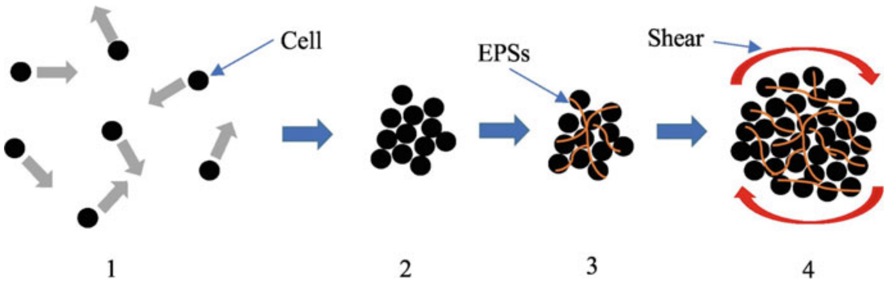


Fig. 6.2 Aerobic granulation mechanism starts with (1) bacterial cell movement and cell-to-cell interaction then (2) cell adhesion and micro-aggregate formation, (3) production of extracellular polymeric substances from aggregate surfaces (orange – extracellular polymeric substances). Finally (4) spherical, compact and matured granular structures are formed (Kent et al. 2018)

A generalized granulation mechanism is described in Fig. 6.2 (Kent et al. 2018).

6.2.2 Extracellular Polymeric Substances-Mediated Granulation

Extracellular polymeric substances are gummy materials secreted on the outer surfaces of microbial cells, which promote cell-to-cell adhesion and granule formation providing long-term granule stability (Tay et al. 2001a; Wang et al. 2006a). Extracellular polymeric substances consist of different exopolysaccharides (Seviour et al. 2010; Lin et al. 2010), exoproteins, humic acid, uronic acid and DNA (deoxyribonucleic acid) which enhance granulation process (Wang et al. 2005; Wang et al. 2015; Wang et al. 2006a).

6.2.3 Role of Hydrophobicity

Liu et al. (2003b) reported surface hydrophobicity as the primary factor behind aerobic granulation. Increasing cell hydrophobicity can decrease the excess Gibbs free energy of bacterial cell surface enhancing cell-to-cell adhesion in granulation process (Tay et al. 2002b).

6.2.4 Cell-to-Cell Adhesion

Zheng et al. (2006) hypothesized that aerobic granulation promotes cell-to-cell adherence which regulates different cellular reactions. Bacterial aggregation is further classified into two categories:

- Auto-aggregation: Adhesion between the cells of genetically identical strains.
- Co-aggregation: Aggregation between genetically different bacterial strains.

6.2.5 Other Mechanisms

Role of dominating microbial species (Barr et al. 2010) and addition of crushed granules inside a sequencing batch reactor (Verawaty et al. 2012) are the other probable granulation mechanisms reported so far.

In another literature, different steps of aerobic granulation are described by Hailei et al. (2006) which are illustrated in Fig. 6.3.

6.3 Characteristics of Aerobic Granules

Characteristics of aerobic granules are determined by physical, chemical and biological parameters.

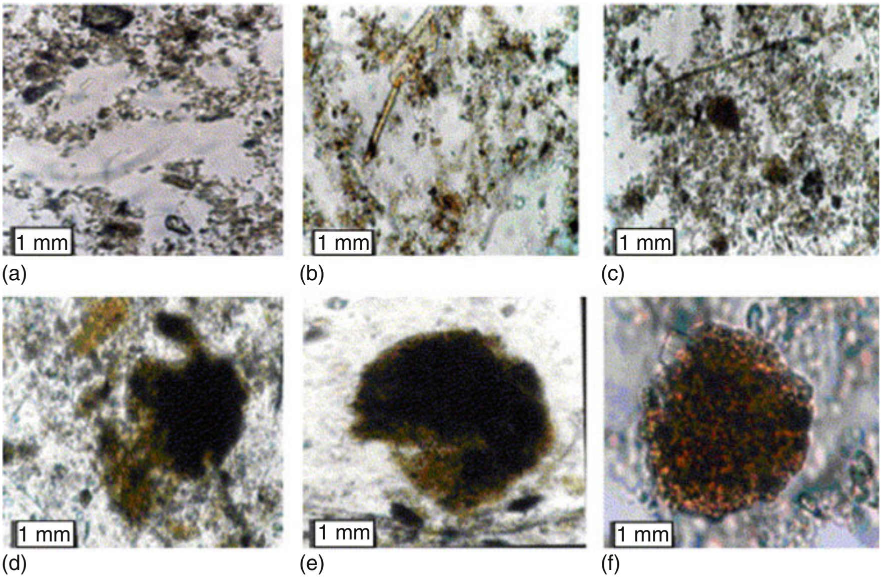


Fig. 6.3 Micrograms of granulation phenomena are illustrated. Picture depicting (**a**) initial sludge; (**b**) multiplication of sludge bacteria; (**c**) appearance of bacterial floc; (**d**) cohesion of the floc; (**e**) maturation of floc; (**f**) formation of aerobic granule (Hailei et al. 2006)

6.3.1 Physical Parameters

Size of Granules

The approximate average granule diameter range lies between 0.2 μm to 16 mm (Beun et al. 1999; Toh et al. 2003; Zheng et al. 2006). High organic loading rate promotes larger granules whereas, smaller granules can be formed under high shear forces (Li et al. 2008; Gao et al. 2011).

Granule Settling Velocity

Granule settling velocity corresponds with granule size and structure which lies between 30 to 70 m/h, which is three times greater than the settling velocity of conventional activated sludge (Liu and Tay 2004). Aerobic granulation is also achievable at settling velocity below 9.5 m/h (Val del Río et al. 2013).

Sludge Volume Index

Sludge volume index determines the volume (in milliliters) required for 1 g of settled sludge after a specific settling time such as 5, 10 or 30 min. Granule settleability is generally represented by sludge volume index. Shorter sludge volume index denotes more compact and stable granular structure. Liu et al. (2003b) observed excellent granule hydrophobicity at sludge volume index values lower than 50 mL/g.

Physical Strength and Density

According to literature, approximately 1 g/mL granule density is observed for matured aerobic granules (Etterer and Wilderer 2001).

Physical Structure

Aerobic granules are either spherical or rod-shaped. They are mainly yellow, brown and black in colour (Zheng et al. 2006) which is dependent on type of carbon source, feed composition and microbial population.

6.3.2 Chemical Parameters

Specific Oxygen Utilization Rate

Specific oxygen utilization rate denotes the activity of microorganisms expressed as milligrams of oxygen consumed by a milligram of cellular proteins per hour. In a case study, specific oxygen utilization rate values in glucose-fed and acetate-fed granules ranged between 55.9 to 69.4 mg O_2/g mixed liquor volatile suspended solids/h (Tay et al. 2002b).

Extracellular Polymeric Substances

Extracellular polymeric substances are metabolic polymers secreted by aerobic granules which help in granule formation. Extracellular polymeric substances mainly contain β-polysaccharides and proteins. In aerobic granules proteins/polysaccharides ratios are generally found between 3.4 to 6.2 which is 0.9 time higher than flocculent-activated sludge (Adav and Lee 2008). Relatively high protein fractions are required as an important feature for matured aerobic granule formation (McSwain et al. 2005).

6.3.3 Biological Parameters

Different light and electronic micrograms like light microscopy, scanning electron microscopy, field emission scanning electron microscopy, fluorescence in situ hybridization along with confocal laser scanning microscopy are mainly employed to reveal aerobic granular structures (Lemaire et al. 2008)**.** Dominancy of ammonia oxidizing bacteria was generally observed on the granule surfaces (Jang et al. 2003). De Kreuk et al. (2005) observed a mixture of heterotrophic phosphate accumulating organisms and autotrophic nitrifiers prevailing in the outer granule layers and phosphate accumulating organisms in the core of granules by using fluorescence in situ hybridization analysis of aerobic granule.

6.3.4 Granule Stability and Storage

Excessive growth of filamentous organisms is the major cause for granule instability during reactor operation. Long solid retention time, dissolved oxygen and nutrient deficiency along with low substrate concentration are the possible reasons behind filamentous outgrowth in aerobic granules (Liu and Liu 2006). Integrity coefficient is a parameter which is used to denote granule physical strength. Integrity coefficient defines the ratio of solids in the supernatant to the total weight of the aerobic granules, expressed in percent (%). Integrity coefficient ranged up to 98% and 97% for aerobic granules cultivated in glucose and acetate, respectively (Tay et al. 2002b). Ghangrekar et al. (2005) reported that lower integrity coefficient determines greater granule strength (Ghangrekar et al. 2005). During storage, extracellular protein content was found to be significantly less due to more protease enzyme (secreted by proteolytic bacteria) activity inside the granules (Adav et al. 2009).

6.4 Granule Characterization Techniques

There are several microscopic characterization techniques available for aerobic granules like normal light microscopy, scanning electron microscope, field emission scanning electron microscope and confocal laser scanning microscopy. Scanning electron microscope analysis explained the dominancy of filamentous bacteria on the outer surface of glucose-fed mature granules, whereas tightly linked microbial cells with compact structure were found in acetate-fed granules (Tay et al. 2001b).

6.5 Factors Affecting Aerobic Granulation

There are number of conditions that should be fulfilled for microbial granular structure formation. The factors affecting aerobic granulation are discussed in this section.

6.5.1 Organic Loading Rate

Aerobic granulation is achievable at different organic loading rates. Moy et al. (2002), Liu et al. (2003a) and Liu et al. (2003b) successfully achieved aerobic granulation at high loading of 15 kg chemical oxygen demand/m^3.day as well as low loading of 2.5 kg chemical oxygen demand/m^3.day organic loading rates. It indicates that aerobic granulation is almost independent of organic loading rate values. However, Tay et al. (2004) suggested that about 4 kg chemical oxygen demand/m^3.day is an optimal organic loading rate of aerobic granulation for achieving 99% of chemical oxygen demand removal efficiency.

6.5.2 Settling Time

Approximately 5 min settling time is required to achieve effective granulation. According to literature, short settling time around 5 min helps to provide high cell polysaccharides to the cell proteins and a rise in granule hydrophobicity (Qin et al. 2004).

6.5.3 Intermittent Feeding Strategy

According to the literature, aerobic granules had been mostly reported in sequencing batch reactors. Sequencing batch reactor operation mode consists of feeding, aeration, sludge settling and effluent decanting in each cycle. In a cycle, the settling time and volume exchange ratio provide a specific pressure to washout loose and non-granular biomass from the reactor eliciting mature granulation (Liu et al. 2007).

6.5.4 Hydrodynamic Force

High hydrodynamic shear force enhances stable and compact granule formation (Khan et al. 2009). Superficial air velocity above 1.2 cm/s is required for aerobic granulation inside a sequencing batch reactor (Liu and Tay 2004). Hence, high shear force promotes faster microbial aggregation leading to rapid biogranulation (Beun et al. 1999).

6.5.5 Augmentation

A study conducted by Jiang et al. (2003) showed that external augmentation of 100 mg Ca^{2+}/L promoted more regular and compact granule morphology as compared to control which was without Ca^{2+}. Liu et al. (2014) observed that augmentation of 500 mg/L of poly aluminum chloride in sequencing batch reactor decreased granulation time from 17 to 7 days. The average size of poly aluminum chloride-fed granules was found to be 3.2 mm having more extracellular polymeric substances content and better settling properties than control reactor.

6.5.6 Seed Sludge

The properties of the initial seed sludge affects aerobic granule formation. Two sequencing batch reactors were seeded with two different types of sludge. One was inoculated with 100% flocculent sludge and another one was added with 10% crushed granules (and 90% flocculent sludge) for studying the aerobic granulation enhancement. Aerobic granules developed faster in 90%-floc sequencing batch reactor and were fully granulated than 100% floc sequencing batch reactor.

However, the mean granule diameter was almost similar in both cases. The removal rate of nitrogen, phosphorous and organic matter were 75%, 93% and 85%, respectively in 100% floc sequencing batch reactor, while in 90% floc sequencing batch reactor the removal rates were found to be 84%, 99% and 80%, respectively (Coma et al. 2012).

6.5.7 Food to Microorganism Ratio

In most of the cases, high food-to-microorganism ratio accelerates faster and larger granulation, and a low food-to-microorganism ratio results into slower and smaller granule formation. Moreover, a high food-to-microorganism ratio enhances granule stability and size (Lobos et al. 2008). But Moy et al. (2002) reported that large and compact granules suffer from air diffusion limitations. Hence, food-to-microorganism ratios should keep changing at different phases of sequencing batch reactor operation to achieve proper granulation. Li et al. (2011) suggested high food-to-microorganism ratio in the initial phase and low food-to-microorganism ratio in the final phase as optimum criteria for aerobic granulation.

6.5.8 Height-to-Diameter Ratio

Height-to-diameter ratio of an aerobic granular reactor column is the major controlling parameter for granular shape and microbial structure formation. Zhu et al. (2008) observed that when the height-to-diameter ratio is very high in an aerobic granular reactor, internal flow patterns helped in strong granule formation. In contrast, Kong et al. (2009) reported that in aerobic granular reactor, height-to-diameter ratio and granule settling velocity had no significant effect on granulation.

6.5.9 Hydraulic Retention Time

Hydraulic retention time determines the average time duration for a soluble compound remains in a bioreactor. For sequencing batch reactor performance optimization, an effective hydraulic retention time should be carefully selected (Fang and Yu 2000, 2001). Beun et al. (1999) observed that shorter hydraulic retention times promote stable granulation. However, a very short hydraulic retention time can suppress the biomass growth due to excessive washout of the flocculent biomass from the reactors.

6.5.10 Volumetric Exchange Ratio

Volumetric exchange ratio defines the volume of the effluent withdrawn in every cycle of the sequencing batch reactor. An exchange ratio of 40%, 50% or 80% was found favourable for granulation. Wang et al. (2006b) observed that rapid granulation was possible in aerobic granular reactors having high volumetric exchange ratios and good settling properties. If settling velocity was less, high volumetric exchange ratio caused excessive biomass washout causing poor granulation.

6.5.11 Substrate Composition

Aerobic granulation occurred in wide varieties of simple carbon substrates like glucose, sucrose, acetate, molasses and ethanol (Adav et al. 2008). Granulation was also observed with recalcitrant compounds like phenol (Tomar and Chakraborty 2018a), thiocyanate (Tomar and Chakraborty 2018b), hydrocarbons (Zhang et al. 2011; Ghosh and Chakraborty 2019) and aniline (Winkler et al. 2018). Granules cultivated in inorganic carbon source with nitrifying bacteria exhibited excellent nitrification efficiencies (Tay et al. 2002; Tsuneda et al. 2003). Aerobic granulation was successfully employed in treating low-strength to high-strength real domestic and industrial effluents generated from municipal, petrochemical, brewery, textile, paper mill, dairy products, seafood, manure and pharmaceutical sectors (Winkler et al. 2018).

However, granule microscopic structure and bacterial community are largely dependent upon the types of substrates in which they are cultivated. Literature evidences proved that glucose-fed granules obtained loosely bound and filamentous structures, whereas acetate-fed granules achieved compact and non-filamentous structures with more stability (Liu and Tay 2004; Tay et al. 2002b).

6.5.12 Environmental Factors

pH

According to Hailei et al. (2006), approximately pH 7.5, which is slightly alkaline, is essential for matured granule formation. However, granulation might be hindered at pH values above 8.5. Acidic pH is favourable for fungi growth inside the granules, whereas an alkaline pH produces bacteria dominating granules ensuring compact microbial structure (Yang et al. 2008).

Effect of Temperature

According to Hailei et al. (2006) temperatures below 41 °C and above 26 °C are favourable for granule formation. Zhiwei et al. (2009) optimized 30 °C temperature to be essential for matured granulation.

Dissolved Oxygen Concentration

Granules are observed to be formed across lower dissolved oxygen concentration range of 0.7–1.0 mg/L (Dangcong et al. 1999) and at higher concentration of 2 mg/L (Tay et al. 2002a) in sequencing batch reactors. It proves that dissolved oxygen is not a significant parameter for aerobic granules. On other hand, Hailei et al. (2006) found that below 2.5 mg/L dissolved oxygen concentrations resulted into unstable and poor granulation. However, Sturm and Irvine (2008) demonstrated more importance of dissolved oxygen concentration and substrate removal kinetics than hydrodynamic shear force in aerobic granulation.

6.6 Applications in Hydrocarbon-Rich Wastewater Treatment

Aerobic granulation technology is regarded as an emerging technology in oily wastewater treatment. High chemical oxygen demand concentration and turbidity of palm oil mill effluent is the major problem to find an efficient treatment process. Abdullah et al. (2011) achieved stable granulation while treating palm oil mill effluent in sequencing batch reactor. Matured compact granules dominated by rods, cocci and spirilli organisms provided very good biomass accumulation and settling characteristics in the reactor. An integrated biological and adsorption method was also employed to treat palm oil mill effluent by Gobi et al. (2011). Aerobic granules were biologically developed inside a sequencing batch reactor and the waste aerobic granules were further utilized as an adsorbent to achieve significant pollutant removal efficiency. In another study, Najib et al. (2017) cultivated microbial granules containing photosynthetic pigments by using palm oil mill effluent as a nutrient source for granulation. Microbial identification revealed the presence of three dominant bacteria *Enterobacter cloacae, Bacillus cereus, Lysinibacillus sp*. and a fungi, *Engyodontium album*, with bacteriochlorophyll a and carotenoids as photosynthetic pigments.

Zhang et al. (2011) cultivated aerobic granule in glucose-fed wastewater and further treated real petrochemical wastewater in a sequencing batch airlift reactor. In the presence of 100% of petrochemical wastewater, the mean granule size and extracellular polymeric substances contents were abruptly reduced. Serious deterioration was also noticed in granule settleability and pollutant removal efficiencies.

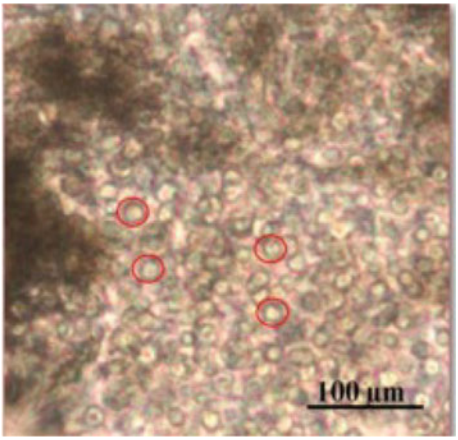


Fig. 6.4 Oil droplet inclusion was visible within the aerobic granules during hypersaline oily wastewater treatment in aerobic granular reactors. It proved the hydrocarbon adsorption capacity of aerobic granular surfaces while treating oily wastewater (Corsino et al. 2015)

Hypersaline oily wastewater was treated by Corsino et al. (2015) in two sequencing batch reactors. Despite high salinity, phosphorous and carbon removal efficiencies were satisfactory. Salinity and hydrocarbons inhibited the autotrophic biomass growth leading to poor nitrification inside the reactors. Small granule size and high extracellular polymeric substances contents increased granule surface area to enhance hydrocarbon adsorption process. Oil droplet inclusion inside the aerobic granules (Fig. 6.4) further proved oil adsorption by the granules.

Milia et al. (2016) used different shear forces, inoculum source and pH in two aerobic granular reactors to achieve stable granulation while treating coal gasification wastewater. Caluwé et al. (2017) demonstrated real petrochemical wastewater treatment in two different conditions, aerobic feast/famine and an anaerobic famine/aerobic feast regime by using aerobic granular sludge inside two sequencing batch reactors. Chen et al. (2019) conducted a study to treat synthetic oily wastewater using aerobic granulation technology. *Propioniciclava, Micropruina, Alphaproteobacteria, Flavobacterium,* and *Sulfuritalea* were isolated as the major petrochemical degrading microbes present inside the granules. However total nitrogen and ammonia-nitrogen removal efficiencies were not satisfactory due to inhibition of nitrobacteria and denitrificans.

In our recent study we have investigated the impacts of different seed sludge on granulation and oil tolerance threshold while treating diesel-contaminated wastewater (Ghosh and Chakraborty 2019). Chemical oxygen demand removal was independent of type of initial inoculums. Refinery sludge granules were found to be most potent in 67.39% oil degradation (influent oil: 320 mg/L) than the other inoculums. Finally, *Brevibacterium paucivorans* strain SG001 isolated from sewage inoculum, *Micrococcus aloeverae* strain SG002 from refinery sludge and *Staphylococcus hominis* strain SG003 isolated from brewery sludge were proved to be the major oil degrading bacterial strains. In another study, we checked the effects of short (12 h), medium (24 h) and long (48 h) hydraulic retention times on aerobic granular reactors treating diesel wastewater (Ghosh and Chakraborty 2020). Shortest retention time (12 h) promoted biggest and most stable granules having 68% hydrocarbon removal among the reactors (influent oil: 250 mg/L). However, longest HRT (12 h) had maximum contact time between granules and pollutants which helped in 90% oil removal. Gas chromatogrphy results predicted degradation of some short and long chain *n*-alkanes (C_6-C_{27}) which followed a pathway of conversion into fatty acids which further undergo ß-oxidation. Nitrogen balancing data suggested that about 2–20% complete nitrification occured inside the aerobic granules. About 24–77 mg/L of efflent oil concentration was recommended to avoid phytotoxic effects after wastewater disposal.

Detailed description of aerobic granular reactor operating conditions, granule characteristics and pollutant removal efficiencies in different types of hydrocarbon-rich wastewater treatment are elaborated in Table 6.2.

6.7 Conclusion

Aerobic granulation technology has been successfully employed in treating both real and synthetic hydrocarbon-rich wastewater. Aerobic granulation provided a very stable and cost-effective treatment process which was able to withstand high organic loads, fluctuation in toxic chemical concentration and finally produced effluents with lower pollutant concentration than the conventional wastewater treatment processes. Microbial diversity in aerobic granules helped to simultaneously degrade carbon, nitrogen and different types of recalcitrant aromatic hydrocarbons.

According to literature, aerobic granulation was able to treat oily wastewater containing hydrocarbons between 5.6 to 320 mg/L. However, everyday oil refineries produce real petrochemical wastewater in million litres volume containing higher oil concentration than the previous reports. Biological treatment and effluent management of large volume of complex oily wastewater is still a big challenge. However some research areas are still unexplored; like literature reporting complete nitrification in petrochemical wastewater treatment are limited, treatability of automobile effluents and heavy motor oil by using aerobic granular sludge is not studied so far, whether bioaugmentation of oil degrading pure strains can improve granule oil removal efficiencies is still unknown, effects on hydrocarbon removal by changing superficial air velocity and feed up-flow velocity of an aerobic granular reactor are not well accounted, potentiality of renewable biomaterial production using oil treated waste granules is also not well explored so far. Hence, these knowledge gaps would reveal new domains of research in aerobic granulation treating hydrocarbon-rich wastewater treatment.

Acknowledgement Authors thankfully acknowledge Centre for the Environment, Indian Institute of Technology, Guwahati, for providing the analytical laboratory and instrumentation facility to conduct the literature survey and research. We are grateful to Dr. Inamuddin for his kind cooperation throughout the book publishing process.

Table 6.2 Aerobic granular reactor operating conditions, granule characteristics and pollutant removal efficiencies in different types of hydrocarbon-rich wastewater treatment (*abbreviations are explained below)

Type of wastewater	Operating conditions	Granule characteristics	Pollutant removal	Reference
Palm oil mill wastewater	i) AGR volume: 1 L; OLR: 2.5 kg COD/m^3.d; VER: 50%; superficial air velocity: 2.5 cm s^{-1}; cycle time: 3 h; operation time: 60 days	Granule size: 2–4 mm, biomass concentration: 7.6 g/L; SVI: 31.3 mL/g SS	COD: 91.1% (I: 700 mg/L); Ammonia: 97.6% (I: 100 mg/L); Colour: 66.0% (I: 600 ADMI)	Abdullah et al. (2011)
	ii) AGR volume: 8 L; OLR: 3-6 kg COD/m^3.d; VER: 25%; superficial air velocity: 5 L/min; cycle time: 6 h; operation time: 170 days; Adsorbent: waste granules treated in 0.1 M NaOH; column study.	Granule size: 0.9 mm, granulation time: 110 days; MLSS: 3.6–2.5 g/l; SVI: 30 mL/g	By granules: COD: 88% (OLR: 3 kg COD/m^3.day); 90% (6 kg COD/m^3.day); by adsorbent: COD: 21%; turbidity: 99%	Gobi et al. (2011)
	iii) AGR volume: 1.2 L; OLR: 2.75 kg COD/m^3.d; VER: 50%; 2.07 cm/s; cycle time: 4 h; operation time: 120 days;	Granule size: 0.3–2.36 mm, SVI: 10.30–14.80 mL/g SS; MLSS: 6.90–8.25 g /L; GSV: 18.0–103.0 m/h; integrity coefficient: 2%	Aerobic granules containing photosynthetic bacteria naturally consumed POME as nutrient source	Najib et al. (2017)
Hypersaline oily wastewater	AGR volume: 3.5 L; VER: 50%; cycle time: R1: 3 h; R2: 12 h; superficial air velocity: 3.5 cm/s; operation time: 100 days	Granule size: 1.9 mm, SVI$_5$: 28–30 mL/g GSV: 70–80 m/h; TSS: 6.5–11; EPS: 550–340 mg/g. VSS; PN:PS: 3–6; granule hydrophobicity: 89%–93%	COD: 98%, 88% (I: 900 ± 15 and 1350 ± 50 mg/L); TN: 50%, 26% (I: 90 ± 5 and 115 ± 10 mg/L); Phosphorus: 50%, 80% (I: 20 ± 2 and 25 ± 3 mg/L); Hydrocarbon: above 90% (I: 6.8 ± 1.5 mg/L)	Corsino et al. (2015)
Coal gasification wastewater	AGR volume: 3 L; VER: 50%; cycle time: 4 h; HRT: 8 h; operation time: 480 days	Granule size: 1300–250 μm, SVI$_8$: 30 ± 8 mL/g. TSS; VSS: 4.9 ± 0.6 g/L; TSS: 260 ± 20 mg/L; GSV: 1.1–6 m/h	COD: 92 ± 6 to 94 ± 2% (I: 240–630 mg/L); NH_4^+-N: 78% (I: 340–610 mg/L)	Milia et al. (2016)

(continued)

Table 6.2 (continued)

Type of wastewater	Operating conditions	Granule characteristics	Pollutant removal	Reference
Real petroleum wastewater	i) AGR volume: 3 L; OLR: 2 kg COD/m^3.d; NLR: 0.16 kg NH_4^+–N/m^3.day; VER: 50%; cycle time: 6 h; superficial air velocity: 2.2 cm/s operation time: 223 days	Granule size: 220 μm, SVI: 26.1–41.5 mL/g; MLVSS/MLSS: 0.9; PS:PN: 1–2	COD: 89% (I: 500 mg/L), NH_4^+–N: (I: 42.9 mg/L) 94% and TN: 67% (I: 70 mg/L)	Zhang et al. (2011)
	ii) SBR_{ae}: aerobic regime; SBR_{an}: anaerobic feast and aerobic famine regime; feeding volume: 1–4 L; VER: 16.6%–28.6%; feeding rate: 1 L/min; cycle time: variable; OLR: 1.0–1.35 kg COD/m^3.d; operation time: 60 days	Granule size: 264.7 μm, 307.4 μm, SVI: 71 mL/g MLSS, 56 mL/g MLSS; MLVSS: 1.8, 3.4 mg/L; GSV: 10 m/h.	COD: 96.1 ± 1.8%, 96.6 ± 0.2% (I: 94.0 ± 26.2 mg/L; 80.4 ± 27.8 mg/L; sCOD: 97.0 ± 1.3%, 97.7 ± 1.3% (I: 66.4 ± 29.8 mg/L, 51.6 ± 29.0 mg/L).	Caluwé et al. (2017)
Synthetic petroleum wastewater	AGR volume: 71 L; VER: 50%; H/D: 5.71; cycle time: 4.8–6 h; operation time: 130 days	Granule size: 0.46–0.9 mm, EPS: 128 mg/g.VSS; MLSS: 8.5–4.5 g/L; SVI_{30}: 30 mL/g; integrality coefficient: 99.8% ± 0.1%	COD: 95% (I: 600 to 900 mg/L); NH_4^+-N: 30–39% (I: 25–40 mg/L); TN: below 35% (I: 30–47 mg/L); oil: 90% (I: 50–200 mg/L)	Chen et al. (2019)
Diesel wastewater	AGR volume: 3 L; VER: 50%; H/D:30.56; cycle time: 8 h; OLR: 1.8 kg COD/m^3.day; NLR: 0.0075–0.075 kg NH_4^+-N /m^3.day; HLR: 0.015–0.48 kg/m^3.day; operation time: 246 days	Granule size: 3.11–3.49 mm, SVI: 39.80 mL/g GSV: 23.21 m/h; VSS: 5.85 g/L; EPS: 172–218 mg/g VSS; PN:PS: 3.56–3.96; granule hydrophobicity: 50–92%	COD: 99.9% (I: 1200 mg/L); NH_4^+-N: 91–92% (I: 50 mg/L); Oil: 61–67% (I: 320 mg/L)	Ghosh and Chakraborty (2019)

**I* influent concentration (mg/L), *AGR* aerobic granular reactor, SBR_{ae} sequencing batch reactor aerobic, SBR_{an} sequencing batch reactor anaerobic, *OLR* organic loading rate (kg COD/m^3/day), *NLR* nitrogen loading rate (kg NH_4^+-N/m^3/day), *HLR* hydrocarbon loading rate (kg/m^3/day), *SVI* sludge volume index (mL/g), *GSV* granule settling velocity (m/h), *VER* volumetric exchange ratio (%), *HRT* Hydraulic retention time (day), *POME* Palm oil mill effluent, *EPS* extracellular polymeric substances, *PN:PS* protein:polysaccharide, *H/D* height/diameter, *MLSS* Mixed liquor suspended solids (g/L), *MLVSS* Mixed liquor volatile suspended solids (g/L), *SS* suspended solids (g/L), *VSS* volatile suspended solids (g/L), *COD*chemical oxygen demand (mg/L), *sCOD* soluble chemical oxygen demand (mg/L), NH_4^+–*N* ammonia-nitrogen (mg/L) *ADMI* American Dye Manufacturer's Institute unit

References

Abdullah N, Ujang Z, Yahya A (2011) Aerobic granular sludge formation for high strength agro-based wastewater treatment. Bioresour Technol 102(12):6778–6781. https://doi.org/10.1016/j.biortech.2011.04.009

Adav SS, Lee D-J (2008) Extraction of extracellular polymeric substances from aerobic granule with compact interior structure. J Hazard Mater 154:1120–1126. https://doi.org/10.1016/j.jhazmat.2007.11.058

Adav SS, Chen MY, Lee DJ, Ren NQ (2007) Degradation of phenol by aerobic granules and isolated yeast Candida tropicalis. Biotechnol Bioeng 96(5):844–852. https://doi.org/10.1002/bit.21148

Adav SS, Lee D-J, Show K-Y, Tay J-H (2008) Aerobic granular sludge: recent advances. Biotechnol Adv 26(5):411–423. https://doi.org/10.1016/j.biotechadv.2008.05.002

Adav SS, Lee D-J, Lai J-Y (2009) Proteolytic activity in stored aerobic granular sludge and structural integrity. Bioresour Technol 100(1):68–73. https://doi.org/10.1016/j.biortech.2008.05.045

Alva-Argáez A, Kokossis AC, Smith R (2007) The design of water-using systems in petroleum refining using a water-pinch decomposition. Chem Eng J 128(1):33–46. https://doi.org/10.1016/j.cej.2006.10.001

Barr JJ, Cook AE, Bond PL (2010) Granule formation mechanisms within an aerobic wastewater system for phosphorus removal. Appl Environ Microbiol 76(22):7588–7597. https://doi.org/10.1128/AEM.00864-10

Beun J, Hendriks A, Van Loosdrecht M, Morgenroth E, Wilderer P, Heijnen J (1999) Aerobic granulation in a sequencing batch reactor. Water Res 33(10):2283–2290. https://doi.org/10.1016/S0043-1354(98)00463-1

Beun J, Van Loosdrecht M, Heijnen J (2002) Aerobic granulation in a sequencing batch airlift reactor. Water Res 36(3):702–712. https://doi.org/10.1016/S0043-1354(01)00250-0

Biswal BK, Tiwari SN, Mukherji S (2009) Biodegradation of oil in oily sludges from steel mills. Bioresour Technol 100(4):1700–1703. https://doi.org/10.1016/j.biortech.2008.09.037

Caluwé M, Dobbeleers T, D'aes J, Miele S, Akkermans V, Daens D, Geuens L, Kiekens F, Blust R, Dries J (2017) Formation of aerobic granular sludge during the treatment of petrochemical wastewater. Bioresour Technol 238:559–567. https://doi.org/10.1016/j.biortech.2017.04.068

Chen C, Ming J, Yoza BA, Liang J, Li QX, Guo H, Liu Z, Deng J, Wang Q (2019) Characterization of aerobic granular sludge used for the treatment of petroleum wastewater. Bioresour Technol 271:353–359. https://doi.org/10.1016/j.biortech.2018.09.132

Coma M, Verawaty M, Pijuan M, Yuan Z, Bond PL (2012) Enhancing aerobic granulation for biological nutrient removal from domestic wastewater. Bioresour Technol 103(1):101–108. https://doi.org/10.1016/j.biortech.2011.10.014

Corsino SF, Campo R, Di Bella G, Torregrossa M, Viviani G (2015) Cultivation of granular sludge with hypersaline oily wastewater. Int Biodeterior Biodegradation 105:192–202. https://doi.org/10.1016/j.ibiod.2015.09.009

Dangcong P, Bernet N, Delgenes J-P, Moletta R (1999) Aerobic granular sludge—a case report. Water Res 33(3):890–893. https://doi.org/10.1016/S0043-1354(98)00443-6

De Kreuk M, Heijnen J, Van Loosdrecht M (2005) Simultaneous COD, nitrogen, and phosphate removal by aerobic granular sludge. Biotechnol Bioeng 90(6):761–769. https://doi.org/10.1002/bit.20470

Etterer T, Wilderer P (2001) Generation and properties of aerobic granular sludge. Water Sci Technol 43(3):19–26. https://doi.org/10.2166/wst.2001.0114

Fang HH, Yu H (2000) Effect of HRT on mesophilic acidogenesis of dairy wastewater. J Environ Eng 126(12):1145–1148. https://doi.org/10.1061/(ASCE)0733-9372(2000)126:12(1145)

Fang HH, Yu H (2001) Acidification of lactose in wastewater. J Environ Eng 127(9):825–831. https://doi.org/10.1061/(ASCE)0733-9372(2001)127:9(825)

Franca RD, Vieira A, Mata AM, Carvalho GS, Pinheiro HM, Lourenço ND (2015) Effect of an azo dye on the performance of an aerobic granular sludge sequencing batch reactor treating a simulated textile wastewater. Water Res 85:327–336. https://doi.org/10.1016/j.watres.2015.08.043

Gao D, Liu L, Liang H, Wu W-M (2011) Aerobic granular sludge: characterization, mechanism of granulation and application to wastewater treatment. Crit Rev Biotechnol 31(2):137–152. https://doi.org/10.3109/07388551.2010.497961

Ghangrekar M, Asolekar S, Joshi S (2005) Characteristics of sludge developed under different loading conditions during UASB reactor start-up and granulation. Water Res 39(6):1123–1133. https://doi.org/10.1016/j.watres.2004.12.018

Ghosh S, Chakraborty S (2019) Influence of inoculum variation on formation and stability of aerobic granules in oily wastewater treatment. J Environ Manag 248:109239. https://doi.org/10.1016/j.jenvman.2019.07.010

Ghosh S, Chakraborty S (2020) Impacts of hydraulic retention time on granule behaviour and reactor activity during hydrocarbon degradation in aerobic granular reactors (AGRs) with phytotoxicity analysis. Int Biodeterior Biodegradation 151:104963

Gobi K, Mashitah M, Vadivelu V (2011) Development and utilization of aerobic granules for the palm oil mill (POM) wastewater treatment. Chem Eng J 174(1):213–220. https://doi.org/10.1016/j.cej.2011.09.002

Hailei W, Guangli Y, Guosheng L, Feng P (2006) A new way to cultivate aerobic granules in the process of papermaking wastewater treatment. Biochem Eng J 28(1):99–103. https://doi.org/10.1016/j.bej.2005.10.002

Jang A, Yoon Y-H, Kim IS, Kim K-S, Bishop PL (2003) Characterization and evaluation of aerobic granules in sequencing batch reactor. J Biotechnol 105(1–2):71–82. https://doi.org/10.1016/S0168-1656(03)00142-1

Jiang H-L, Tay J-H, Liu Y, Tay ST-L (2003) Ca^{2+} augmentation for enhancement of aerobically grown microbial granules in sludge blanket reactors. Biotechnol Lett 25(2):95–99. https://doi.org/10.1023/A:1021967914544

Kent TR, Bott CB, Wang ZW (2018) State of the art of aerobic granulation in continuous flow bioreactors. Biotechnol Adv 36(4):1139–1166. https://doi.org/10.1016/j.biotechadv.2018.03.015

Khan F, Zain Khan M, Qamar Usmani S, Sabir S (2009) Biodegradation of phenol by aerobic granulation technology. Water Sci Technol 59(2):273–278. https://doi.org/10.2166/wst.2009.863

Kong Y, Liu Y-Q, Tay J-H, Wong F-S, Zhu J (2009) Aerobic granulation in sequencing batch reactors with different reactor height/diameter ratios. Enzym Microb Technol 45(5):379–383. https://doi.org/10.1016/j.enzmictec.2009.06.014

Lemaire R, Webb RI, Yuan Z (2008) Micro-scale observations of the structure of aerobic microbial granules used for the treatment of nutrient-rich industrial wastewater. ISME J 2(5):528–541

Li Y, Liu Y, Shen L, Chen F (2008) DO diffusion profile in aerobic granule and its microbiological implications. Enzym Microb Technol 43(4–5):349–354. https://doi.org/10.1016/j.enzmictec.2008.04.005

Li A-j, Li X-y, H-q Y (2011) Effect of the food-to-microorganism (F/M) ratio on the formation and size of aerobic sludge granules. Process Biochem 46(12):2269–2276. https://doi.org/10.1016/j.procbio.2011.09.007

Lin Y, de Kreuk M, Van Loosdrecht M, Adin A (2010) Characterization of alginate-like exopolysaccharides isolated from aerobic granular sludge in pilot-plant. Water Res 44(11):3355–3364. https://doi.org/10.1016/j.watres.2010.03.019

Liu Y, Liu Q-S (2006) Causes and control of filamentous growth in aerobic granular sludge sequencing batch reactors. Biotechnol Adv 24(1):115–127. https://doi.org/10.1016/j.biotechadv.2005.08.001

Liu Y, Tay J-H (2002) The essential role of hydrodynamic shear force in the formation of biofilm and granular sludge. Water Res 36(7):1653–1665. https://doi.org/10.1016/S0043-1354(01)00379-7

Liu Y, Tay J-H (2004) State of the art of biogranulation technology for wastewater treatment. Biotechnol Adv 22(7):533–563. https://doi.org/10.1016/j.biotechadv.2004.05.001

Liu Q, Tay J, Liu Y (2003a) Substrate concentration-independent aerobic granulation in sequential aerobic sludge blanket reactor. Environ Technol 24(10):1235–1242. https://doi.org/10.1080/09593330309385665

Liu Y, Yang S-F, Liu Q-S, Tay J-H (2003b) The role of cell hydrophobicity in the formation of aerobic granules. Curr Microbiol 46(4):0270–0274. https://doi.org/10.1007/s00284-002-3878-3

Liu Y-Q, Wu W-W, Tay J-H, Wang J-L (2007) Starvation is not a prerequisite for the formation of aerobic granules. Appl Microbiol Biotechnol 76(1):211–216. https://doi.org/10.1007/s00253-007-0979-8

Liu Z, Liu Y, Zhang A, Zhang C, Wang X (2014) Study on the process of aerobic granule sludge rapid formation by using the poly aluminum chloride (PAC). Chem Eng J 250:319–325. https://doi.org/10.1016/j.cej.2014.04.025

Lobos J, Wisniewski C, Heran M, Grasmick A (2008) Sequencing versus continuous membrane bioreactors: effect of substrate to biomass ratio (F/M) on process performance. J Membr Sci 317 (1–2):71–77. https://doi.org/10.1016/j.memsci.2007.08.041

Manzetti S (2012) Ecotoxicity of polycyclic aromatic hydrocarbons, aromatic amines, and nitroarenes through molecular properties. Environ Chem Lett 10:349–361. https://doi.org/10.1007/s10311-012-0368-0

McSwain B, Irvine R, Hausner M, Wilderer P (2005) Composition and distribution of extracellular polymeric substances in aerobic flocs and granular sludge. Appl Environ Microbiol 71 (2):1051–1057. https://doi.org/10.1128/AEM.71.2.1051-1057.2005

Milia S, Malloci E, Carucci A (2016) Aerobic granulation with petrochemical wastewater in a sequencing batch reactor under different operating conditions. Desalin Water Treat 57 (57):27978–27987. https://doi.org/10.1080/19443994.2016.1191778

Mondal PK, Ahmad R, Usmani SQ (2010) Anaerobic biodegradation of triphenylmethane dyes in a hybrid UASFB reactor for wastewater remediation. Biodegradation 21(6):1041–1047. https://doi.org/10.1007/s10532-010-9364-x

Moy BP, Tay JH, Toh SK, Liu Y, Tay SL (2002) High organic loading influences the physical characteristics of aerobic sludge granules. Lett Appl Microbiol 34(6):407–412. https://doi.org/10.1046/j.1472-765X.2002.01108.x

Najib M, Ujang Z, Salim M, Ibrahim Z (2017) Developed microbial granules containing photosynthetic pigments for carbon dioxide reduction in palm oil mill effluent. Int Biodeterior Biodegradation 116:163–170. https://doi.org/10.1016/j.ibiod.2016.10.031

Novaković M, Ramadan MMA, Knudsen TŠ, Antić M, Beškoski V, Gojgić-Cvijović G, Vrvić MM, Jovančićević B (2012) Degradation of methyl-phenanthrene isomers during bioremediation of soil contaminated by residual fuel oil. Environ Chem Lett 10:287–294. https://doi.org/10.1007/s10311-012-0354-6

Qin L, Tay J-H, Liu Y (2004) Selection pressure is a driving force of aerobic granulation in sequencing batch reactors. Process Biochem 39(5):579–584. https://doi.org/10.1016/S0032-9592(03)00125-0

Sengar A, Basheer F, Aziz A, Farooqi IH (2018) Aerobic granulation technology: laboratory studies to full scale practices. J Clean Prod 197:616–632. https://doi.org/10.1016/j.jclepro.2018.06.167

Seviour T, Lambert LK, Pijuan M, Yuan Z (2010) Structural determination of a key exopolysaccharide in mixed culture aerobic sludge granules using NMR spectroscopy. Environ Sci Technol 44(23):8964–8970. https://doi.org/10.1021/es102658s

Show K-Y, Lee D-J, Tay J-H (2012) Aerobic granulation: advances and challenges. Appl Biochem Biotechnol 167(6):1622–1640. https://doi.org/10.1007/s12010-012-9609-8

Sturm B, Irvine R (2008) Dissolved oxygen as a key parameter to aerobic granule formation. Water Sci Technol 58(4):781–787. https://doi.org/10.2166/wst.2008.393

Tay J-H, Liu Q-S, Liu Y (2001a) The effects of shear force on the formation, structure and metabolism of aerobic granules. Appl Microbiol Biotechnol 57(1–2):227–233. https://doi.org/10.1007/s002530100766

Tay JH, Liu QS, Liu Y (2001b) Microscopic observation of aerobic granulation in sequential aerobic sludge blanket reactor. J Appl Microbiol 91(1):168–175. https://doi.org/10.1046/j.1365-2672.2001.01374.x

Tay J-H, S-F Y, Y L (2002) Hydraulic selection pressure-induced nitrifying granulation in sequencing batch reactors. Appl Microbiol Biotechnol 59(2–3):332–337. https://doi.org/10.1007/s00253-002-0996-6

Tay J-H, Liu Q-S, Liu Y (2002a) Aerobic granulation in sequential sludge blanket reactor. Water Sci Technol 46(4–5):13–18. https://doi.org/10.2166/wst.2002.0540

Tay J, Liu Q, Liu Y (2002b) Characteristics of aerobic granules grown on glucose and acetate in sequential aerobic sludge blanket reactors. Environ Technol 23(8):931–936. https://doi.org/10.1080/09593332308618363

Tay J-H, Jiang H-L, Tay ST-L (2004) High-rate biodegradation of phenol by aerobically grown microbial granules. J Environ Eng 130(12):1415–1423. https://doi.org/10.1061/(ASCE)0733-9372(2004)130:12(1415

Toh S, Tay J, Moy B, Ivanov V, Tay S (2003) Size-effect on the physical characteristics of the aerobic granule in a SBR. Appl Microbiol Biotechnol 60(6):687–695. https://doi.org/10.1007/s00253-002-1145-y

Tomar SK, Chakraborty S (2018a) Characteristics of aerobic granules treating phenol and ammonium at different cycle time and up flow liquid velocity. Int Biodeterior Biodegradation 127:113–123. https://doi.org/10.1016/j.ibiod.2017.11.024

Tomar SK, Chakraborty S (2018b) Effect of air flow rate on development of aerobic granules, biomass activity and nitrification efficiency for treating phenol, thiocyanate and ammonium. J Environ Manag 219:178–188. https://doi.org/10.1016/j.jenvman.2018.04.111

Tsuneda S, Nagano T, Hoshino T, Ejiri Y, Noda N, Hirata A (2003) Characterization of nitrifying granules produced in an aerobic upflow fluidized bed reactor. Water Res 37(20):4965–4973. https://doi.org/10.1016/j.watres.2003.08.017

Val del Río A, Figueroa M, Mosquera-Corral A, Campos J, Méndez R (2013) Stability of aerobic granular biomass treating the effluent from a seafood industry. Int J Environ Res 7(2):265–276. https://doi.org/10.22059/IJER.2013.606

Vashi H, Iorhemen O, Tay J (2019) Extensive studies on the treatment of pulp mill wastewater using aerobic granular sludge (AGS) technology. Chem Eng J 359:1175–1194. https://doi.org/10.1016/j.cej.2018.11.060

Verawaty M, Pijuan M, Yuan Z, Bond P (2012) Determining the mechanisms for aerobic granulation from mixed seed of floccular and crushed granules in activated sludge wastewater treatment. Water Res 46(3):761–771. https://doi.org/10.1016/j.watres.2011.11.054

Wang Z-W, Liu Y, Tay J-H (2005) Distribution of EPS and cell surface hydrophobicity in aerobic granules. Appl Microbiol Biotechnol 69(4):469. https://doi.org/10.1007/s00253-005-1991-5

Wang Z-W, Li Y, Zhou J-Q, Liu Y (2006a) The influence of short-term starvation on aerobic granules. Process Biochem 41(12):2373–2378. https://doi.org/10.1016/j.procbio.2006.06.009

Wang Z-W, Liu Y, Tay J-H (2006b) The role of SBR mixed liquor volume exchange ratio in aerobic granulation. Chemosphere 62(5):767–771. https://doi.org/10.1016/j.chemosphere.2005.04.081

Wang L, Liu X, X-f C, Lee D-J, Tay J-H, Zhang Y, C-l W (2015) Biosorption of Sr (II) from aqueous solutions using aerobic granules: equilibrium and mechanisms. J Radioanal Nucl Chem 306(1):193–202. https://doi.org/10.1007/s10967-015-4084-7

Winkler M-KH, Meunier C, Henriet O, Mahillon J, Suárez-Ojeda ME, Del Moro G, De Sanctis M, Di Iaconi C, Weissbrodt DG (2018) An integrative review of granular sludge for the biological removal of nutrients and recalcitrant organic matter from wastewater. Chem Eng J 336:489–502. https://doi.org/10.1016/j.cej.2017.12.026

Yang S, Li X, Yu H (2008) Formation and characterisation of fungal and bacterial granules under different feeding alkalinity and pH conditions. Process Biochem 43(1):8–14. https://doi.org/10.1016/j.procbio.2007.10.008

Zhang H, He Y, Jiang T, Yang F (2011) Research on characteristics of aerobic granules treating petrochemical wastewater by acclimation and co-metabolism methods. Desalination 279(1–3):69–74. https://doi.org/10.1016/j.desal.2011.05.060

Zhang Q, Hu J, Lee D-J (2016) Aerobic granular processes: current research trends. Bioresour Technol 210:74–80. https://doi.org/10.1016/j.biortech.2016.01.098

Zheng Y-M, Yu H-Q, Liu S-J, Liu X-Z (2006) Formation and instability of aerobic granules under high organic loading conditions. Chemosphere 63(10):1791–1800. https://doi.org/10.1016/j.chemosphere.2005.08.055

Zhiwei S, Nanqi R, Zhang K, Longyan T (2009) Influence of temperature on the characteristics of aerobic granulation in sequencing batch airlift reactors. J Environ Sci 21(3):273–278. https://doi.org/10.1016/S1001-0742(08)62263-9

Zhu L, Xu X, Luo W, Tian Z, Lin H, Zhang N (2008) A comparative study on the formation and characterization of aerobic 4-chloroaniline-degrading granules in SBR and SABR. Appl Microbiol Biotechnol 79(5):867–874. https://doi.org/10.1007/s00253-008-1476-4

Chapter 7
Biodegradation of Hydrocarbons in Marine Environment

R. Denaro, F. Di Pippo, F. Crisafi, and S. Rossetti

Contents

Abstract Oil pollution in marine environment is a serious issue that impacts human health, animal wellness, environmental health, and finally the economy of impaired areas, mainly coastal regions. Sustainable treatments (bioremediation) can attenuate the toxicity of the affected habitats, because they are inspired by natural processes carried out by bacteria and algae in synergistic actions targeted at degradation of hydrocarbons. We reviewed the specific key role of the synergy between bacteria

---

R. Denaro (✉) · F. Di Pippo · S. Rossetti
Water Research Institute, National Research Council of Italy (IRSA - CNR), Rome, Italy
e-mail: denaro@irsa.cnr.it; dipippo@irsa.cnr.it; rossetti@irsa.cnr.it

F. Crisafi
Institute for Biological Resources and Marine Biotechnology, National Research Council of Italy (IRBIM - CNR), Messina, Italy
e-mail: francesca.crisafi@irbim.cnr.it

Inamuddin et al. (eds.), *Water Pollution and Remediation: Organic Pollutants*, Environmental Chemistry for a Sustainable World 54,
https://doi.org/10.1007/978-3-030-52395-4_7

and algae during the degradation of hydrocarbons in the sea, pointing out the importance of two crucial evidences: (1) the exchange of mutual benefits that help to cope with the variability of the aquatic environment and (2) the syntrophic behavior in the consumption of hydrocarbons. Moreover, according to the literature, it appeared that phycosphere is a complex system that should be studied by a holistic approach to understand the natural occurring interaction between algae and bacteria that can contribute to the success of in situ bioremediation processes.

Keywords Algae bacteria interaction · Bioremediation in marine environment · Hydrocarbon-degrading bacteria

7.1 Introduction

7.1.1 Oil Pollution in Marine Environment

Petroleum is an important industrial raw material and power source widely used in multiple fields. Given the common understanding on the necessity to use renewable energy sources, the projection on the use of fossil fuel in the countries belonging to the Organisation for Economic Co-operation and Development shows a decline by 2050 (Itopf.com 2016), notwithstanding the fact that the global demand for energy is expected to rise by 25% in the period 2014–2040 and in 2040, one-third of the world's energy would be still provided by oil (Selin 2013). This is not consequence-free as historically demonstrated by the number and severity of the incidents that have occurred during oil extraction, refinery, naval operation and transport, especially in marine environment (O' Brien 2004; Gomez and Sartaj 2014; Khudur et al. 2015). According to Fernandez-Macho (2016), European Atlantic countries are at greater risk of oil pollution, followed by Mediterranean coastlines, where Italy and Greece seem to be much more exposed to the hazard. Moreover, Mediterranean coastline is littered with several oil-polluted sites, which have experienced intensive industrialization (Daffonchio et al. 2013). Some of these (i.e., Gela and Priolo, Italy) were declared "at high risk of environmental crisis" in 1990, but little has been done for the cleaning-up of the polluted sites and to reduce environmental damages attributable to pollution exposure (Guerriero et al. 2011). Such conditions dramatically reduce the extent of marine areas contributing to ecosystems services (Sousa et al. 2016). Oil pollution in marine environment threatens public and animal well-being, impairs environmental health, not to mention socioeconomic relapses, overall for marine and maritime activities and industries and related jobs. The source of oil pollution in marine environment can have natural origin as seepage, but a large proportion derives from anthropic activities such as offshore production, shipping, refinery operations, and industrial and urban runoff (Group of Experts on the Scientific Aspects of Marine Environmental Protection 2007; Farrington and McDowell 2004; Lindgren et al. 2016). Generally, oil spillages can be distinguished into large (macro) and small (micro) spills (Sardi et al. 2017). Macro oil-spill, caused by marine oil well blowouts or shipping disaster (Jewett et al. 1999; Valentine et al. 2014), dramatically impact on the marine environment. However, also frequent micro spills due to urban/industrial runoff and shipping may generate chronic and long-term effects (Camphuysen 2007; Silva et al. 2009; Lindgren et al. 2012; Troisi et al. 2016; Frometa et al. 2017; Klotz et al. 2018; Xie et al. 2018; Szczybelski et al. 2018; Liu et al. 2019). Lindgren et al. (2012) investigated the effect of polycyclic aromatic hydrocarbons on benthos and found evident impacts on meiofauna and microbial communities even at low concentrations of polycyclic aromatic hydrocarbons. The contamination by oil fractions may be observed for many years after an oil-spill (Tansel 2014). A fairly quick natural recovery (within 2–10 years) may occur in areas such as mangrove swamps or salt marshes (Kingston 2002) but the contamination can persist for more than 25 years where the physical removal of oil is not performed (Kingston 2002).

7.1.2 Oil Composition

Crude oil is a mixture that includes hydrocarbons as the most abundant fraction, varying in a range of 50–98% of the total composition (Clark and Brown 1977), and the majority of oils include higher relative percentage of aliphatic hydrocarbons. Moreover, consistent elements are also oxygen, nitrogen, and sulfur, both as elemental or heterocyclic constituents (e.g., dibenzothiophene) and functional groups. Hydrocarbons generally consist of alkanes (also called paraffins, on average 30%), naphtenes (or cycloalkanes) (on average 49%), aromatic (on average 15%), asphaltenes (porphyrins, esters, phenols, fatty acids, ketones), and resins (amides, pyridines, carbazoles, quinolines, sulfoxides) ranging from 0 to 40%. Alkanes and naphtenes (also called saturates) linear or branched, lack double bonds. Cycloalkanes (mainly cyclopentanes and cyclohexanes) have one or more rings of carbon atoms and frequently show alkyl substituent(s). Aromatics exhibit one or more aromatic rings (Matar and Hatch 1994). Asphaltene and resins contain non-hydrocarbon polar compounds. Oil also contains trace constituents, comprising less than 1% (v/v), including phosphorus and heavy metals such as vanadium and nickel. Petroleomics analyses have allowed the identification of more than 17,000 distinct chemical components, revealing the complexity of such organic mixtures. Furthermore, chemical and physical properties can vary between different type of crude oils and accordingly their susceptibility to biodegradation and fate in aquatic environment.

7.1.3 Fate of Oil in Marine Environment

Oil in seawater medium is affected by several processes that change its distribution and composition. Oil physical and chemical changes may occur in different chronological events. An early stage, which occurs over days, is characterized by spreading, evaporation, dispersion, emulsification, and dissolution. Diversely, at later stage, oxidation, sedimentation, and biodegradation occur over years, determining the ultimate fate of the oil spilled (Harayama et al. 1999; Dutta and Harayama 2001). Each fraction of crude oil has different behavior in marine environment: hydrocarbons having lower molecular weight form slicks on the surface and are subjected to spreading, mixing, and volatilization/evaporation whereas heavier resins form persistent tar balls with low surface area. The effect of mixing, but even more tension-active substances produced by microorganisms (biosurfactants), creates emulsions that are more easily degradable (Harayama et al. 1999; Yamada et al. 2003; Xue et al. 2015; Atlas and Hazen 2011). Sunlight radiation causes photo-oxidation of floating petroleum hydrocarbon molecules and in presence of algae the response of microbial community to oil is differently modulated (Medina-Sánchez et al. 2002; Aksmann and Tukaj 2008; Huang et al. 2014; Bacosa et al. 2015).

Processes occurring during the early phase result in the partitioning of oil components among the sea surface, air, water column, and sediments. After extensive alterations, however, many petroleum hydrocarbons persist unchanged and consequently their toxicity is diluted but not diminished. Petroleum residues, asphaltenes, and nonvolatile hydrocarbons persist indefinitely. Natural occurring biological and chemical degradation processes become increasingly significant over months. Because marine microorganisms ingest, metabolize, and utilize the petroleum as a carbon source, petroleum hydrocarbons and residues in the environment do not exist in greater abundance. Without microorganisms, the abundance of hydrocarbons would increase at possibly undesirable rates. Isolation and identification of microorganisms responsible for hydrocarbon transformations have long been acknowledged and include bacteria, yeasts, fungi, and algae (Atlas 1981; Leahy and Colwell 1990; Atlas and Cerniglia 1995). The biodegradation efficiency was shown to range from 6% to 82% for soil fungi (Bovio et al. 2017), from 0.13% to 50% for soilbacteria (Jones et al. 1970), and from 0.003% to 100% for marine bacteria (Mulkins-Phillips and Stewart 1974).

The use of microbial community for the recovery of impacted marine areas is the subject of bioremediation, a biotechnology mainly targeted to exploit processes carried out by single type of microorganisms. Indeed, hydrocarbons degradation processes in the natural environment are too complicated to be entirely comprehended, and therefore a system biology approach is required to investigate networks and interaction at the molecular, cellular, and ecosystem levels.

In this chapter, we outline the existing knowledge about the interaction between bacteria and algae during the petroleum biodegradation process; whereafter, we will specifically focus on the bacterial and algal actions under aerobic conditions.

7.2 Microbial Hydrocarbon Biodegradation

7.2.1 Bacterial Hydrocarbons Biodegradation

Several marine ecological niches, both extreme and conventional, host hydrocarbon-degrading bacteria. The biogeography of hydrocarbon-degrading bacteria has been continuously updating and has demonstrated that they are widely distributed around the world (Oliveira et al. 2017), including in the polar region (Crisafi et al. 2016), hydrothermal vents (He et al. 2015), deep-sea (Liu et al. 2019), and hypersaline environments (Fathepure 2014). Coastal zones disturbed by frequent oil input together with chronically oil-polluted sites (ports, the surroundings of refineries, mining marine sites) show an increase of hydrocarbon-degrading bacteria relative density (Denaro et al. 2005; Yakimov et al. 2005; Yakimov et al. 2007; Crisafi et al. 2016; Zhang et al. 2017; McFarlin et al. 2018). The potential of hydrocarbons-degrading bacteria has been known for decades. Zobell (1946) perceived an interesting opportunity on the use of hydrocarbon-degrading bacteria for the clean-up of oil-polluted areas. Cutting-edge omics technologies have allowed to deeply investigate structural and functional features of natural bacterial communities, together with genome of bacterial strains, their genes, enzymes, metabolites, and degradation pathway and network as crucial components of biodegradation processes (Bargiela et al. 2015; Zhang et al. 2019). Biodegradation of petroleum depends on the nature and on the amount of the hydrocarbons, which determine their availability to bacteria (Cooney et al. 1985; Chaudhry et al. 2005; Rojo 2009; Beskoski et al. 2011; Chandra et al. 2013). In particular, the susceptibility of hydrocarbons to microbial degradation is generally ranked as follows: linear alkanes > branched alkanes > low-molecular-weight alkyl aromatics > monoaromatics > cyclic alkanes > polyaromatics > asphaltenes (Atlas 1981; Leahy and Colwell 1990; Atlas and Bragg 2009; Varjani 2017). Hydrocarbon degradation can be influenced by the bioavailability of nutrients such as nitrogen and phosphorous (Bootpathy 2000; Rahman et al. 2006; Varjani et al. 2015). Temperature, pH, and oxygen can also limit the efficiency of the process (Atlas 1991; McKew et al. 2007; Chandra et al. 2013; Taffi et al. 2014). Moreover, high amount of organic matter associated with long-term hydrocarbon contamination can reduce the bioavailability of the pollutant (Santos et al. 2003). Among biotic factors affecting oilbiodegradation, predation is considered as a positive event because it creates a nutritional loop, but at the same time may cause a decrease in the number of hydrocarbon-degrading bacteria in comparison to a predator-less condition (Bootpathy 2000).

7.2.2 Bacteria-Degrading Aliphatic Hydrocarbons

Although 75 different bacterial genera have been so far described as hydrocarbons-degraders (Prince 2005), little is known on marine strains, likely due to their known

Table 7.1 List of the main bacteria genera used in studies on hydrocarbonsbiodegradation

Bacterial genus	Hydrocarbons	References
Alcanivorax sp.	Aliphatics alkanes up to C32 and branched aliphatic, as isoprenoid hydrocarbons, alkylarenes and alkylcycloalkanes, cycloalkanes	Yakimov et al. (1998)
Marinobacter sp.	Aliphatics alkanes C16-C20, heptadecano, tetradecano, dodecylbenzene, phenantrene, pristine fluoranthene	Gauthier et al. (1992)
Halomonas sp.	Aromatics diesel fuel, alkanes C11-C22	Melcher et al. (2002)
Novosphingobium sp.	Aromatics pyrene, benz(a)anthracene, benz (b) fluoranthene, benzo(a) pyrene	Xu et al. (2018)
Alteromonas sp.	Aliphatics and aromatics naphthalene, phenanthrene	Teramoto et al. (2011)
Oleiphilus sp.	Aliphatics aliphatic hydrocarbons C11 -C20, alkanoates alkanoles	Golyshin et al. (2002)
Oleispira sp.	Aliphatics aliphatic hydrocarbons C10-C18 and their fatty alcohols and acids, cycloalkanes	Yakimov et al. (2003)
Pseudoalteromonas sp.	Aliphatics and aromatic naphthalene, 1/2 methylnaphtalene, biphenyl, phenantrene, fluorine linear alkanes (decane, tetradecane, and eicosane), branched alkanes (pristane and squalane)	Liu et al. (2019)
Thalassolituus sp.	Aliphatics C12–C32 aliphatic hydrocarbons and their oxidized derivatives	Yakimov et al. (2003)
Neptunomonas sp.	Aromatics naphthalene, phenantrene, 1-methylnaphtalene, 2-methylnaphtalene, 2,6 dimethylnaphtalene	Hedlund et al. (2001)
Roseobacter sp.	Aliphatics and aromatics	Viggor et al. (2013)
Cycloclasticus sp.	Aromatics naphtalene, phenanthrene, methylnaphtalene, fluorene, anthracene, biphenyl, acenaphtene, fluoranthene, pyrene, chrysene, bezo(a)pyrene	Dyksterhouse et al. (1995)
Eritrobacter sp.	Aromatics	Zhang et al. (2017)
Oleibacter sp.	Aliphatic	Teramoto et al. (2011)
Thalassospira sp.	Aromatic	
Sphingomonas sp.	Aromatics	Demaneche et al. (2004)

low cultivability. Table 7.1 lists a selection of marine strains frequently detected in oil-polluted environments both in natural samples and in culture conditions. The structure of the microbial communities associated to oil-polluted marine areas depends on environmental conditions that select for distinct site-specific bacterial assemblage and affect the physico-chemical properties of hydrocarbons by increasing or reducing their bioavailability (Coulon et al. 2007; Duran and Cravo-Laureau 2016; Dashti et al. 2015; Potts et al. 2018). The most representative class, *Gammaproteobacteria*, includes *Alcanivorax* sp. comprising more than 11 species.

Alcanivorax borkumensis SK2 (Yakimov et al. 1998) is the first described of the five genera of obligate hydrocarbonoclastic marine bacteria. *Alcanivorax*, together with *Thalassolituus*, *Cycloclasticus*, *Oleispira* and *Oleiphilus* genera, includes specialist bacterial strains that are able to use hydrocarbons as sole carbon and energy source. Obligate hydrocarbon-degrading bacteria are extremely specialized in consuming exclusively certain petroleum fractions for which their genes have been evolving. By contrast, generalist hydrocarbon-degrading bacteria can, in some cases, use both aliphatic and aromatic hydrocarbons. *Alcanivorax-like*bacteria have been identified in oil-polluted marine areas across the globe, along the coast in Mediterranean Sea (Denaro et al. 2005; Yakimov et al. 2007; Yakimov et al. 2019), in the Mid-Atlantic Ridge near Antarctica (Alcaide et al. 2015) and in deep-sea sediments from eastern Pacific Ocean (Liu and Shao 2005). Natural environments affected by an oil-spill and artificial system as during oil-spill simulation in micro/mesocosms show similar biodiversity pattern with a significant dominance of *Alcanivorax* sp. during the first 1–2 weeks, corresponding to a severe decrease in aliphatic relative fraction of oil (Kasai et al. 2002; Hara et al. 2003; Yakimov et al. 2005; McKew et al. 2007; Li et al. 2019). Strains belonging to *Alcanivorax* genus benefit from a selective advantage because they are able to use aliphatic hydrocarbons (Table 7.1) including branched-chain alkanes such as pristane, naturally produced by marine plankton (Hara et al. 2003; Head et al. 2006; Sevilla et al. 2017; Wang and Shao 2014). *Alcanivorax* outcompetes with *Thalassolituus* sp. for the use of *n*-tetradecane and oil (Yakimov et al. 2005; McKew et al. 2007). *Thalassolituus*-like bacteria were found in microbial communities described in the Mediterranean, Baltic, Barents, Atlantic, Pacific, Polar Oceans, North, Okhotsk, South China seas (Yakimov et al. 2007, 2010); moreover, it was also detected in the oil plume in the Gulf of Mexico (Hazen et al. 2010; Camilli et al. 2010) and terrestrial sites (caves and groundwater) (Mou et al. 2008). In addition, *Thalassolituus* spp. was the dominant member of microbial communities representative of seawater samples collected from oil production wells in Canada (Kryachko et al. 2012). It is capable of special adaptation to different temperatures (from 4 °C to 28 °C) and shows an interesting versatility on the use of acetate or tetradecane according to the temperature (Mckew et al. 2007). Species affiliated to *Marinobacter* genus are both heterotrophic and mixotrophic (Dhillon et al. 2005; Handley et al. 2009a, b). Strains belonging to *Marinobacter* genus were found in a wide range of environments, marine and saline terrestrial settings, including various low-temperature hydrothermal environments (Shieh et al. 2003; Moyer and Morita 2007), showing also capability to adapt to aerobic and anaerobic conditions (Li et al. 2013; Gao et al. 2012). Indeed, only 4 out of the 41 already described species belonging to *Marinobacter* genus showed hydrocarbons degradation capability (Handley and Lloyd 2013). Moreover, some species have also the ability to reduce nitrates, potentially useful in oilfield maintenance and for the strains themselves as an advantage to colonize different ecological niches (phycospheres). *Oleiphilus messinensis* is a mono-species mono-genus strain, growing preferentially on aliphatic hydrocarbons as sole carbon sources; it inhabits preferentially marine sediments (Golyshin et al. 2002). This strain harbors the largest genome among obligate hydrocarbon-degrading bacteria, with a high presence of mobile genetic elements and proteins for signal transduction, but it shows a very narrow substrate profile (Toshchakov et al. 2017). The psychrophilic strains belonging to *Oleispira* sp. are able to use hydrocarbons as carbon source (Table 7.1) in a range of temperature comprised between 4 °C and 20 °C (Yakimov et al. 2003; Kube et al. 2013; Crisafi et al. 2016). *Oleispira* have been detected and isolated both in polar region and deep-sea waters demonstrating that *Oleispira* spp. has peculiar capability in the adaptation to extreme parameters such as high hydrostatic pressure and low temperature (Marietou et al. 2018; Jensen et al. 2019). Strictly related to *Thalassolituus* genus, *Oleibacter* sp. was isolated from tropical region and showed capability to degrade petroleum aliphatic hydrocarbons growing between the range 10–40 °C but the optimum is 25–30 °C (Teramoto et al. 2011). It was also described in high-polluted marine sediments (Catania et al. 2015). Marine aliphatic-degrading strains show similar metabolic pathways. On the base of *Alcanivorax* model, the best-known obligate hydrocarbon-degrading bacteria specialists, together with the knowledge about the generalist *Pseudomonas* sp., a general degradation pathway for the aerobic alkane degradation has been proposed. The alkane-activating enzymes, mono-oxygenases, generate a primary alcohol by the oxidation of a terminal methyl group. The primary alcohol is oxidized to aldehyde, and then converted into a fatty acid that is conjugated to coenzyme A, which is further processed by β-oxidation to generate acetyl-coenzyme A (Morgan and Watkinson 1990; van Hamme et al. 2003; Ashraf 1994; Schneiker et al. 2006; Wentzel et al. 2007; Gregson et al. 2018). Subterminal oxidation of n-alkanes generates a secondary alcohol that is then converted to the corresponding ketone, and transformed in ester by the oxidation catalyzed by Baeyer–Villiger mono-oxygenase. (Whyte et al. 1998; Kotani et al. 2006). The action of an esterase generates an alcohol and a fatty acid (Forney and Markovetz 1970; Sakuradani et al. 2013). Both terminal and subterminal oxidation can coexist in some microorganisms as in *Thalassolituus* sp. that express this pathway with long-chain alkanes growth (Gregson et al. 2018). *Alcanivorax* sp. and *Oleispira* sp. strains show similar patterns of expression profile. Their central operon is a cluster of genes: $alkSB_1GHJ$ for hydrocarbons catabolism (Kube et al. 2013; Schneiker et al. 2006), in particular $AlkB_1$ and $AlkB_2$ alkane hydroxylase (monoxygenase) oxidize medium-chain alkanes (C5–C12) medium-chain alkanes in the range (C8–C16), respectively. (Schneiker et al. 2006; van Beilen et al. 2006). An additional gene *AlmA*, a flavin-binding monooxygenase, was recently identified in *Alcanivorax dieselolei* and seems to be upregulated in presence of long-chain alkanes (Wang and Shao 2014). Moreover, genes involved in the expression of ferredoxin, an alcohol dehydrogenase, FAD-dependent oxido-reductase are involved in the terminal oxidation of alkanes. In *Alcanivorax SK2* the presence of isoprenoid hydrocarbons determined the specifically expression of three cytochromes P450, while in *Oleispira* they are differentially expressed in tetradecane and acetate (Schneiker et al. 2006; Kube et al. 2013; Sevilla et al. 2017). Also *Marinobacter* sp. shows similar patterns with a key role of homologous genes. By contrast, the orthologous to *AlmA*, a flavin-binding monooxygenase gene involved in long-chain hydrocarbon (>32 carbons) degradation in *Acinetobacter* and

Alcanivorax species, showed no change in expression profile growing under the same conditions (Wang and Shao 2012; Mounier et al. 2014). Biosurfactants, a distinctive feature of hydrocarbon-degrading bacteria, enhance bioavailability of hydrocarbons and improve the biodegradation capability of these hydrophobic organic substrates (Kubicki et al. 2019). The *Alcanivorax borkumensis* SK2 produces anionic glycolipids biosurfactants with four varying chain lengths fatty acids and surface-active secondary metabolites (Qiao and Shao 2010), *Marinobacter* sp. exhibits a wide range of biosurfactants, which includes rhamnolipids (Tripathi et al. 2019), but also amphiphilic siderophore (Martinez et al. 2000). To date, no relevant evidences for biosurfactants production in *Thalassolituus* sp. *and Oleispira* sp. have been reported, although they showed a differential expression, in oily and non-oily seawater, of a *LolA-like* gene codifying for a lipoprotein, involved in biosurfactant production (Schneiker et al. 2006; Sabirova et al. 2011; Gregson et al. 2018). *Alcanivorax* genome includes putative genes for exopolysaccharides biosynthesis, export, modification, and polymerization (Sabirova et al. 2011). Moreover, cluster for alginate biosynthesis and a number of determinants for a Type II secretion system together with genes encoding for secretion proteins have been identified in *Marinobacter* (Handley and Lloyd 2013; Mounier et al. 2018) and *Thalassolituus* sp. (Morohoshi et al. 2018).

Bacteria-Degrading Aromatic Hydrocarbons

Different pattern of genes and enzymes have been described for polycyclic aromatic hydrocarbons degradation. The widespread diffusion of polycyclic aromatic hydrocarbons in marine environment determines the presence of these compounds in remote deep-sea sediments and hydrothermal vent sulfide minerals (Vila et al. 2015). In spite of their high toxicity, the marine bacteria can use the polycyclic aromatic hydrocarbons as both carbon and energy sources. Table 7.1 shows some of the strains described as polycyclic aromatic hydrocarbons-degraders. The classical strategy for aromatic-ring cleavage, which is restricted to aerobic microorganisms, comprises firstly the oxidation of the benzene ring to form cis-dihydrodiols catalyzed by dioxygenase enzymes that are then dehydrogenated to form dihydroxylated intermediates, further metabolized via catechols to water and carbon dioxide. Marine bacteria show a wide biodiversity in metabolic pathways identified for polycyclic aromatic hydrocarbons degradation. As an example, halophilic bacteria as *Halomonas* use several downstream pathways, such as protocatechuic acid pathway, gentisic acid pathway, and catechol pathway. Moreover, several downstream pathways to rapidly transform intermediates have been identified (Wang et al. 2018). *Cycloclasticus* genus, one of the key players of polycyclic aromatic hydrocarbons degradation in marine environment, can also degrade chlorinated derivatives of polycyclic aromatic hydrocarbons (Dyksterhouse et al. 1995; Yakimov et al. 2007; Yakimov et al. 2014). It has been detected in estuaries (Niepceron et al. 2010), coastal areas (Genovese et al. 2014; Ding et al. 2017), deep-sea sediments (Wang et al. 2008), and polar oceans (Hazen et al. 2010; Brakstad et al. 2015). Recently, Rubin-Blum et al. (2017) described*Cycloclasticus* as a symbiont with mussels and sponges dwelling in deep-sea gas and oil seeps (Rubin-Blum et al. 2017) and oil-aggregates to diatoms in Arctic region (Netzer et al. 2018). The halophilic strain *Thalassospira* sp. SL5–1 (Zhou et al. 2016) is able to degrade pyrene through both o-phthalic acid and gentisic acid. Particularly, identification of phthalic acid and salicylic acid showed that phthalate and salicylic acid routes were simultaneously contained in the pyrene degradation, which was remarkably different from those for other pyrene-degraders. The polycyclic aromatic hydrocarbons metabolic pathway occurring in mixed microbial consortia is expected to be a more complex combination than those described in pure cultures considering that the metabolic intermediates can be used and transferred among different microorganisms (Zhou et al. 2016). *Cycloclasticus* genus includes strains specialized in the degradation of polycyclic aromatic hydrocarbons. Strains belonging to this genus harbor three large operons encoding for a set of four different classes of dioxygenases (Messina et al. 2016). The role of *Alphaproteobacteria* on the polycyclic aromatic hydrocarbons degradation is particularly interesting, due to their putative capability to conclude polycyclic aromatic hydrocarbons degradation by using intermediate action, which both eliminates toxic compounds from the medium and maintains enzymatic action at the same rate. A recent comparative genomic study of genera affiliated with *Alphaproteobacteria*, for example, marine *Roseobacter*, *Thalassospira*, and *Erytrobacter* clade, revealed the presence of numerous pathways for the catabolism of structurally diverse aromatic substrates.

7.3 Biodegradation of Hydrocarbons by Microalgae and Cyanobacteria

7.3.1 Microalgae Oil Degradation

Microalgae and cyanobacteria have, firstly, a pivotal role in the primary production, but due to their capability in the carbon fixation and nutrients recycling, their involvement on hydrocarbonsbiodegradation processes was hypothesized (Ghosal et al. 2016; Srivastava and Kumar 2019). Many marine phototrophic microorganisms exhibit the capability to survive in marine areas seriously affected by oil pollution, especially those species adapted to coastal areas where oil inputs can frequently occur (Abed et al. 2006). Some cyanobacteria and diatoms are particularly abundant even in oil-contaminated sediments (Coulon et al. 2012). The capability of chlorophytes and diatoms but also cyanobacteria, to degrade hydrocarbons, especially aromatic fractions, is rarely reported (Table 7.2 and Table 7.3), often with conflicting results. Accordingly, it is still an open question whether microalgae and cyanobacteria would cooperate with specialist aerobic hydrocarbonoclastic bacteria to break down hydrocarbons or they are involved only in the partial oxidation (Cerniglia et al. 1980b). As an example, first experiments were performed on

Table 7.2 List of the main microalgal species used in studies on hydrocarbonbiodegradation

Species	Hydrocarbon	References
Diatoms		
Amphora sp.	Naphtalene	Cerniglia et al. (1980b)
Cylindrotheca sp.	Dichlorodiphenyltrichloroethane, naphthalene	Cerniglia et al. (1980b), Kobayashi and Rittman (1982), and de Llasera et al. (2016)
Navicula pelliculosa	Naphthenic acids	Mahdavi et al. (2015)
Navicula sp.	Naphtalene	Cerniglia et al. (1982)
Nitzschia sp.	Fluoranthene, phenanthrene, naphtalene	Cerniglia et al. (1982) and Hong et al. (2008)
Skeletonema costatum	Fluoranthene, phenanthrene	Hong et al. (2008)
Synedra sp.	Naphtalene	Cerniglia et al. (1982)
Chlorophytes		
Ankistrodesmus braunii	Benzo [α]pyrene	Warshasky et al. (1995a, b)
Chlamydomonas angulosa	Naphthalene	Soto et al. (1975) and Soto et al. (1977)
Chlamydomonas reinhardtii	Benzo [α]pyrene, naphthalene	Kobayashi and Rittman (1982) and de Llasera et al. (2016)
Chlamydomonas ulvaensis	Phenol	Ellis (1997)
Chlorella autotrophica	Naphthalene	Cerniglia et al. (1980b)
Chlorella kessleri	Aromatic hydrocarbons	Ichor et al. (2016)
Chlorella pyrenoidosa	Phenol	Ellis (1997)
Chlorella sorokiniana	Naphthalene	Cerniglia et al. (1980b)
Chlorella spp.	Toxaphene	Kobayashi and Rittman (1982) and de Llasera et al. (2016)
Chlorella vulgaris	Fluoranthene	Lei et al. (2007)
Closterium spp.	Crude oil	Uzoh et al. (2015)
Desmodesmus sp.	Biphenol	Wang et al. (2017)
Dunaliella sp.	Dichlorodiphenyltrichloroethane, naphthalene	Kobayashi and Rittman (1982) and de Llasera et al. (2016)
Euglena gracilis	Benzo [α]pyrene, dichlorodiphenyltrichloroethane, naphtalene, biphenol	Kobayashi and Rittman (1982), Ellis (1997), and de Llasera et al. (2016)
Monorafidium braunii	Biphenol	Gattullo et al. (2012)
Scenedesmus acutus	Benzo [α]pyrene	Warshawsky et al. (1995a, b)

(continued)

Table 7.2 (continued)

Species	Hydrocarbon	References
Scenedesmus baleniensis	Phenol	Ellis (1997)
Scenedesmus obliquus	Naphtalene sulfonic acid, dichlorodiphenyltrichloroethane, naphtalene	Kobayashi and Rittman (1982), Luther and Soeder (1987), Luther (1990), and de Llasera et al. (2016)
Scenedesmus platydiscus	Fluoranthene	Lei et al. (2007)
Scenedesmus quadricauda	Fluoranthene	Lei et al. (2007)
Selenastrum capricornutus	Fluoranthene, benzene,benzopyrene, benzo [α]pyrene, chlorobenzene, 1,2-dichlorobenzene, nitrobenzene, pyrene	Kobayashi and Rittman (1982), Warshawsky et al. (1990), Simple et al. (1999), and de Llasera et al. (2016)
Chrysophytes		
Ochromonas malhamensis	Benzo [α]pyrene	Warshasky et al. (1995a, b)

naphthalene, using the chlorophyte *Chlamydomonas angulosa* (Soto et al. 1975; Soto et al. 1977). The microalgae were able only to intracellularly accumulate naphthalene without metabolizing the pollutant. Further, Cerniglia et al. (1979, 1980a, b, c, 1982; Cerniglia 1981) showed the capability of microalgae and diatoms *Navicula* sp., a *Nitzschia* sp., and a *Synedra* sp. to oxidize naphthalene-producing metabolites as α-naphthol or aromatic diols. Successive studies showed that the green algae *Scenedesmus obliquus* is able to use different substituted aromatic compounds, that is, some naphthalene sulfonic acids, as nutrient source (Luther and Soeder 1987, 1991; Luther 1990).

Species *Skeletonema costatum* and *Nitzschia* sp., isolated from mangrove, exhibited the capability to degrade phenanthrene and fluoranthene simultaneously, with high efficiency (Hong et al. 2008). Similar results were obtained using *Chlorella vulgaris*, *Scenedesmus platydiscus*, *Scenedesmus quadricauda*, and *Selenastrum capricornutum* to break down a mixture of fluoranthene and pyrene (Lei et al. 2007). More detailed studies were conducted to evaluate the potential benzo[a]-pyrene biodegradation ability of the chlorophyte alga *Selenastrum c.* (Lindquist and Warshawsky 1985a, b; Schoeny et al. 1988; Warshawsky et al. 1988, 1990, 1995a, b). *Selenastrum capricornutum* utilizes a dioxygenase enzyme system to metabolize benzo[a]-pyrene to cis-dihydrodiols (cis-4,5-, 7,8-, 9,10-, 11,12- dihydrodiols), which is then transformed in an ester. More recent studies (Ke et al. 2010; Luo et al. 2014) reported transformation of a mixture of polycyclic aromatic hydrocarbons by the green algae *Selenastrum c.* under different spectral irradiance. The capability to degrade crude oil by microalgae in absence of light has also been tested (Walker et al. 1975; Cerniglia 1992; Uzoh et al. 2015). The heterotrophic strains of the achlorophyllous alga *Prototheca zopfii* and of the

Table 7.3 List of the main cyanobacterial species used in studies on hydrocarbonbiodegradation

Species	Hydrocarbon	References
Agmenellum quadruplicatum	Phenenthrene, naphtalene	Cerniglia et al. (1980b) and Narro et al. (1992)
Anabaena cycadae	Crude oil	Ichor et al. (2016)
Anabaena spp.	Naphtalene	Cerniglia et al. (1980b)
Anabaena flos-aquae	Benzo [α]pyrene	Warshasky et al. (1995a, b)
Anabaena spp.	n-octadecane, naphtalene	Cerniglia et al. (1980b), Ibraheem (2010)
Aphanocapsa sp.	Crude oil	Raghukumar et al. (2001)
Aphanothece conferta	n-Octadecane	Ibraheem (2010)
Leptolyngbya sp.	Crude oil	Ichor et al. (2016)
Microcoleus chthonoplastes	n-hexadecanen-nonadecane, naphthalene	Cerniglia et al. (1980b), Al-Hasan et al. (1998)
Microcoleus sp.	Crude oil	Ichor et al. (2016)
Mycrocystis elabens	Crude oil	Ichor et al. (2016)
Mycrocystis halsatica	Crude oil	Ichor et al. (2016)
Nostoc spp.	n-octadecane, naphtalene	Cerniglia et al. (1980b), Ibraheem (2010)
Oscillatoria salina	Crude oil	Raghukumar et al. (2001)
Oscillatoria spp.	Naphtalene	Cerniglia et al. (1980b)
Phormidium corium	n-Hexadecanen-Nonadecane	Al-Hasan et al. (1998)
Phormidium faveolaurum	Phenol, crude oil	Ellis (1997) and Ichor et al. (2016)
Phormidium sp.	n-Octadecane, crude oil	Ibraheem (2010) and Ichor et al. (2016)
Plectonema terebrans	Crude oil	Raghukumar et al. (2001)
Pseudoanabaena minima	Crude oil	Ichor et al. (2016)
Synechococcus spp.	Crude oil	Ichor et al. (2016)
Synechocystis aquatilis	n-Octadecane	Ibraheem (2010)

chlorophyte*Closterium* sp. isolated from oil-polluted environments seem to utilize crude oil as a unique substrate (Walker et al. 1975; Uzoh et al. 2015).

7.3.2 *Cyanobacteria Oil Degradation*

Cyanobacteria, also known as blue green algae, are oxygen-evolving photosynthetic prokaryotes occupying a broad range of habitats across all latitudes. The metabolic activity of cyanobacteria, including photosynthesis, can affect the oxygen and pH conditions of the environment and modify the amounts of available organic compounds and nutrients (Oliver and Ganf 2000; Ichor et al. 2016). The capability of cyanobacteria to degrade compounds including petroleum hydrocarbons has been widely documented (Abed et al. 2000; Grotzschel et al. 2002; Sanchez et al. 2005;

Ichor et al. 2016). Ellis (1997) reported that *Anabaena cylindrica* and *Phormidium foveolarum* are able to metabolize hydrocarbons. Further studies conducted on *Agmenellum quadruplicatum* and *Oscillatoria* sp. showed the transformation of simple aromatic hydrocarbons as naphthalene to their metabolites under photautotrophic conditions (Cerniglia et al. 1979; Cerniglia et al. 1980a, b, c). Other studies showed that *Oscillatoria* sp. oxidizes biphenyl to 4-hydroxybiphenyl and *Agmenellum q.* is able to oxidize phenanthrene (Narro et al. 1992). The oxidation of methylnaphthalene and biphenyl phenanthrene by cyanobacteria has been also proved (Ibraheem 2010). Many authors have demonstrated that cyanobacteria are able to metabolize aliphatic hydrocarbons. As an example, *Microcoleus chthonoplastes* and *Phormidium corium*, isolated from marine oil-polluted environment, produced galactolipids and sulfolipids that included fatty acid derived from the degradation of aliphatic hydrocarbons (Al-Hasan et al. 1998). The isolated cyanobacteria *Aphanothece conferta* and *Synechocystis aquatilis* exhibited different degradation efficiencies of aliphatic hydrocarbons, in relation to species and alkane used (Ibraheem 2010). Other studies monitored degradation of petroleum hydrocarbons by the cyanobacteria *Nostoc punctiforme* and *Spirulina platensis* and showed the total removal of decane, pentacosane, hexacosane, octacosane, and nonacosane (Raghukumar et al. 2001; Radwan and Al-Hasan 2000; Cohen 2002). However, many authors suggest that these findings were often ambiguous and, consequently, the role of cyanobacteria on hydrocarbons degradation is not still clear (Radwan and Al-Hasan 2000). As an example, the need of autotrophic microorganisms to use carbon deriving from oil is also questioned by many authors (Sorkhoh et al. 1992; Rippka 1988; Radwan and Al-Hasan 2000). It is noticeable that most of the studies were conducted under non-axenic conditions, due to the difficult to obtain separated bacterial and algal cultures (Abed and Koster 2005). On the other hand, several authors have demonstrated the dominance of cyanobacteria in microbial communities occurring in many hydrocarbon-polluted sites (Sorkhoh et al. 1992; Raghukumar et al. 2001; De Oteyza et al. 2004; Ibraheem 2010). Cyanobacteria indeed frequently dominate microbial mats, laminated benthic microbial communities developing on the sediments of shallow protected water, such as estuaries, lagoons, or sheltered beaches (Stal 2010; Stal et al. 2017). Oil-pollution in environment, both for natural seepage or caused by human activities can favor the development of microbial mats, where cyanobacteria are certainly associated to hydrocarbon-degrading bacteria and fungi (Goñi-Urriza and Duran 2018). In particular, the surface layer of the mats, where the dominant members were cyanobacteria and aerobic heterotrophic bacteria, shows a special capability in hydrocarbons degradation (Abed et al. 2002; Cohen 2002; Abed and Koster 2005; Abed et al. 2006; Sanchez et al. 2005; Abed 2010; Goñi-Urriza and Duran 2018), probably due to bacteria present in the microbial consortium (i.e., *Marinobater* and *Alcanivorax*-related members as well as species belonging to *Rhodococcus*, *Sphingomonas*, *Microbacterium* genera) (Abed and Koster 2005). Microalgae and cyanobacteria could participate to hydrocarbons degradation by performing biotransformation of aromatic compounds into their hydroxylated intermediates that can be more easily degraded by bacteria. Although they are not able to totally degrade pollutants, they are able to modify their physical and chemical nature, making them bioavailable for hydrocarbons-degrading bacteria.

7.4 Synergistic Action Algae-Bacteria in Oil-Polluted Marine Environment

7.4.1 Algae Bacteria Mutual Benefits During Degradation Processes

The oil input in marine environment induces a shift in the bacterial community structure with a consequent increase of the relative cell density of hydrocarbon-degrading bacteria (Yakimov et al. 2005; McKew et al. 2007; Yakimov et al. 2007). However, the natural occurring oilbiodegradation is a concerted action resulting from the interaction between hydrocarbon-degrading bacteria and other microorganisms, such as fungi or microalgae and cyanobacteria (Coulon et al. 2012; Bovio et al. 2017). The association of algae-bacteria can be defined as a "microbial module" (McGenity et al. 2012) that can contribute to the success of Bioremediation in marine environment. For this reason,knowledge about algae–bacteria interaction as physiological, biochemical, and ecological aspects will be fundamental to exploit this biotechnological potential.

In general, the interaction between algae and bacteria can generate both, positive or negative effects for the two components of the consortium and consequently for the biodegradation processes. The crucial events of algae–bacteria interaction occur within the phycosphere, the region that surrounds phytoplankton cells enriched in organic substrates and algal exudates. It may also include associated bacterial communities (Seymour et al. 2017). In a mixed algae/bacteria consortium as it occurs in the natural environment, a cooperation was reported between algae and bacteria in the biodegradation of available organic substrate, including hydrocarbons (McGenity et al. 2012; Tang et al. 2012). The success of such cooperation depends, among several biotic and abiotic factors, also on the type of interaction between algae and bacteria that can be synergic or antagonist (Fig. 7.1). With special attention to the synergic action within the phycosphere, the interexchange of gases for mutual benefits can significantly improve the biodegradation processes (Cole 1982; Gutierrez et al. 2012; Amin et al. 2015; Palacios et al. 2016). In general, oxygen produced by algae enhances bacterial growth and in turn CO_2 deriving from bacteria promotes microalgae growth (Ramanan et al. 2016). During bioremediation processes, the oxygen demand increases and its limitation can reduce the yield of biocatalyses. Within the phycosphere, algae can provide sufficient amount of oxygen, reducing the total energy requirement of the process (Sforza et al. 2018). The same benefit could be determinant to enhance the natural occurring biodegradation processes as for example within marine aggregates such as marine oily snow (Suja et al. 2019). Moreover, further advantages of algae–bacteria

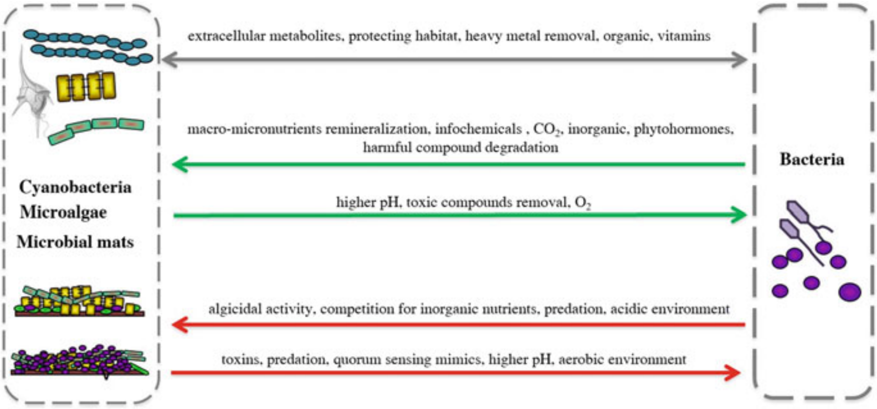


Fig. 7.1 Possible interactions between microalgae/cyanobacteria and bacteria that can affect oil degradation in marine environment. Factors underlined with green arrows indicate products or activities carried out by both sides (see arrows direction) that can positively influence the life of the members of the consortium. Red arrows indicate elements that may negatively affect microorganisms' cooperation during biodegradation processes. Gray arrow represents mutual benefits deriving from synergistic interaction

interaction are with regard to nutrients exchange. Nitrogen and phosphorous availability can seriously limit biodegradation processes in marine environment; algae–bacteria syntrophy in the recycling or mutual provision of organic and inorganic nutrients can sustain both algal growth and available nutrients for hydrocarbons-degrading bacteria (Clarens et al. 2010; Müller and Overmann 2011; Lian et al. 2018). Similarly, iron is a growth-limiting nutrient in marine environment due to its poor availability both for algae and bacteria (Landry et al. 2000; Amin et al. 2009; Sanchez et al. 2018). Marine bacteria have developed the capability to produce iron-chelating compounds, siderophores, exhibiting a high affinity for iron. Such organic small molecules can be excreted to scavenge iron, bind and transport it within the cells (Butler 2005; Denaro et al. 2014). Bacteria are equipped with specific receptors and transport systems for different groups of siderophores. On the contrary, there is no evidence on the production of siderophores by algae. However, many algae can access iron from siderophores, utilizing ferrireductases and adjacent Fe (II) transporters on their outer cell membranes, for which there is genomic evidence in diatoms and green algae (Amin et al. 2009). Algae-associated bacterial strains can provide both, iron or iron-siderophore complexes to algae, dealing with their iron demand. For instance, bacterial strains belonging to *Marinobacter* genus, associated with dinoflagellates and coccolithophores, have been shown to produce vibrioferrin, a siderophore that releases iron in the presence of sunlight, increasing microalgal iron uptake more than 20-fold (Amin et al. 2009).

The phycosphere can also serve as a habitat where a mutual protection may occur. Algae may protect bacteria from adverse environmental conditions, ensuring stability during grazing events and, in turn, microalgae may benefit from antibiotics produced by bacteria against algicidal or infective microbes (Amin et al. 2012;

Amin et al. 2015; Ramanan et al. 2016; Mayali 2018). Also, bacterial extracellular polymeric substances can protect algae from toxic compounds such as heavy metals (Decho and Gutierrez 2017). Other metabolites can be exchanged within the algae–bacteria consortium. Bacterial vitamin B1 and B12 may enhance the microalgae growth (Croft et al. 2005; Helliwell 2017), and phytohormones have positive effect on lipid accumulation in algae (Bruhn et al. 2007; Amin et al. 2009; Seyedsayamdost et al. 2011; Wahl et al. 2012; Danchin and Braham 2017). Moreover, algal exudates represent a carbon source for bacteria. However, hydrocarbons of different origin, accumulated from external source (oil-polluted areas) or produced by algae may be trapped within the phycosphere. In the latter case, the role of hydrocarbons in algae includes water balance, self-defense, signaling, and membrane architecture (Binark et al. 2000).

7.4.2 Algae–Bacteria Synergy Within Phycosphere in Oil Pollution Conditions

Amin and coauthors (2015) evaluated the positive effect of coastal diatom *Pseudo-nitzschia multiseries*–bacteria interaction on the diatom growth. They hypothesized that hydrocarbons-degrading bacteria associated to the diatom (*Alcanivorax, Marinobacter, Pseudoalteromonas, Thalassospira*) produce auxin phytohormone indole-3 acetic acid that stimulates algal growth. Accordingly, Hedlund et al. (2001) have demonstrated the role of *Marinobacter* dioxygenase (involved in polycyclic aromatic hydrocarbons degradation) in the indole-3 acetic acid production.

Additionally, associated bacteria serve as helper for their hosts during environmental perturbation such as changing salinity (Xie et al. 2013; Dittami et al. 2016). For instance, *Picochlorum* sp., a green alga can survive in a wide range of salinity (from 0.35% to 10.8%) (Wang and Shao 2014); Foflonker and coauthors (2014) have shown that the genome of this algal strain harbors 24 additional genes derived from bacteria that are responsible for the response to saline stress.

Moreover, Lea-Smith et al. (2015) assessed alkane and alkene production capacity by cyanobacteria *Prochlorococcus* and *Synechococcus*. Derivatives of phytol, such as pristane and phytane produced by algae and utilized as biomarkers for monitoring hydrocarbonsbiodegradation, can even be degraded by some hydrocarbonoclastic bacterial taxa (e.g., pseudomonads) (Rontani et al. 1999; Dawson et al. 2013). Likewise, benzokinones and naphthoquinones (isoprenoids), produced and utilized by algae during photosynthesis and respiration, have a structure whose skeleton consists of hydrocarbons (Nowicka and Kruk 2010); strains belonging to the genus *Shewanella* can use isoprenoids as electron acceptors during the degradation of humic acids (Newman and Kolter 2000). Moreover, McGenity et al. (2012) hypothesized that similar compounds, isoprene by algae, could have a role in feeding specialist hydrocarbon-degrading bacteria because of their restricted pattern of substrates, in pristine marine sites. In addition, the ability to adsorb and accumulate polycyclic aromatic hydrocarbons molecules from the surrounding seawater by algae would create a polycyclic aromatic hydrocarbons enriched zone around the phytoplankton cell surface, where polycyclic aromatic hydrocarbons-degrading bacteria can proliferate (Gutierrez and Aitken 2014). Such association was proved to be also functional for polycyclic aromatic hydrocarbons removal, particularly during periods of bloom. With special attention to bioremediation, algae–bacteria consortia seem to enhance the rate of biodegradation processes. For instance, the alga *Chlorella sorokiniana* associated with *Pseudomonas migulae* (Munoz et al. 2003), as well as microalgae*Selenastrum c.* and *Mycobacterium* sp. (Luo et al. 2014) exhibit best performance in the degradation of hydrocarbons than algae or bacteria alone. *Synechocystis* sp. coupled with *Pseudomonas* sp. and *Bacillus* sp. showed an enhancement of the growth rate together with an ameliorated capability in the polycyclic aromatic hydrocarbon degradation (Patel and Hellgardt 2015). Tang et al. (2012) demonstrated that a microalgal–bacterial consortium formed by one axenic *Scenedesmus obliquus* and four hydrocarbon-degrading bacteria was able to reduce the aromatic hydrocarbons contamination faster than bacterial consortium alone.

Marine microalgal extracellular polymeric substances can contain many complex nonpolar molecules (e.g., poly-unsaturated fatty acids) incorporated into macromolecular protein/lipid/polysaccharide matrices (Flemming et al. 2007; Dewapriya and Kim 2014; Neu and Lawrence 2016). Potential complexation of petroleum hydrocarbons to extracellular polymeric substances molecules would influence distribution/partitioning and therefore the fate of hydrocarbons (Sikkema et al. 1995; Kalmykova et al. 2013). Gutierrez et al. (2013) and Quigg et al. (2016) argue the role of marine oil snow (MOS) upon the in situ biodegradation processes. In fact, the aggregates of hydrocarbonoclastic bacteria and phytoplankton, kept together by bacterial-produced extracellular polymeric substances, sink along water column as flocculent accumulation to the seafloor where the rate of catalyses could be significantly slowed down due to environmental constraints (pressure, temperature, and oxygen). Extracellular polymeric substances produced by another algal-associated oil-degrading bacterium (*Halomonas*) exhibit trace metal binding capacities (Ca, Fe, Mn, Mg, Al) and may be involved in nutrient sharing between bacteria and microalgae (Gutierrez et al. 2012).

It is also noticeable that the oil-resisting consortia show a decrease in biodiversity due to the toxic effect of oil. Parsons and coauthors (2015) showed that after the Deepwater Horizon oil-spill, diatoms and cyanobacteria dominated the survivor phytoplankton. The differential behavior is likely species-dependent and could be expressed as different tolerance to oil (Ozhan and Bargu 2014), or different biodegradation capability (Prouse et al. 1976; Jung et al. 2012; Parsons et al. 2015). In a recent microcosm study, phytoplankton-associated bacterial community showed an improvement on degradation capability when bacteria were associated to phytoplankton (Thompson et al. 2017). Also, bacteria associated with the mucilaginous sheath/capsule of cyanobacteria show interesting biodegradation capability (Sorkhoh et al. 1995; Radwan et al. 2002; Abed and Koster 2005; Chaillan et al. 2006). Al-Hasan et al. (1998) identified four genera of heterotrophic bacteria

(*Rhodococcus rhodochrous*, *Arthrobacter nicotianae*, *Pseudomonas* sp., and *Bacillus* sp.), associated with cyanobacterial cultures of *Microcoleus c.* and *Phormidium c.*, able to oxidize n-alkanes although cyanobacteria directly contributed to hydrocarbon uptake and oxidation.

Recently, Severin and Erdner (2019) have explained the presence of hydrocarbon-degrading taxa in the microbiome of dinoflagellates with their high content of triacylglycerols, a precursor of biodiesel (Harrington et al. 1970; Vasudevan and Briggs 2008; Fuentes-Grünewald et al. 2009). Hydrocarbon-degrading bacteria are listed among the few examples of microorganisms that produce triacylglycerols as reserve compounds, which could be used as a feedstock by dinoflagellates. Moreover, they have evidenced a correlation with the capability of consortium to resist and degrade oil.

According to the evidence reported above, the natural occurring hydrocarbonsbiodegradation processes can be certainly inferred in the light of synergic actions of a consortium, more than a monotype organism. Moreover, it seems that the mechanism of positive interaction is species-specific as the phycosphere different algae (Ramanan et al. 2016; Fuentes-Grünewald et al. 2016). Indeed, the algae–bacteria association can have a negative influence. For example, in limiting-nutrients conditions, competition for the use of bioavailable nutrients can occur. Furthermore, the pH of the medium can vary causing alkalization and acidification of the phycosphere. For instance, the metabolic activity during the flowering of cyanobacteria induces an increase of pH, while the production of poly-g-glutamic acid by bacteria significantly reduces aquatic pH and inhibits the growth of microalgae. Moreover, substances produced both by algae and bacteria can interfere with bacterial quorum sensing and inhibit cyanobacteria photosynthesis.

In order to produce the desired effects (e.g., bioremediation) from the concerted action of algae and bacteria, it is necessary to investigate the regulation of interactions at the molecular level. The biotechnological application of this knowledge is already applied not only in the field of bioremediation but also in the sectors of wastewater treatment and sustainable aquaculture.

7.5 Conclusions

- Algae–bacteria consortia have been described as efficient systems for hydrocarbons degradation, even for tough substrates as aromatic ones.
- Few studies report in situ investigation and are mostly carried out in artificial systems.
- The mechanisms of interaction during bioremediation processes are still unclear. Axenic cultures of microalgae do not seem able to degrade hydrocarbons while the degradation of hydrocarbons is observed if a microbiome (hydrocarbons-degraders) is associated with the same species There is no evidence of the presence of the classical genetic signatures specific for hydrocarbons degradation

in microalgae. On the contrary, cyanobacteria *Synechocystis* harbors gene coding for dioxygenase involved in polycyclic aromatic hydrocarbons degradation (Goñi-Urriza and Duran 2018), suggesting a specific function in the aerobic biodegradation processes.

7.6 Needs

- Further investigation on the phycosphere developed in marine oil-polluted areas should be carried out by means of -omic approaches in order to interpret the organization of microbial communities inhabiting the phycosphere, the interaction between the consortium members, their diversity and their function
- The use of engineering systems, as modular microcosms, to investigate the influence of chemical-physical parameters (in combination with oil) on the bacterial community succession within the phycosphere
- Further studies to comprehend mechanism(s) that defines microbiome–algae associations and mode of interexchange occurring during biodegradation processes, also coupling ecogenomics and analytical chemistry
- Specific efforts toward the isolation and identification of novel hydrocarbon-degrading bacteria inhabiting the phycosphere
- Well-designed experiments with environmentally appropriate model systems in simple biological condition (one-to-one species)
- Monitoring natural environment with selective molecular targets with both taxonomical and functional significance in oil-polluted environment

References

Abed RMM (2010) Interaction between cyanobacteria and aerobic heterotrophic bacteria in the degradation of hydrocarbons. Intern Biodet Biodegr 64:58–64. https://doi.org/10.1016/j.ibiod.2009.10.008

Abed RMM, Koster J (2005) The direct role of aerobic heterotrophic bacteria associated with cyanobacteria in the degradation of oil compounds. Int Biodeterior Biodegrad 55:29–37. https://doi.org/10.1016/j.ibiod.2004.07.001

Abed RMM, Safi NMD, Koster J et al (2000) Microbial diversity of a heavily polluted microbial mat and its community changes following degradation of petroleum compounds. Appl Environ Microbiol 68:1674–1683. https://doi.org/10.1128/AEM.68.4.1674-1683.2002

Abed RMM, Safi NMD, Koster J, de Beer D et al (2002) Microbial diversity of a heavily polluted microbial mat and its community changes following degradation of petroleum compounds. Appl Environ Microbiol 68:1674–1683. https://doi.org/10.1128/AEM.68.4.1674-1683.2002

Abed RMM, Al-Thukair A, de Beer D (2006) Bacterial diversity of a cyanobacterial mat degrading petroleum compounds at elevated salinities and temperatures. FEMS Microbiol Ecol 57:290–301. https://doi.org/10.1111/j.1574-6941.2006.00113.x

Aksmann A, Tukaj Z (2008) Intact anthracene inhibits photosynthesis in algal cells: a fluorescence induction study on Chlamydomonas reinhardtii cw92 strain. Chemosphere 74(1):26–32. https://doi.org/10.1016/j.chemosphere.2008.09.064

Alcaide M, Stogios PJ, Lafraya A et al (2015) Pressure adaptation is linked to thermal adaptation in salt-saturated marine habitats. Environ Microbiol 17:332–345. https://doi.org/10.1111/1462-2920.12660

Al-Hasan RH, Al-Bader DA, Sorkhoh NA, Radwan SS (1998) Evidence for n-alkane consumption and oxidation by filamentous cyanobacteria from oil-contaminated coasts of the Arabian Gulf. Marine Biology 130(3):521–527

Amin SA, Green DH, Hart MC et al (2009) Photolysis of iron-siderophore chelates promotes bacterial-algal mutualism. Proc Natl Acad Sci U S A 106:17071–17076. https://doi.org/10.1073/pnas.0905512106

Amin SA, Parker MS, Armbrust EV (2012) Interactions between diatoms and bacteria. Microbiology and Molecular Biology Reviews 76(3):667–684

Amin SA, Hmelo LR, van Tol HM et al (2015) Interaction and signaling between a cosmopolitan phytoplankton and associated bacteria. Nature 522:98–101. https://doi.org/10.1038/nature14488

Ashraf M (1994) Genetic variation for salinity tolerance in spring wheat. Hereditas 120:99–104. https://doi.org/10.1111/j.1601-5223.1994.00099.x

Atlas RM (1981) Microbial degradation of petroleum hydrocarbon: an environmental perspective. Microbiol Rev 45:180–209

Atlas RM (1991) Microbial hydrocarbon degradation, bioremediation of oil spills. J Chem Technol 52:149–156. https://doi.org/10.1002/jctb.280520202

Atlas R, Bragg J (2009) Bioremediation of marine oil spills: when and when not-the Exxon Valdez experience. Microbial Biotech 2(2):213–221. https://doi.org/10.1111/j.1751-7915.2008.00079.x

Atlas RM, Cerniglia CE (1995) Bioremediation of petroleum pollutants. Bioscience 45(5):1–10. https://doi.org/10.2307/1312494

Atlas RM, Hazen TC (2011) Oil biodegradation and bioremediation: a tale of the two worst spills in U.S. history. Environ Sci Technol 45(16):6709–6715. https://doi.org/10.1021/es2013227

Bacosa HP, Liu Z, Erdner DL (2015) Natural sunlight shapes crude oil-degrading bacterial communities in northern Gulf of Mexico surface waters. Front Microbiol 6:1325. https://doi.org/10.3389/fmicb.2015.01325

Bargiela R, Mapelli F, Rojo D et al (2015) Bacterial population and biodegradation potential in chronically crude oil-contaminated marine sediments are strongly linked to temperature. Sci Rep 5:11651. https://doi.org/10.1038/srep11651

Beskoski VP, Gojgic-Cvijovic G, Milic J et al (2011) Ex-situ bioremediation of a soil contaminated by mazut (heavy residual fuel oil) – a field experiment. Chemosphere 83:34–40. https://doi.org/10.1016/j.chemosphere.2011.01.020

Binark N, Guven KC, Gezgin T et al (2000) Oil pollution of marine algae. Bull Environ Contam Toxicol 64:866–872. https://doi.org/10.1007/s0012800083

Bootpathy R (2000) Factors limiting bioremediation technologies. BioresTechnol 74:63–67. https://doi.org/10.1016/S0960-8524(99)00144-3

Bovio E, Gnavi G, Prigione V et al (2017) The culturable mycobiota of a Mediterranean marine site after an oil spill: isolation, identification and potential application in bioremediation. Sci Total Environ 576:310–318. https://doi.org/10.1016/j.scitotenv.2016.10.064

Brakstad OG, Nortug T, Throne-Holst M (2015) Biodegradation of dispersed Macondo oil in seawater at low temperature and different oil droplet sizes. Mar Pollut Bull 93:144–152. https://doi.org/10.1016/j.marpolbul.2015.02.006

Bruhn JB, Gram L, Belas R (2007) Production of antibacterial compounds and biofilm formation by Roseobacter species are influenced by culture conditions. Applied and environmental microbiology 73(2):442–450

Butler A (2005) Marine siderophores and microbial iron metabolism. Biometals 18:369–374. https://doi.org/10.1007/s10534-005-3711-0

Camilli R, Reddy CM, Yoerger DR et al (2010) Tracking hydrocarbon plume transport and biodegradation at deepwater horizon. Science 330:201–204. https://doi.org/10.1126/science.1195223

Camphuysen CJ (2007) Chronic oil pollution in Europe, a status report. Report Royal Netherlands Institute for Sea Research, commissioned by International Fund for Animal Welfare (IFAW), Brussels, p 85

Catania V, Santisi S, Signa G et al (2015) Intrinsic bioremediation potential of a chronically polluted marine coastal area. Mar Pollut Bull 99:138–149. https://doi.org/10.1016/j.marpolbul.2015.07.042

Cerniglia CE (1981) Aromatic hydrocarbons: metabolism by bacteria, fungi and algae. In: Hodgson E, Bend JR, Philpot RM (eds) Reviews in biochemical toxicology. Elsevier/North Holland, New York, pp 321–361

Cerniglia C (1992) Biodegradation of polycyclic aromatic hydrocarbons. Biodegradation 3:351–368. https://doi.org/10.1007/BF00129093

Cerniglia CE, Gibson DT, Van Baalen C (1979) Algal oxidation of aromatic hydrocarbons: formation of 1-naphthol from naphthalene by *Agmenellum quadruplicatum* strain PR-6. Biochem Biophys Res Comm 88:50–58. https://doi.org/10.1016/0006-291X(79)91695-4

Cerniglia C, Van Baalen C, Gibson DT (1980a) Metabolism of naphthalene by the cyanobacterium *Oscillatoria* sp., strain JCM. Microbiology 116:485–494. https://doi.org/10.1099/00221287-116-2-485

Cerniglia CE, Gibson DT, Van Baalen C (1980b) Oxidation of naphthalene by cyanobacteria and microalgae. J of Gen Microbiol 116:495–500. https://doi.org/10.1099/00221287-116-2-495

Cerniglia CE, Van Baalen C, Gibson DT (1980c) Oxidation of biphenyl by the cyanobacterium *Oscillatoria* sp. strain JCM. Arch Microbiol 125:203–209. https://doi.org/10.1007/BF00446877

Cerniglia CE, Gibson DT, Van Baalen C (1982) Naphthalene metabolism by diatoms isolated from the Kachemak Bay Region of Alaska. J Gen Microbiol 128:987–990. https://doi.org/10.1099/00221287-128-5-987

Chandra S, Sharma R, Singh K et al (2013) Application of bioremediation technology in the environment contaminated with petroleum hydrocarbon. Ann Microbiol 63:417–431. https://doi.org/10.1007/s13213-012-0543-3

Chaillan F, Gugger M, Saliot A, Coute A, Oudot J (2006) Role of cyanobacteria in the biodegradation of crude oil by a tropical cyanobacterial mat. Chemosphere 62(10):1574–1582

Chaudhry Q, Blom-Zandstra M, Gupta S et al (2005) Utilising the synergy between plants and rhizosphere microorganisms to enhance breakdown of organic pollutants in the environment. Environ Sci Pollut Res 12:34–48. https://doi.org/10.1065/espr2004.08.213

Clarens A, Resurreccion E, White M et al (2010) Environmental life cycle comparison of algae to other bioenergy feedstocks. Environ Sci Technol 44:1813–1819. https://doi.org/10.1021/es902838n

Clark RC, Brown DW (1977) Petroleum: properties and analyses in biotic and abiotic systems. In: Malins DC (ed) Effects of petroleum on arctic and subarctic marine environments and organisms, vol I. Academic Press, New York, pp 1–89

Cohen Y (2002) Bioremediation of oil by marine microbial mats. Int Microbiol 5:189–193. https://doi.org/10.1007/s10123-002-0089-5

Cole JJ (1982) Interactions between bacteria and algae in aquatic ecosystems. Ann rev Ecol sys 13:291– 314. https://doi.org/10.1146/annurev.es.13.110182.001451

Cooney JJ, Silver SA, Beck EA (1985) Factor influencing hydrocarbon degradation at three freshwater lakes. Microb Ecol 11:127–137. https://doi.org/10.1007/BF02010485

Coulon FBA, McKew AM, Osborn TJ et al (2007) Effects of temperature and biostimulation on oil-degrading microbial communities in temperate estuarine waters. Environ Microbiol 9:177–186. https://doi.org/10.1111/j.1462-2920.2006.01126.x

Coulon F, Chronoupolou P-M, Fahy A et al (2012) Central role of dynamic tidal biofilms dominated by aerobic hydrocarbonoclastic bacteria and diatoms in the biodegradation of hydrocarbons in coastal mudflats. Appl Environ Microbiol 78:3638–3648. https://doi.org/10.1128/AEM.00072-12

Crisafi F, Giuliano L, Yakimov MM et al (2016) Isolation and degradation potential of a cold-adapted oil/PAH-degrading marine bacterial consortium from Kongsfjorden (Arctic region). Rend Lincei Sci Fis Nat 27(1):261–270. https://doi.org/10.1007/s12210-016-0550-6

Croft MT, Lawrence AD, Raux-Deery E et al (2005) Algae acquire vitamin B12 through a symbiotic relationship with bacteria. Nature 438:90–93. https://doi.org/10.1038/nature04056

Daffonchio D, Ferrer M, Mapelli F et al (2013) Bioremediation of southern Mediterranean oil polluted sites comes of age. New Biotechnol 30:743–748. https://doi.org/10.1016/j.nbt.2013.05.006

Danchin A, Braham S (2017) Coenzyme B12 synthesis as a baseline to study metabolite contribution of animal microbiota. Microb Biotechnol 10:688–701. https://doi.org/10.1111/1751-7915.12722

Dashti N, Ali N, Eliyas M et al (2015) Most hydrocarbonoclastic bacteria in the total environment are diazotrophic, which highlights their value in the bioreme-diation of hydrocarbon contaminants. Microbes Environ 30:70–75. https://doi.org/10.1264/jsme2.ME14090

Dawson KS, Schaperdoth I, Freeman KH et al (2013) Anaerobic biodegradation of the isoprenoid biomarkers pristane and phytane. Org Geochem 65:118–126. https://doi.org/10.1016/j.orggeochem.2013.10.010

Demaneche S, Meyer C, Micoud J, Louwagie M, Willison JC, Jouanneau Y (2004) Identification and functional analysis of two aromatic-ring-hydroxylating dioxygenases from a Sphingomonas strain that degrades various polycyclic aromatic hydrocarbons. Applied and Environmental Microbiology 70(11):6714–6725

de Llasera MPO, de Jesus O-EJ, Diaz-Flores G et al (2016) Biodegradation of benzo[α] pyrene by two freshwater microalgae *Selenastrum capricornutum* and *Scenedesmus acutus*: a comparative study useful for bioremediation. Environ Sci Pollut Res 23:3365–3375. https://doi.org/10.1007/s11356-015-5576-2

De Oteyza TG, Grimalt JO, Diestra E et al (2004) Changes in the composition of polar and a polar crude oil fractions under the action of *Microcoleus* consortia. Appl Microbiol Biotechnol 66:226–232. https://doi.org/10.1007/s00253-004-1694-3

Decho AW, Gutierrez T (2017) Microbial extracellular polymeric substances (EPSs) in ocean systems. Front Microbiol 8(922). https://doi.org/10.3389/fmicb.2017.00922

Denaro R, D'Auria G, Di Marco G et al (2005) Assessing terminal restriction fragment length polymorphism suitability for the description of bacterial community structure and dynamics in hydrocarbon-polluted marine environments. Environ Microbiol 7:78–87. https://doi.org/10.1111/j.1462-2920.2004.00685.x

Denaro R, Crisafi F, Russo D et al (2014) Alcanivorax borkumensis produces an extracellular siderophore in iron-limitation condition maintaining the hydrocarbon-degradation efficiency. Mar Genomics 17:43–52. https://doi.org/10.1016/j.margen.2014.07.004

Dewapriya P, Kim SK (2014) Marine microorganisms: an emerging avenue in modern nutraceuticals and functional foods. Food Res Int 56:115–125. https://doi.org/10.1016/j.foodres.2013.12.022

Dhillon A, Edwards KJ, Webb E et al (2005) Marinobacter aquaeolei gene expression studies for clues to neutrophilic iron oxidation. In: NASA astrobiology institute biennial meeting, abstract 829. University of Colorado, Boulder

Ding Q, Huang X, Hu H et al (2017) Impact of pyrene and cadmium co-contamination on prokaryotic community in coastal sediment microcosms. Chemosphere 188:320–328. https://doi.org/10.1016/j.chemosphere.2017.08.124

Dittami SM, Duboscq-Bidot L, Perennou M et al (2016) Host–microbe interactions as a driver of acclimation to salinity gradients in brown algal cultures. ISME J 10:51–63. https://doi.org/10.1038/ismej.2015.104

Duran R, Cravo-Laureau C (2016) Role of environmental factors and microorganisms in determining the fate of polycyclic aromatic hydrocarbons in the marine environment. FEMS Microbiol Rev 40:814–830. https://doi.org/10.1093/femsre/fuw031

Dutta TK, Harayama S (2001) Biodegradation of n-alkylcycloalkanes and n-alkylbenzenes via new pathways in *Alcanivorax* sp. strain MBIC 4326. Appl Environ Microb 67:1970–1974. https://doi.org/10.1128/AEM.67.4.1970-1974.2001

Dyksterhouse SE, Gray JP, Herwig RP et al (1995) *Cycloclasticus pugetii* gen. nov. sp. nov., an aromatic hydrocarbon-degrading bacterium from marine sediments. Int J Syst Bacteriol 45:116–123. https://doi.org/10.1099/00207713-45-1-116

Ellis B (1997) Degradation of phenolic compounds by fresh water algae. Plant Sci Let 8 (3):213–216. https://doi.org/10.1016/0304-4211(77)90183-3

Eliana Gattullo C, Bährs H, Steinberg CEW, Loffredo E (2012) Removal of bisphenol A by the freshwater green alga Monoraphidium braunii and the role of natural organic matter. Science of The Total Environment 416:501–506

Farrington JF, McDowell JE (2004) Mixing and water. Oceanus 43(1):46–49. https://doi.org/10.1002/pfi.4140430210

Fathepure BZ (2014) Recent studies in microbial degradation of petroleum hydrocarbons in hypersaline environments. Front Microbiol 5:1–16. https://doi.org/10.3389/fmicb.2014.00173

Fernández-Macho J (2016) Risk assessment for marine spills along European coastlines. Mar Pollut Bull 113(1–2):200–210. https://doi.org/10.1016/j.marpolbul.2016.09.015

Flemming H-C, Neu TR, Wozniak DJ (2007) The EPS matrix: the 'house of biofilm cells'. J Bacteriol 189:7945–7947. https://doi.org/10.1128/JB.00858-07

Foflonker F, Price DC, Qiu H et al (2014) Genome of the halotolerant green alga *Picochlorum* sp. reveals strategies for thriving under fluctuating environmental conditions. Environ Microbiol. https://doi.org/10.1111/1462-2920.12541

Forney FW, Markovetz AJ (1970) Subterminal oxidation of aliphatic hydrocarbons. J Bacteriol 102:281–282

Frometa J, De Lorenzo ME, Pisarski EC et al (2017) Toxicity of oil and dispersant on the deep water gorgonian octocoral Swiftia exserta, with implications for the effects of the Deepwater Horizon oil spill. Mar Pollut Bull 122:91–99. https://doi.org/10.1016/j.marpolbul.2017.06.009

Fuentes-Grünewald C, Garcés E, Rossi S et al (2009) Use of the dinoflagellate *Karlodinium veneficum* as a sustainable source of biodiesel production. J Indus Microbiol Biotechnol 36 (9):1215–1224. https://doi.org/10.1007/s10295-009-0602-3

Fuentes-Grünewald C, Bayliss C, Fonlut F, Chapuli E (2016) Long-term dinoflagellate culture performance in a commercial photobioreactor: Amphidinium carterae case. Bioresource technology 218:533–540

Gao W, Cui Z, Li Q et al (2012) Marinobacter nanhaiticus sp. nov., polycyclic aromatic hydrocarbon-degrading bacterium isolated from sediment of the South China Sea. Anton Van Leeuwen. https://doi.org/10.1007/s10482-012-9830-z

Gauthier MJ, Lafay B, Christen R et al (1992) *Marinobacter hydrocarbonoclasticus* gen. nov., sp. nov., a new, extremely halotolerant, hydrocarbon-degrading marine bacterium. Int J Syst Bacteriol 42:568–576. https://doi.org/10.1099/00207713-42-4-568

Genovese M, Crisafi F, Denaro R et al (2014) Effective bioremediation strategy for rapid in situ cleanup of anoxic marine sediments in mesocosm oil spill simulation. Front Microbiol 5:162. https://doi.org/10.3389/fmicb.2014.00162

GESAMP Group of Experts on the Scientific Aspects of Marine Environmental Protection (2007) Estimates of oil entering the marine environment from sea-based activities. Rep Stud GESAMP No. 75. London

Ghosal D, Ghosh S, Dutta TK et al (2016) Current state of knowledge in microbial degradation of polycyclic aromatic hydrocarbons (PAHs): a review. Front Microbiol 7:1369. https://doi.org/10.3389/fmicb.2016.01369

Golyshin PN, Chernikova TN, Abraham WR et al (2002) Oleiphilaceae fam. Nov., to include *Oleiphilus messinensis* gen. Nov., sp nov., a novel marine bacterium that obligately utilizes hydrocarbons. Int J Syst Evol Microbiol 52:901–911. https://doi.org/10.1099/ijs.0.01890-0

Gomez F, Sartaj M (2014) Optimization of Field scale biopiles for bioremediation of petroleum hydrocarbon contaminated soil at low temperature conditions by response surface methodology (RSM). Int Biodet Biodegr 89:103–109. https://doi.org/10.1016/j.ibiod.2014.01.010

Goñi-Urriza M, Duran R (2018) Impact of petroleum contamination on microbial Mats. Microbial Commun Utilizing Hydrocarbons Lipids Members Metagenomics Ecophysiol 2018:1–17. https://doi.org/10.1007/978-3-319-60063-5_14-1

Gregson BH, Metodieva G, Metodiev MV et al (2018) Differential protein expression during growth on medium versus long-chain alkanes in the obligate marine hydrocarbon-degrading bacterium *Thalassolituus oleivorans* MIL-1. Front Microbiol 9:3130. https://doi.org/10.3389/fmicb.2018.03130

Grotzschel S, Koster J, Abed RMM, de Beer D (2002) Degradation of petroleum model compounds immobilized on clay by a hypersaline microbial mat. Biodegradation 13:273–283. https://doi.org/10.1023/A:1021263009377

Guerriero C, Bianchi F, Cairns J et al (2011) Policies to clean-up toxic industrial contaminated sites of Gela and Priolo: a cost-benefit analysis. Environ Health 10:68. https://doi.org/10.1186/1476-069X-10-68

Gutierrez T, Aitken MD (2014) Role of methylotrophs in the degradation of hydrocarbons during the Deepwater horizon oil spill. ISME J 8:2543–2545. https://doi.org/10.1038/ismej.2014.88

Gutierrez T, Nichols PD, Whitman WB et al (2012) Porticoccus hydrocarbonoclasticus sp. nov., an aromatic hydrocarbon-degrading bacterium identified in laboratory cultures of marine phytoplankton. Appl Environ Microbiol 78:628–637. https://doi.org/10.1128/AEM.06398-11

Gutierrez T, Berry D, Yang T et al (2013) Role of bacterial exopolymers in the fate of the oil released during the Deepwater Horizon oil spill. PLoS One 8:e67717. https://doi.org/10.1139/f76-098

Handley KM, Lloyd JR (2013) Biogeochemical implications of the ubiquitous colonization of marine habitats and redox gradients by *Marinobacter* species. Front Microbiol 4:136. https://doi.org/10.3389/fmicb.2013.00136

Handley KM, Héry M, Lloyd JR (2009a) Marinobacter santoriniensis sp. nov., an arsenate-respiring and arsenite-oxidizing bacterium isolated from hydrothermal sediment. Int J Syst Evol Microbiol 59:886–892. https://doi.org/10.1099/ijs.0.003145-0

Handley KM, Héry M, Lloyd JR (2009b) Redox cycling of arsenic by the hydrothermal marine bacterium *Marinobacter santoriniensis*. Environ Microbiol 11:1601–1611. https://doi.org/10.1111/j.1462-2920.2009.01890.x

Hara A, Syutsubo K, Harayama S (2003) *Alcanivorax* which prevails in oil-contaminated seawater exhibits broad substrate specificity for alkane degradation. Environ Microbiol 5:746–753. https://doi.org/10.1046/j.1468-2920.2003.00468.x

Harayama S, Kishira H, Kasai Y et al (1999) Petroleum biodegradation in marine environments. J Mol Microbiol Biotechnol 1:63–70

Harrington GW, Beach DH, Dunham JE et al (1970) The polyunsaturated fatty acids of marine dinoflagellates. J Protozool 17:213–219. https://doi.org/10.1111/j.1550-7408.1970.tb02359.x

Hazen TC, Dubinsky EA, De Santis TZ et al (2010) Deep-sea oil plume enriches indigenous oil-degrading bacteria. Science 330:204–208. https://doi.org/10.1126/science.1195979

He Y, Feng X, Fang J et al (2015) Metagenome and metatranscriptome revealed a highly active and intensive sulfur cycle in an oil-immersed hydrothermal chimney in Guaymas Basin. Front Microbiol 6:1236. https://doi.org/10.3389/fmicb.2015.01236

Head IM, Jones DM, Roling WFM (2006) Marine microorganisms make a meal of oil. Nature Rev Microbiol 4:173–182. https://doi.org/10.1038/nrmicro1348

Hedlund BP, Geiselbrecht AD, Staley JT (2001) *Marinobacter* strain NCE312 has a *Pseudomonas*-like naphthalene dioxygenase. FEMS Microbiol Lett 201:47–51. https://doi.org/10.1016/S0378-1097(01)00238-5

Helliwell KE (2017) The roles of B vitamins in phytoplankton nutrition: new perspectives and prospects. New Phytol 216:62–68. https://doi.org/10.1111/nph.14669

Hong Y, Yuan D, Lin Q, Yang T (2008) Accumulation and biodegradation of phenanthrene and fluoranthene by the algae enriched from a mangrove aquatic ecosystem. Mar Poll Bull 56:1400–1405. https://doi.org/10.1016/j.marpolbul.2008.05.003

Huang HB, Huang HL, Zhang L et al (2014) Photooxidation of gaseous benzene by 185 nm VUV irradiation. Environ Eng Sci 31:481–486. https://doi.org/10.1089/ees.2014.0100

Ibraheem IBM (2010) Biodegradability of hydrocarbons by cyanobacteria. J Phycol 46:818–824. https://doi.org/10.1111/j.1529-8817.2010.00865.x

Ichor T, Okerentugba PO, Okpokwasili GC (2016) Biodegradation of Total petroleum hydrocarbon by a consortium of cyanobacteria isolated from crude oil polluted brackish waters of Bodo Creeks in Ogoniland, Rivers State. Res J Environ Toxicol 10(1):16–27. https://doi.org/10.3923/rjet.2016.16.27

Itopf.com (2016) Environmental Effects - ITOPF. Available at: http://www.itopf.com/knowledge-resources/documents-guides/environmental-effects/

Jensen S, Hovland M, Lynch MDJ et al (2019) Diversity of deep-water coral-associated bacteria and comparison across depth gradients. FEMS Microbiol Ecol 95:7. https://doi.org/10.1093/femsec/fiz091

Jung HA, Islam MN, Lee CM, Jeong HO, Chung HY, Woo HC, Choi JS (2012) Promising antidiabetic potential of fucoxanthin isolated from the edible brown algae Eisenia bicyclis and Undaria pinnatifida. Fisheries Science 78(6):1321–1329

Jewett SC, Dean TA, Smith RO et al (1999) ‘Exxon Valdez’ oil spill: impacts and recovery in the soft-bottom benthic community in and adjacent to eelgrass beds. Mar Ecol Prog Ser 185:59–83. https://doi.org/10.3354/meps185059

Jones JG, Knight M, Byron JA (1970) Effect of gross pollution by kerosine hydrocarbons on the microflora of a moorland soil. Nature 227:1166. https://doi.org/10.1038/2271166a0

Kalmykova Y, Björklund K, Strömvall AM et al (2013) Partitioning of polycyclic aromatic hydrocarbons, alkylphenols, bisphenol A and phthalates in landfill leachates and stormwater. Water Res 47:1317–1328. https://doi.org/10.1016/j.watres.2012.11.054

Kasai Y, Kishira H, Harayama S (2002) Bacteria belonging to the genus *Cycloclasticus* play a primary role in the degradation of aromatic hydrocarbons released in a marine environment. Appl Environ Microbiol 68:5625–5633. https://doi.org/10.1128/AEM.68.11.5625-5633.2002

Ke L, Luo L, Wang P et al (2010) Effects of metals on biosorption and biodegradation of mixed polycyclic aromatic hydrocarbons by a freshwater green alga *Selenastrum capricornutum*. Bioresour Technol 101:6961–6972. https://doi.org/10.1016/j.biortech.2010.04.011.ß

Khudur LS, Shahsavari E, Miranda AF et al (2015) Evaluating the efficacy of bioremediating a diesel-contaminated soil using ecotoxicological and bacterial community indices. Envir Scien Poll Res Int 22(14809):14819. https://doi.org/10.1007/s11356-015-4624-2

Kingston PF (2002) Long-term environmental impact of oil spills. Spill Sci Technol Bull 7:53–61. https://doi.org/10.1016/S1353-2561(02)00051-8

Klotz P, Schloss IR, Dumont D (2018) Effects of a chronic oil spill on the planktonic system in San Jorge Gulf, Argentina: a one-vertical-dimension modeling approach. Oceanography 31 (4):81–91. https://doi.org/10.5670/oceanog.2018.413

Kobayashi H, Rittman BE (1982) Microbial removal of hazardous organic compounds. Environ Sci Technol 16:170–183. https://doi.org/10.1021/es00097a002

Kotani T, Kawashima Y, Yurimoto H et al (2006) Gene structure and regulation of alkane monooxygenases in propane-utilizing *Mycobacterium* sp. TY-6 and *Pseudonocardia* sp. TY-7. J Biosci Bioeng 102(3):184–192. https://doi.org/10.1263/jbb.102.184

Kryachko Y, Dong X, Sensen C et al (2012) Compositions of microbial communities associated with oil and water in a mesothermic oil field. Anton Leeuw 101(3):493–506. https://doi.org/10.1007/s10482-011-9658-y

Kube M, Chernikova TN, Al-Ramahi Y et al (2013) Genome sequence and functional genomic analysis of the oil-degrading bacterium Oleispira Antarctica. Nat Commun 4:2156. https://doi.org/10.1038/ncomms3156

Kubicki S, Bollinger A, Katzke N et al (2019) Marine biosurfactants: biosynthesis, structural diversity and biotechnological applications. Mar Drugs 17(7):408. https://doi.org/10.3390/md17070408

Landry MR, Constantinou J, Latasa M et al (2000) Biological response to iron fertilization in the eastern equatorial Pacific (IronEx II). III. Dynamics of phytoplankton growth and microzooplankton grazing. Mar Ecol Prog Ser 201:73–83. https://doi.org/10.3354/meps201057

Leahy JG, Colwell RR (1990) Microbial degradation of hydro- carbons in the environment. Microbiol Rev 54:305–315

Lea-Smith JD, Biller SJ, Davey MP et al (2015) Contribution of cyanobacterial alkane production to the ocean hydrocarbon cycle. Proc Natl Acad Sci U S A 112:13591–13596. https://doi.org/10.1073/pnas.1507274112

Lei AP, Hu ZL, Wong YS et al (2007) Removal of fluoranthene and pyrene by different microalgal species. Bioresour Technol 98:273–280. https://doi.org/10.1016/j.biortech.2006.01.012

Li R, Zi X, Wang X et al (2013) Marinobacter hydrocarbonoclasticus NY-4, a novel denitrifying, moderately halophilic marine bacterium. Spring 2:346. https://doi.org/10.1186/2193-1801-2-346

Li W, Huang JM, Zhang PW et al (2019) Periodic and spatial spreading of alkanes and Alcanivorax Bacteria in deep waters of the Mariana trench. Appl Environ Microbiol. https://doi.org/10.1128/AEM.02089-18

Lian Z, Xu J, Wang Z et al (2018) Nanosecond laser induced underwater superoleophobic and underoil superhydropho–bic mesh for oil/water separation. Langmuir 34(9):2981–2988. https://doi.org/10.1021/acs.langmuir.7b03986

Lindgren JF, Hassellov IM, Dahllof I (2012) Meiofaunal and bacterial community response to diesel additions in a microcosm study. Mar Pollut Bull 64:595–601. https://doi.org/10.1016/j.marpolbul.2011.12.014

Lindgren JF, Wilewska-Bien M, Granhag L (2016) Discharges to the Sea. In: Andersson K, Brynolf S, Lindgren FJ, Wilewska-Bien M (eds) Shipping and the environment: improving environmental performance in marine transportation. Springer, Berlin, Heidelberg, pp 125–295. https://doi.org/10.1007/978-3-662-49045-7_4

Lindquist B, Warshawsky D (1985a) Stereospecificity in algal oxidation of the carcinogen benzo[a] pyrene. Experientia 41:767–769. https://doi.org/10.1007/BF02012587

Lindquist B, Warshawsky D (1985b) Identification of the 11,12- dihydro-11,12 dihydroxybenzo[a] pyrene as a major metabolite produced by the green alga *Selenastrum capricornutum*. Biochem Biophys Res Commun 130:71–75. https://doi.org/10.1016/0006-291X(85)90383-3

Liu C, Shao Z (2005) Alcanivorax dieselolei sp. nov., a novel alkane-degrading bacterium isolated from sea water and deep-sea sediment. Int J Syst Evol Microbiol 55:1181–1186. https://doi.org/10.1099/ijs.0.63443-0

Liu Y, Liu Y, Li N et al (2019) Effect of oil spill stress on fatty acid stable carbon isotope composition of *Ulva pertusa*. Sci Total Environ 649:1443–1451. https://doi.org/10.1016/j.scitotenv.2018.08.377

Luo L, Wang P, Lin L et al (2014) Removal and transformation of high molecular weight polycyclic aromatic hydrocarbons in water by live and dead microalgae. Process Biochem 49 (10):1723–1732. https://doi.org/10.1016/j.procbio.2014.06.026

Luther M (1990) Degradation of different substituted aromatic compounds as nutrient sources by the green alga *Scenedesmus obliquus*. Dechema Biotechnol 4:613–615

Luther M, Soeder CJ (1987) Some naphthalene sulphonic acids as Sulphur sources for the green microalga, *Scenedesmus obliquus*. Chemosphere 16:1565–1578. https://doi.org/10.1016/0045-6535(87)90097-X

Luther M, Soeder CJ (1991) 1-Naphthalenesulfonic acid and sulfate as sulfur sources for the green alga *Scenedesmus obliquus*. Wat Res 25(3):299–307. https://doi.org/10.1016/0043-1354(91)90009-F

Marietou A, Chastain R, Scoma A et al (2018) The effect of hydrostatic pressure on enrichments of hydrocarbon degrading microbes from the Gulf of Mexico following the Deepwater Horizon oil spill. Front Microbiol 9:808. https://doi.org/10.3389/fmicb.2018.00808

Martinez JS, Zhang GP, Holt PD et al (2000) Self-assembling amphiphilic siderophores from marine bacteria. Science 287:1245–1247. https://doi.org/10.1126/science.287.5456.1245

Matar S, Hatch LF (1994) Chemistry of petrochemical processes. Gulf Publishing Company, Houston

Mahdavi H, Prasad V, Yang L, Ulrich AC (2015) In situ biodegradation of naphthenic acids in oil sands tailings pond water using indigenous algae–bacteria consortium. Bioresource Technology 187:97–105

Mayali X (2018) Editorial: metabolic interactions between bacteria and phytoplankton. Front Microbiol 9:727. https://doi.org/10.3389/fmicb.2018.00727

McFarlin KM, Perkins MJ, Field JA et al (2018) Biodegradation of crude oil and Corexit 9500 in arctic seawater. Front Microbiol 9:1788. https://doi.org/10.3389/fmicb.2018.01788

McGenity TJ, Folwell BD, McKew BA et al (2012) Marine crude-oil biodegradation: a central role for interspecies interactions. Aquat Biosyst 8:10. https://doi.org/10.1186/2046-9063-8-10

McKew BA, Coulon F, Yakimov MM et al (2007) Efficacy of intervention strategies for bioremediation of crude oil in marine systems and effects on indigenous hydrocarbonoclastic bacteria. Environ Microbiol 9:1562–1571. https://doi.org/10.1111/j.1462-2920.2007.01277.x

Medina-Sánchez JM, Villar-Argaiz M, Carrillo P (2002) Modulation of the bacterial response to spectral solar radiation by algae and limiting nutrients. Freshw Biol 47:2191–2204. https://doi.org/10.1046/j.1365-2427.2002.00969.x

Melcher RJ, Apitz SE, Hemmingsen BB (2002) Impact of irradiation and polycyclic aromatic hydrocarbon spiking on microbial populations in marine sediment for future aging and biodegradability studies. Appl Environ Microbiol 68:2858–2868. https://doi.org/10.1128/AEM.68.6.2858-2868.2002

Messina E, Denaro R, Crisafi F et al (2016) Genome sequence of obligate marine polycyclic aromatic hydrocarbons-degrading bacterium *Cycloclasticus* sp. 78-ME, isolated from petroleum deposits of the sunken tanker Amoco Milford Haven, Mediterranean Sea. Mar Genomics 25:11–13. https://doi.org/10.1016/j.margen.2015.10.006

Mou X, Sun S, Edwards RA, Hodson RE, Moran MA (2008) Bacterial carbon processing by generalist species in the coastal ocean. Nature 451(7179):708–711

Morgan P, Watkinson RJ (1990) Assessment of the potential for in situ biotreatment of hydrocarbon-contaminated soils. Water Sci Technol 22(6):63–68. https://doi.org/10.2166/wst.1990.0052

Morohoshi T, Oi T, Aiso H et al (2018) Biofilm formation and degradation of commercially available biodegradable plastics films by bacterial consortiums in freshwater environments. Microbes Environ 33:332–335. https://doi.org/10.1264/jsme2.ME18033

Mounier J, Camus A, Mitteau I et al (2014) The marine bacterium *Marinobacter hydrocarbonoclasticus* SP17 degrades a wide range of lipids and hydrocarbons through the formation of oleolytic biofilms with distinct gene expression profiles. FEMS Microbiol Ecol 90 (3):816–831. https://doi.org/10.1111/1574-6941.12439

Mounier J, Hakil F, Branchu P, Naïtali M, Goulas P, Sivadon P, Grimaud R (2018) AupA and AupB are outer and inner membrane proteins involved in alkane uptake in marinobacter hydrocarbonoclasticus SP17. Mbio 9(3)

Moyer CL, Morita RY (2007) Psychrophiles and psychrotrophs. In: eLS Chichester: John Wiley and Sons Ltd https://doi.org/10.1002/9780470015902.a0000402.pub2

Mulkins-Phillips GJ, Stewart JE (1974) Distribution of hydrocarbon-utilizing bacteria in orthwestern Atlantic waters and coastal sediments. Can J Microbiol 20:955–962. https://doi.org/10.1139/m74-147

Müller J, Overmann J (2011) Close interspecies interactions between prokaryotes from sulfureous environments. Front Microbiol 2:146. https://doi.org/10.3389/fmicb.2011.00146

Munoz R, Guieysse B, Mattiasson B (2003) Phenanthrene biodegradation by an algal-bacterial consortium in two-phase partitioning bioreactors. Appl Microbiol Biotechnol 61(3):261–267. https://doi.org/10.1007/s00253-003-1231-9

Narro ML, Cerniglia CE, van Baalen C et al (1992) Metabolism of phenanthrene by the marine cyanobacterium *Agmenellum quadruplicatum* PR-6. Appl Environ Microbiol 58:1351–1359

Netzer R, Henry IA, Ribicic D et al (2018) Petroleum hydrocarbon and microbial community structure successions in marine oil-related aggregates associated with diatoms relevant for Arctic conditions. Mar Pollut Bull 135:759–768. https://doi.org/10.1016/j.marpolbul.2018.07.074

Neu TR, Lawrence JR (2016) The extracellular matrix: an intractable part of biofilm systems. In: Flemming H-C, Wingender J, Neu TR (eds) The perfect slime – microbial extracellular polymeric substances. IWA Publishing, London, pp 25–60

Newman DK, Kolter R (2000) A role for excreted quinones in extracellular electron transfer. Nature 405:94–97. https://doi.org/10.1038/35011098

Niepceron M, Portet-Koltalo F, Merlin C et al (2010) Both *Cycloclasticus* spp. and *Pseudomonas* spp. as PAH-degrading bacteria in the Seine estuary (France). FEMS Microbiol Ecol 71:137–147. https://doi.org/10.1111/j.1574-6941.2009.00788.x

Nowicka B, Kruk J (2010) Occurrence, biosynthesis and function of isoprenoid quinones. Biochem Biophys Acta 1797:1587–1605. https://doi.org/10.1016/j.bbabio.2010.06.007

O' Brien RD (ed) (2004) Fats and oils formulation and processing for application. CRC Press, New York

Oliver RL, Ganf GG (2000) Freshwater blooms. In: Whitton BA, Potts M (eds) The ecology of cyanobacteria: their diversity in time and space. Kluwer, Dordrecht, pp 149–194. https://doi.org/10.1007/0-306-46855-7_6

Oliveira FR, Patel AK, Jaisi DP et al (2017) Environmental application of biochar: Current status and perspectives. Bioresour Technol 246:110–122. https://doi.org/10.1016/j.biortech.2017.08.122

Ozhan K, Bargu S (2014) Distinct responses of Gulf of Mexico phytoplankton communities to crude oil and the dispersant Corexit® EC9500A under different nutrient regimes. Ecotoxicology 23(3):370–384. https://doi.org/10.1007/s10646-014-1195-9

Palacios OA, Gomez-Anduro G, Bashan Y et al (2016) Tryptophan, thiamine and indole-3-acetic acid exchange between *Chlorella sorokiniana* and the plant growth-promoting bacterium *Azospirillum brasilense*. FEMS Microbiol Ecol 92:1–11. https://doi.org/10.1093/femsec/fiw077

Parsons ML, Morrison W, Rabalais NN (2015) Phytoplankton and the Macondo oil spill: a comparison of the 2010 phytoplankton assemblage to baseline conditions on the Louisiana shelf. Environm Pollut 207:152–160. https://doi.org/10.1016/j.envpol.2015.09.019

Patel B, Hellgardt K (2015) Hydrothermal upgrading of algae paste in a continuous flow reactor. Bioresour Technol 191:460–468. https://doi.org/10.1016/j.biortech.2015.04.012

Potts LD, Perez-Calderon LJ, Gontikaki E et al (2018) Effect of spatial origin and hydrocarbon composition on bacterial consortia community structure and hydrocarbon biodegradation rates. FEMS Microbiol Ecol 94:127. https://doi.org/10.1093/femsec/fiy127

Prince RC (2005) The microbiology of marine spill bioremediation. In: Olivier B, Magot M (eds) Petroleum microbiology. ASM press, Washington, pp 35–54. https://doi.org/10.1128/9781555817589.ch16

Prouse NJ, Gordon DC, Keizer PD (1976) Effects of low concentration of oil accommodated in sea water on the growth of unialgal marine phytoplankton cultures. J Fish Res Board Can 33:810–818

Qiao N, Shao Z (2010) Isolation and characterization of a novel biosurfactant produced by hydrocarbon degrading bacterium *Alcanivoraxdieselolei* B-5. J Appl Microbiol 108:1207–1216. https://doi.org/10.1111/j.1365-2672.2009.04513.x

Quigg A, Passow U, Chin WC et al (2016) The role of microbial exopolymers in determining the fate of oil and chemical dispersants in the ocean: interactions of microbial exopolymers in oil and chemical dispersants. Limnol Oceanogr Lett 1:3–26. https://doi.org/10.1002/lol2.10030

Radwan SS, Al-Hasan RH (2000) Oil pollution and cyanobacteria. In: Whitton BA, Potts M (eds) The ecology of cyanobacteria. Kluwer, Dortretch, pp 307–319. https://doi.org/10.1007/0-306-46855-7_11

Radwan SS, Al-Hasan RH, Salamah S et al (2002) Bioremediation of oily sea water by bacteria immobilized in biofilms coating macroalgae. Int Biodeterior Biodegrad 50:55–59. https://doi.org/10.1016/S0964-8305(02)00067-7

Raghukumar C, Vipparty V, David JJ et al (2001) Degradation of crude oil by marine cyanobacteria. Appl Microbiol Biotechnol 57:433–436. https://doi.org/10.1007/s002530100784

Rahman RNZA, Ghazali FM, Salleh AB et al (2006) Biodegradation of hydrocarbon contamination by immobilized bacterial cells. J Microbiol 44(3):354–359

Ramanan R, Kim BH, Cho DH et al (2016) Algae–bacteria interactions: evolution, ecology and emerging applications. Biotechnol Adv 34:14–29. https://doi.org/10.1016/j.biotechadv.2015.12.003

Rippka R (1988) Isolation and purification of cyanobacteria. Meth Enzymol 167:3–27. https://doi.org/10.1016/0076-6879(88)67004-2

Rojo F (2009) Degradation of alkanes by bacteria. Environ Microbiol 11:2477–2490. https://doi.org/10.1111/j.1462-2920.2009.01948.x

Rontani JF, Bonin PC, Volkman JK (1999) Production of wax esters during aerobic growth of marine bacteria on isoprenoid compounds. Appl Environ Microbiol 65:221–230

Rubin-Blum M, Antony CP, Borowski C et al (2017) Short-chain alkanes fuel mussel and sponge *Cycloclasticus* symbionts from deep-sea gas and oil seeps. Nat Microbiol 2:17093. https://doi.org/10.1038/nmicrobiol.2017.93

Sabirova JS, Becker A, Lünsdorf H et al (2011) Transcriptional profiling of the marine oil-degrading bacterium *Alcanivorax borkumensis* during growth on *n*-alkanes: Transcriptomic responses of *Alcanivorax borkumensis*. FEMS Microbiol Lett 319:160–168. https://doi.org/10.1111/j.1574-6968.2011.02279.x

Sakuradani E, Ando A, Shimizu S et al (2013) Metabolic engineering for the production of polyunsaturated fatty acids by oleaginous fungus *Mortierella alpina* 1S-4. J Biosci Bioeng 116:417–422. https://doi.org/10.1016/j.jbiosc.2013.04.008

Santos FJ, Galceran MT (2003) Modern developments in gas chromatography-mass spectrometry-based environmental analysis. J Chromatogr A 1000: 125–51. https://doi.org/10.1016/S0021-9673(03)00305-4

Sanchez O, Diestra E, Esteve I et al (2005) Molecular characterization of an oil degrading cyanobacterial consortium. Microb Ecol 50:580–588. https://doi.org/10.1007/s00248-005-5061-4

Sanchez N, Brown EA, Olsen Y (2018) Effect of siderophore on iron availability in a diatom and a dinoflagellate species: contrasting response in associated bacteria. Front Mar Sci 5(2):118. https://doi.org/10.3389/fmars.2018.00118

Sardi AE, Renaud PE, Morais GC et al (2017) Effects of an in situ diesel oil spill on oxidative stress in the clam Anomalocardia flexuosa. Environ Pollut 230:891–901. https://doi.org/10.1016/j.envpol.2017.07.040

Schneiker S, Martins dos Santos VA, Bartels D et al (2006) Genome sequence of the ubiquitous hydrocarbon-degrading marine bacterium *Alcanivorax borkumensis*. Nat Biotechnol 24:997–1004. https://doi.org/10.1038/nbt1232

Schoeny R, Cody T, Warshawsky D, Radike MJ (1988) Metabolism of mutagenic polycyclic aromatic hydrocarbons by photosynthetic algal species. Mutat Res 197:289–302. https://doi.org/10.1016/0027-5107(88)90099-1

Selin R (2013) The outlook for energy: a view to 2040. In: proceedings of the 2013 South East Asia Petroleum Exploration Society (SEAPEX) Conference, Singapore, 8–11 April 2013

Severin T, Erdner DL (2019) The phytoplankton taxon-dependent oil response and its microbiome: correlation but not causation. Front Microbiol 10:385. https://doi.org/10.3389/fmicb.2019.00385

Sevilla E, Yuste L, Moreno R, Rojo F (2017) Differential expression of the three Alcanivorax borkumensis SK2 genes coding for the P450 cytochromes involved in the assimilation of hydrocarbons. Environ Microbiol Rep 9(6):797–808

Seyedsayamdost MR, Carr G, Kolter R et al (2011) Roseobacticides: small molecule modulators of an algal-bacterial symbiosis. J Am Chem Soc 133:18343–18349. https://doi.org/10.1021/ja207172s

Seymour JR, Amin SA, Raina JB, Stocker R (2017) Zooming in on the phycosphere: the ecological interface for phytoplankton–bacteria relationships. Nature microbiology 2(7):1–12

Sforza E, Pastore M, Spagni A, Bertucco A (2018) Microalgae-bacteria gas exchange in wastewater: how mixotrophy may reduce the oxygen supply for bacteria. Environmental Science and Pollution Research 25(28):28004–28014

Shieh WY, Jean WD, Lin Y-T, Tseng M (2003) Marinobacter lutaoensis sp. nov., a thermotolerant marine bacterium isolated from a coastal hot spring in Lutao, Taiwan. Can J Microbiol 49:244–252. https://doi.org/10.1139/w03-032

Sikkema J, De Bont JAM, Poolman B (1995) Mechanisms of membrane toxicity of hydrocarbons. Microbiol Rev 59:201–222

Silva AC, Fernando JS, de Oliveira S et al (2009) Bioremediation of marine sediments impacted by petroleum. Appl Biochem Biotechnol 153:58–66. https://doi.org/10.1007/s12010-008-8457-z

Simple KT, Cain RB, Schmidt S (1999) Biodegradation of aromatic compounds by microalgae. FEMS Microbiol Lett 170:291–300. https://doi.org/10.1111/j.1574-6968.1999.tb13386.x

Sorkhoh N, Al-Hasan R, Radwan et al (1992) Self-cleaning of the Gulf. Nature (Lond) 359:109. https://doi.org/10.1038/359109a0

Sorkhoh NA, Al-Hasan RH, Khanafer M et al (1995) Establishment of oil-degrading bacteria associated with cyanobacteria in oil-polluted soil. J Appl Bacteriol 78:194–199. https://doi.org/10.1111/j.1365-2672.1995.tb02842.x

Soto C, Hellebust JA, Hutchinsonan T et al (1975) Effect of naphthalene and aqueous crude oil extracts on the green flagellate *Chlamydomonas angulosa*. I. Growth. Can J Bot 53:109–117. https://doi.org/10.1139/b75-017

Soto C, Hellebust JA, Hutchinson TC (1977) Effect of naphthalene and aqueous crude oil extracts on the green flagellate *Chlamydomonas angulosa*. II. Changes in cellular composition. Can J Bot 55:2765–2777. https://doi.org/10.1139/b77-315

Sousa LP, Sousa AI, Alves FL et al (2016) Ecosystem services provided by a complex coastal region: challenges of classification and mapping. Sci Rep 6:22782. https://doi.org/10.1038/srep22782

Srivastava S, Kumar M (2019) Biodegradation of polycyclic aromatic hydrocarbons (PAHs): a sustainable approach. In: Shah S, Venkatramanan V, Prasad R (eds) Sustainable Green Technologies for Environmental Management. Springer, Singapore, pp 111–139. https://doi.org/10.1007/978-981-13-2772-8_6

Stal LJ (2010) Microphytobenthos as a biogeomorphological force in intertidal sediment stabilization. Ecol Engin 36:236–245. https://doi.org/10.1016/j.ecoleng.2008.12.032

Stal LJ, Bolhuis H, Cretoiu MS (2017) Phototrophic microbial Mats. In: Hallenbeck PC (ed) Modern Topics in the Phototrophic Prokaryotes Colorado. Springs, Boston, pp 295–318. https://doi.org/10.1007/978-3-319-46261-5_9

Suja LD, Chen X, Summers S, Paterson DM, Gutierrez T (2019) Chemical dispersant enhances microbial exopolymer (EPS) production and formation of marine oil/dispersant snow in surface waters of the subarctic northeast Atlantic. Frontiers in Microbiology 10:553

Szczybelski S, Kampen T, Vromans J et al (2018) Avoidance tests as a tool to detect sublethal effects of oil-impacted sediments. Environ Toxicol Chem 37(6):1757–1766. https://doi.org/10.1002/etc.4129

Taffi M, Paoletti N, Angione C (2014) Bioremediation in marine ecosystems: a computational study combining ecological modeling and flux balance analysis. Front Genet 5:319. https://doi.org/10.3389/fgene.2014.00319

Tang HY, Chen M, Ng S et al (2012) Continuous microalgae cultivation in a photobioreactor. Biotechnol Bioeng 109:2468–2474. https://doi.org/10.1002/bit.24516

Tansel B (2014) Propagation of impacts after oil spills at sea: categorization and quantification of local vs regional and immediate vs delayed impacts. Int J Disaster Risk Red 7:1–8. https://doi.org/10.1016/j.ijdrr.2013.11.001

Teramoto M, Ohuchi M, Hatmanti A et al (2011) Oleibacter marinus gen. nov., sp. nov., a bacterium that degrades petroleum aliphatic hydrocarbons in a tropical marine environment. Int J Syst Evol Microbiol 61:375–380. https://doi.org/10.1099/ijs.0.018671-0

Thompson H, Angelova A, Bowler B, Jones M, Gutierrez T (2017) Enhanced crude oil biodegradative potential of natural phytoplankton-associated hydrocarbonoclastic bacteria. Environmental microbiology 19(7):2843–2861

Toshchakov SV, Korzhenkov AA, Chernikova TN et al (2017) The genome analysis of Oleiphilus messinensis ME102 (DSM 13489T) reveals backgrounds of its obligate alkane-devouring marine lifestyle. Mar Genomics 36:41–47. https://doi.org/10.1016/j.margen.2017.07.005

Tripathi L, Twigg MS, Zompra A et al (2019) Biosynthesis of rhamnolipid by a *Marinobacter* species expands the paradigm of biosurfactant synthesis to a new genus of the marine microflora. Microb Cell Factories 18:164. https://doi.org/10.1186/s12934-019-1216-8

Troisi G, Barton S, Bexton S (2016) Impacts of oil spills on seabirds: unsustainable impacts of non-renewable energy. Int J Hydrogen Energ 41:16549–16555. https://doi.org/10.1016/j.ijhydene.2016.04.011

Uzoh CV, Ifeanyi V, Okwuwe C et al (2015) Effect of light on the biodegradation of crude oil by the algae *Closterium* species. J Nat Sci Res 5(22):112–118

Valentine DL, Fisher GB, Bagby SC et al (2014) Fallout plume of submerged oil from Deepwater horizon. Proc Natl Acad Sci U S A 111(45):15906–15911. https://doi.org/10.1073/pnas.1414873111

van Beilen JB, Marin MM, Smits THM (2006) Cytochrome P450 alkane hydroxylases of the CYP153 family are common in alkane-degrading eubacteria lacking integral membrane alkane hydroxylases. Appl Environ Microbiol 72:59–65. https://doi.org/10.1073/pnas.1414873111

Van Hamme JD, Singh A, Ward OP (2003) Recent advances in petroleum microbiology. Microbiol Mol Biol Rev 67:503–549. https://doi.org/10.1128/MMBR.67.4.503-549.2003

Varjani SJ (2017) Microbial degradation of petroleum hydrocarbons. Bioresour Technol 223:277–286. https://doi.org/10.1128/MMBR.67.4.503-549.2003

Varjani SJ, Rana DP, Jain AK et al (2015) Synergistic ex-situ biodegradation of crude oil by halotolerant bacterial consortium of indigenous strains isolated from on shore sites of Gujarat, India. Int Biodeterior Biodegrad 103:116–124. https://doi.org/10.1016/j.ibiod.2015.03.030

Vasudevan PT, Briggs M (2008) Biodiesel production - current state of the art and challenges. J Ind Microbiol Biot 35:421–430. https://doi.org/10.1007/s10295-008-0312-2

Vila J, Tauler M, Grifoll M (2015) Bacterial PAH degradation in marine and terrestrial habitats. Curr Op Biotechnol 33:95–102. https://doi.org/10.1016/j.copbio.2015.01.006

Viggor S, Juhanson J, Jõesaar M, Mitt M, Truu J, Vedler E, Heinaru A (2013) Dynamic changes in the structure of microbial communities in Baltic Sea coastal seawater microcosms modified by crude oil, shale oil or diesel fuel. Microbiological Research 168(7):415–427

Wahl M, Goecke F, Labes A et al (2012) The second skin: ecological role of epibiotic biofilms on marine organisms. Front Microbiol 3:292. https://doi.org/10.3389/fmicb.2012.00292

Walker JD, Colwell RR, Petrakis L (1975) Degradation of petroleum by an alga. Prototheca zopfii Appl Microbiol 30:79–81

Wang W, Shao Z (2012) Genes involved in alkane degradation in the *Alcanivorax hongdengensis* strain A-11-3. Appl Microbiol Biotechnol 94:437–448. https://doi.org/10.1007/s00253-011-3818-x

Wang W, Shao Z (2014) The long-chain alkane metabolism network of *Alcanivorax dieselolei*. Nat Commun 5:5755. https://doi.org/10.1038/ncomms6755

Wang BJ, Lai QL, Cui ZS et al (2008) A pyrene-degrading consortium from deep-sea sediment of the West Pacific and its key member *Cycloclasticus* sp P1. Environ Microbiol 10:1948–1963. https://doi.org/10.1111/j.1462-2920.2008.01611.x

Wang R, Diao P, Chen Q, Wu H, Xu N, Duan S (2017) Identification of novel pathways for biodegradation of bisphenol A by the green alga Desmodesmus sp. WR1, combined with mechanistic analysis at the transcriptome level. Chemical Engineering Journal 321:424–431

Warshawsky D, Radike M, Jayasimhulu K et al (1988) Metabolism of benzo[a]pyrene by a dioxygenase enzyme system of the freshwater alga *Selenastrum capricornutum*. Biochem Biophys Res Commun 152:540–544. https://doi.org/10.1016/S0006-291X(88)80071-8

Warshawsky D, Kenan TH, Reilman R et al (1990) Conjugation of benzo[a]pyrene metabolites by the freshwater alga *Selenastrum capricornutum*. Chem Biol Interact 74:93–105. https://doi.org/10.1016/0009-2797(90)90061-Q

Warshawsky D, Cody T, Radike M et al (1995a) Biotransformation of benzo[a]pyrene and other polycyclic aromatic hydrocarbons and heterocyclic analogs by several green algae and other algal species under gold and white light. Chem Biol Interact 97:131–148. https://doi.org/10.1016/0009-2797(95)03610-X

Warshawsky D, Schneider J, Reilman R et al (1995b) Detection of polycyclic aromatic hydrocarbon metabolites in aquatic organisms. In: Munawar M, Hanninen O, Roy S, Munawar N, Karenlampi L, Brown D (eds) Bioindicators of environmental health. Backhuys Publishers, Dortretch, pp 1–12

Wentzel A, Ellingsen TE, Kotlar H-K et al (2007) Bacterial metabolism of long-chain n-alkanes. Appl Microbiol Biotechnol 76:1209–1221. https://doi.org/10.1007/s00253-007-1119-1

Whyte LG, Hawari J, Zhou E (1998) Biodegradation of variable-chain-length alkanes at low temperatures by a psychrotrophic *Rhodococcus* sp. Appl Environ Microbiol 64:2578–2584

Xie EY, Liu DC, Jia C et al (2013) Artificial seed production and cultivation of the edible brown alga *Sargassum naozhouense* Tseng et Lu. J Appl Phycol 25:513–522. https://doi.org/10.1007/s10811-012-9885-2

Xie Y, Zhang X, Yang J (2018) eDNA-based bioassessment of coastal sediments impacted by an oil spill. Environ Pollut 238:739–748. https://doi.org/10.1016/j.envpol.2018.02.081

Xue C-H, Li Y-R, Hou J-L et al (2015) Self-roughened superhydrophobic coatings for continuous oil–water separation. J Mater Chem A 3:10248–10253. https://doi.org/10.1039/C5TA01014D

Xu X, Liu W, Tian S et al (2018) Petroleum hydrocarbon-degrading bacteria for the remediation of oil pollution under aerobic conditions: a perspective analysis. Front Microbiol 9:2885. https://doi.org/10.3389/fmicb.2018.02885

Yakimov MM, Golyshin PN, Lang S et al (1998) Alcanivorax borkumensis gen. nov., sp. nov., a new, hydrocarbon-degrading and surfactant-producing marine bacterium. Int J Syst Evol Microbiol 48:339–348. https://doi.org/10.1099/00207713-48-2-339

Yakimov MM, Giuliano L, Gentile G et al (2003) Oleispira antarctica gen. nov., sp. Nov., a novel hydrocarbonoclastic marine bacterium isolated from Antarctic coastal sea waterInt. J Syst Evol Microbiol 53:779–785. https://doi.org/10.1099/ijs.0.02366-0

Yakimov MM, Denaro R, Genovese M et al (2005) Natural microbial diversity in superficial sediments of Milazzo Harbor (Sicily) and community successions during microcosm enrichment with various hydrocarbons. Environ Microbiol 7:1426–1441. https://doi.org/10.1111/j.1462-5822.2005.00829.x

Yakimov MM, Timmis KN, Golyshin PN (2007) Obligate oil-degrading marine bacteria. Curr Opin Biotechnol 18:257–266. https://doi.org/10.1016/j.copbio.2007.04.006

Yakimov MM, Genovese M, Denaro R (2010) Thalassolituus. In: Timmis KN (ed) Handbook of hydrocarbon and lipid microbiology. Springer, Berlin, pp 1765–1772. https://doi.org/10.1007/978-3-540-77587-4_126

Yakimov MM, La Cono V, Smedile F et al (2014) Heterotrophic bicarbonate assimilation is the main process of de novo organic carbon synthesis in hadal zone of the Hellenic Trench, the deepest part of Mediterranean Sea. Environ Microbiol Rep 6(6):709–722. https://doi.org/10.1111/1758-2229.12192

Yakimov MM, Golyshin PN, Crisafi F et al (2019) Marine, aerobic hydrocarbon-degrading Gammaproteobacteria: the family Alcanivoracace. In: McGenity T (ed) Taxonomy, genomics and ecophysiology of hydrocarbon-degrading microbes. Handbook of hydrocarbon and lipid microbiology. Springer, Cham, pp 1–13. https://doi.org/10.1007/978-3-319-60053-6_24-1

Yamada M, Takada H, Toyoda K et al (2003) Study on the fate of petroleum-derived polycyclic aromatic hydrocarbons (PAHs) and the effect of chemical dispersant using an enclosed ecosystem, mesocosm. Mar Pollut Bull 47(16):105–113. https://doi.org/10.1016/S0025-326X(03)00102-4

Zhang C, Yang D, Zhang T et al (2017) Synthesis of MnO_2/poly(n-butylacrylate-co-butyl methacrylate-co-methyl methacrylate) hybrid resins for efficient oils and organic solvents absorption. J Clean Prod 148:398–406. https://doi.org/10.1016/j.jclepro.2017.02.009

Zhang S, Hu Z, Wang H (2019) Metagenomic analysis exhibited the co-metabolism of polycyclic aromatic hydrocarbons by bacterial community from estuarine sediment. Environ Int 129:308–319. https://doi.org/10.1016/j.envint.2019.05.028

Zhou H, Wang H, Huang Y et al (2016) Characterization of pyrene degradation by halophilic *Thalassospira* sp. strain TSL5-1 isolated from the coastal soil of Yellow Sea, China. Int Biodeterior Biodegrad 107:62–69. https://doi.org/10.1016/j.ibiod.2015.10.022

ZoBell CE (1946) Action of microorganisms on hydrocarbons. Bacteriol Rev 10:1–49

Chapter 8
Treatment of Petroleum Hydrocarbon Pollutants in Water

Monalisha Samanta and Debarati Mitra

> *Thousands have lived without love, not one without water.*
>
> – British poet W.H. Auden

Contents

Abstract Due to industrialization, worldwide demand of hydrocarbons is escalating day by day and so is the growth of petroleum industries. The petroleum industries (refineries and petrochemicals) can create a detrimental impact on the environment

---

M. Samanta · D. Mitra (✉)
Department of Chemical Technology, University of Calcutta, Kolkata, India

Inamuddin et al. (eds.), *Water Pollution and Remediation: Organic Pollutants*, Environmental Chemistry for a Sustainable World 54,
https://doi.org/10.1007/978-3-030-52395-4_8

by their discharges, oil spillage and waste generation during storage, processing and transportation. The earth's surface water and ground water may be affected by the polluted wastewater from petroleum industries, thereby disturbing the ecosystem. Hence, all operations of hydrocarbon industries should ensure compliance with the applicable regulations related to emissions and waste management. All industries are bound to obey some regulations like occupational safety and health administration, oil pollution act, spill prevention control, clean air act, clean water act and safe drinking water act, which are related to water as well as environmental protection. According to these acts, all petroleum industries should have wastewater treatment plants. Hydrocarbons are the potential pollutants from these industries.

The effluents from petroleum industries have high pH (>7), high biochemical oxygen demand (>30 mg/L), high chemical oxygen demand (>125 mg/L) and high total suspended solids (>30 mg/L). So, this type of wastewater must be treated by preliminary, primary, secondary and tertiary treatments to achieve the specified effluent quality standards. In preliminary and primary treatment process, there is only physical separation of pollutants. The biochemical oxygen demand is decreased by biological processes in secondary treatment. In tertiary process, the effluents are treated with chemicals and thereby lowering the chemical oxygen demand of wastewater. This chapter describes about the different sources and various kinds of water pollutants from petroleum industries and their abatement process.

Keywords Petroleum refinery effluents · Hydrocarbon pollutants · Biochemical oxygen demand · Chemical oxygen demand · Environmental impact

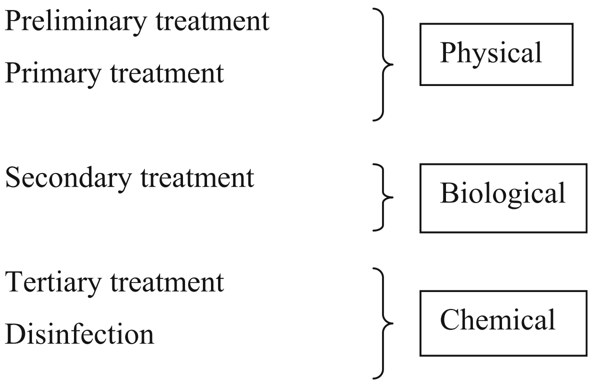
8.1 Introduction

The growth of petroleum industries is increasing with the rising demand for global energy and petrochemicals. Petroleum industries have main two sectors – upstream and downstream. The upstream sector includes exploration and production of crude oil, whereas the downstream refers to all the refinery operations, that is processing of crude oil for production of marketable fuel oil as well as the petrochemical industries (Damian 2013; Palaniandy et al. 2017). In upstream section, for the purpose of drilling and exploration, different chemicals such as drilling mud are used. While drilling, some of these chemicals are contaminated with ground water and surface water. After drilling, crude oil is transported to refineries through pipelines or via ships. During transportation, sea water, ground water and surface water might be contaminated with oil by oil spillage due to leakage in pipelines and ships (Helmy and Kardena 2015; Olajire 2014).

Water pollution can also occur during crude oil processing, handling and transportation. Refinery wastewater includes process water form distillation columns, extractors, heat exchangers, rejected boiler feed-water, blow-down water from cooling tower, washing of equipment, etc. During refining, hydrocarbon-contaminated water must be treated in the wastewater treatment facility prior to discharge or reuse. In petroleum industries, laboratory sink water is also treated as wastewater, because this water is already mixed with different types of impurities (International Petroleum Industry Environmental Conservation Association 2010). During crude oil processing, the water gets contaminated by different aromatic compounds such as benzene, toluene, xylene, polyaromatic hydrocarbons and also organometallic compounds. From different petrochemical industries, water pollutants, like soaps, detergents, dyes, spent solvents, resins, packaging wastes, fabric scraps and waxes, are ejected during washing and purification of products. Some toxic water pollutants from petrochemical industries include acetic acid, benzene, ethyl-benzene, phenol, formaldehyde, urea, naphthenic acids etc. (Sharma et al. 2017; Vineta et al. 2014; Sengupta 2019; Porwal 2015; Sher et al. 2013). The presence of such pollutants is distinguished by offensive odours and accumulation of debris.

Water is essential for healthy growth of life. However, when water gets polluted, then the health of humans, animals and plants is threatened by the usage of such contaminated water and also results in shortage of usable water. Hence, in order to save water or in other words to save life on earth, some rules and regulations must be followed by the petroleum industries. Several acts, like clean water act of 1972, safe drinking water act of 1974, oil pollution act of 1990 and spill prevention control and countermeasure plans of 2010, have been implemented for the purpose of protecting the environment (Department of energy, United States 1998; Speight 2014; Environmental Protection Agency, United States 2004; Environmental Protection Agency, United States 2010; Environmental Protection Agency, United States 2017; Environmental Update #12, 2003).

Several processes are implemented for wastewater treatment in petroleum industries, which mostly involves physical, chemical and biological methods; these methods are conveniently grouped under five heads though all wastewater treatment methods are co-related and also connected with consecutive techniques (Central Pollution Control Board, India 2018; Mareddy 2017).



8.2 Sources of Petroleum-Related Water Pollutants

In the petroleum industries, huge quantities of chemicals are involved for exploration of oil-gas, processing of fractions including water treatment to meet up market necessities that generate wastes. Water pollution is caused by the existence of solid, liquid and gaseous pollutants in quantities above allowable level as well as addition of heat to water, thereby affecting water quality adversely (Olajire 2014). The sources of hydrocarbon-related water pollutants are mainly from oil exploration industries, petroleum refineries and petrochemical units (textile industries, fertilizers, plastics and polymer industries) as well as by oil spillage during storage, handling and transportation (Patwardhan 2008). Figure 8.1 shows the sources of petroleum-related wastewater in petroleum industry.

8.2.1 Oil and Gas Industry

The exploration and production of oil-gas are increasing in leaps and bounds due to the regular rise in demand of fuel. The main sources of water pollutants resulting from exploration and production activities are drilling fluids, hydraulic fluids,

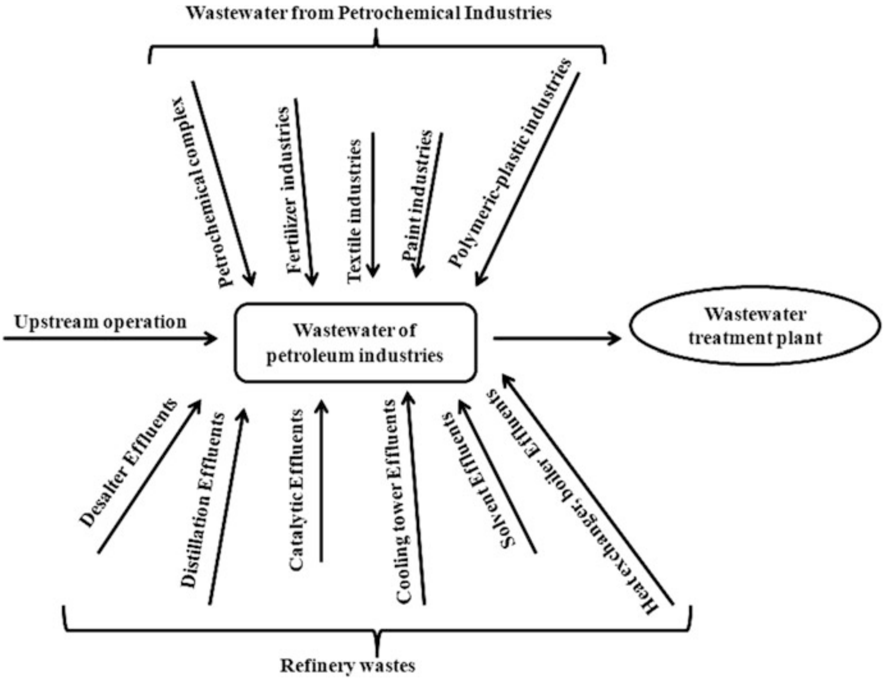


Fig. 8.1 Sources of petroleum-related wastewater in petroleum industry

lubricants in cutting tools, additives, well treatment chemicals, ballast water, boiler blowdown, process water, oil sludge, oil spills and cooling water. The water pollutants that are generally produced during different exploration and production operations are discussed below (Olajire 2014; Helmy and Kardena 2015).

Seismic Survey

The presence of oil-gas is located by geophysical method, that is seismic operation. During seismic operation, the ground water and surface water are contaminated with explosive waste and equipment maintenance waste. At this stage of operation, waste volumes are minimal.

Exploratory Drilling

After identifying the probable reservoir of oil-gas via seismic survey, exploratory drilling of reservoir and source rocks is performed to detect the occurrence of oil and gas. The common water pollutants from this stage include drilling mud, drilling and cutting fluids, drilling chemicals (barite, bentonite), stimulation fluids, cementing waste, explosive chemicals, process water and production testing wastes.

Construction

Following the drilling, the oil and gas are transported through pipeline after treatment. The suitable infrastructure required for oil-gas processing includes pipes, cables, tubing, tanks, cooling system, etc. During this phase, the wastes generated are lubricants, solvents, paints, etc.

Production

Once the appropriate construction is built, the production of oil-gas from the reservoir is started. Throughout the production activity, production chemicals, sludge bottom and work over wastes are produced as pollutants.

Maintenance

All exploration and production activities require maintenance such as inspection and repair of vehicles, drilling rigs and all other equipment. During maintenance, the surface water and ground water are polluted with contaminants like used lubricants, spent solvents, etc.

The volumes of all wastes generated depend on the geological-seismic operation, chemicals dosage and time duration of oil and gas exploration. The earth water is polluted by hazardous compounds like potassium formate, cementing waste (drilling mud), lubricants, rubbing alcohol (cutting fluids) and bio-acids (well treatment chemicals) to aid in the drilling of boreholes. The drilling fluids and cutting chemicals have adverse influences on groundwater as well as surface water due to their high pH as well as high salt content, during discharge and transportation.

8.2.2 Petroleum Refinery

After exploration and production, the crude is transported to the refinery. The petroleum refineries convert crude oil into more than 2500 items including liquefied petroleum gas, gasoline, kerosene, aviation fuel, diesel, lubricating oil and petrochemical feedstock to meet the market requirements. The petroleum refinery has great influence on environment pollution (water, air and soil pollution) during processing of crudes. During the various refinery operations and processes, the water is contaminated with harmful hydrocarbons. These operations and processes mainly include desalting, distillation, hydrotreating, cooling system, wash unit, drainage of tank, flushing of equipment, surface water run-off. (Helmy and Kardena 2015; Damian 2013; Olajire 2014; Mareddy 2017; Central Pollution Control Board, India 2018) According to the Environmental Protection Agency, a normal refinery (production capacity; 150,000 barrel/day fuel oil) generates 357–476 barrel/day of oily wastes (Environmental Protection Agency, Washington 1974).

Desalting Effluents

In the refinery, the first step for refining the crude oil is desalting for the removal of different types of salts, drilling mud, cutting fluids, clay and other chemicals which may cause corrosion of equipment or act as poisons to the catalysts. De-emulsifier is usually added to break the oil-water emulsion during desalting. So, the desalter effluents contain de-emulsifiers, organic-inorganic salts and oily water. The temperature of the wash water is also high (110–150 °C) which reduces the dissolved oxygen content of water (Central Pollution Control Board, India 2018).

Atmospheric Distillation

After desalting, the oil is subjected to atmospheric distillation unit for the production of light fractions, naphtha, liquefied petroleum gas, gasoline, kerosene, diesel and feedstock of lube oil. In this unit, the stripping stream comes in contact with different hydrocarbon fractions, mercaptans, disulphide compounds, hydrogen sulphide and ammonia. So, the wastewater (condensed steam) from atmospheric distillation unit is mostly oily sour water (Central Pollution Control Board, India 2018).

Vacuum Distillation

The heavier fractions cannot be refined in atmospheric distillation at high temperature and hence are sent to the vacuum distillation unit where distillation is carried out at a low pressure. From vacuum distillation, the main wastewater is oily sour water similar to atmospheric effluents. Sometimes, vacuum pump and surface condenser are used in vacuum distillation unit in place of barometric condenser to do away with the generation of oily wastewater (Central Pollution Control Board, India 2018).

Cracking (Thermal and Catalytic)

In cracking unit, heavy and long-chain hydrocarbons are cracked into smaller-size and lighter molecules as per market demand in presence of catalyst (catalytic cracking), or by applying high pressure and temperature (thermal cracking). The quantity of wastewater produced during coking is 25 litres per unit feedstock (approximately). The typical wastewater generated from this type of unit contains pollutants like phenol, cyanides, sludge containing heavy hydrocarbons, sulphur compounds and fine coke particles and heavy metals etc. So, this wastewater has high chemical oxygen demand, biochemical oxygen demand, total suspended solid, pH and temperature. This water is directly dispatched to the refinery water treatment plant (Central Pollution Control Board, India 2018).

Catalytic Reforming

Catalytic reforming is a process to upgrade the octane number of gasoline and naphtha. From this unit, the main constituents of wastewater are organometallic compounds, high levels of oil, suspended solids, mercaptans, hydrocarbons related to spillage along with other inorganic compounds like chloride, ammonia, hydrogen sulphide as well as sour water (Central Pollution Control Board, India 2018).

Solvent Extraction

Solvent extraction, dewaxing and propane deasphalting are required for removal of aromatics, wax and asphalts from lube base oil for improving viscosity index, oxidation stability, colour and pour point. The common solvents used are furfural, phenol, toluene, methyl-ethyl-ketone and propane. So, these used solvents when disposed contaminate the water (Central Pollution Control Board, India 2018).

Acid Gas Removal and Sulphur Recovery Unit

The undesirable elements, like sulphur, nitrogen and water, are removed from crude oil by different chemical treatment methods such as merox treatment, olamine process, glycol treatment, etc. During merox treatment, the mercaptans are removed. The sulphur dioxide, nitrogen dioxide and carbon dioxide are removed in olamine process using amine solution. For removal of water, glycol is used. Generally, the noxious wastes of these units are mercaptans, organic acids, spent amine solution and spent glycol (Central Pollution Control Board, India 2018).

Heat Exchanger

All petroleum industries use heat exchangers for heating or cooling the different streams. Routine maintenance of the heat exchangers is required by removing sludge and scale from tubes, pipes and bundles to maintain efficiency. The effluents from heat exchangers contain oily sludge including heavy metals like lead, chromium, etc. (Central Pollution Control Board, India 2018).

Cooling Tower

Cooling tower plays an important role in petroleum refineries. After cooling the different fractions of hydrocarbons using water in heat exchangers, this hot process water is passed through the cooling tower for heat removal. But sometimes, the process water is contaminated with hydrocarbons due to some leakage problems. From the cooling tower, cold water is mixed with oily sour water, suspended and dissolved solids, etc. This wastewater has high chemical oxygen demand, biochemical oxygen demand and pH. So, this cooling water blowdown must be treated in the refinery effluent plant before reuse (Central Pollution Control Board, India 2018; International Petroleum Industry Environmental Conservation Association 2010).

Blowdown

Blow-down system is a collection unit in which most refinery process units are manifolded to offer safe handling and disposal of liquid and gases from different units. The liquid from the blow-down system typically contains water contaminated with hydrocarbons, sulphur compounds, heavy metals, organic nitrogen, different solvents, etc. which is dispatched to the wastewater treatment plant (Central Pollution Control Board, India 2018; International Petroleum Industry Environmental Conservation Association 2010). Table 8.1 shows the characteristics of effluents from refinery units.

Table 8.1 Characteristics of effluents from different refinery units

Unit operation	Characteristic of wastewater	Concentration (mg/L)	Total effluents (kg/L)	References
Desalter	Suspended solids	50–100	0.05–0.1	Speight (2014), Central Pollution Control Board, India (2018), and International Petroleum Industry Environmental Conservation Association (2010)
	Dissolved hydrocarbons	50–300		
	Phenol	5–30		
	Benzene	30–100		
	Biochemical oxygen demand	300–600		
	Chemical oxygen demand	500–2000		
	Nitrogen compounds	15–30		
	Sulphur compound	Up to 50		
Atmospheric distillation	Mercaptan	50–100	0.01–0.6	Speight (2014), Central Pollution Control Board, India (2018), International Petroleum Industry Environmental Conservation Association (2010), and Malakar et al. (2015)
	Hydrogen sulphide	Up to 50		
	Chlorides	730		
	Chemical oxygen demand	400–1000		
	Suspended hydrocarbons	Up to 1000		
Vacuum distillation	Phenol	0.35	0.004–0.01	Speight (2014), Central Pollution Control Board, India (2018), International Petroleum Industry Environmental Conservation Association (2010), and Malakar et al. (2015)
Cracking	Biochemical oxygen demand	240–570	0.024–0.35	Speight (2014), Central Pollution Control Board, India (2018), International Petroleum Industry Environmental Conservation Association (2010), and Malakar et al. (2015)
	Chemical oxygen demand	400–1400		
	Suspended solids (fine cokes)	500		
	Phenol	10–50		
	o,m,p-cresol	11–16.5		
	Ammonia	Up to 100		
	Oily sour water	Up to 250		
	Hydrogen cyanide	10–20		

(continued)

Table 8.1 (continued)

Unit operation	Characteristic of wastewater	Concentration (mg/L)	Total effluents (kg/L)	References
Reforming	Suspended solids	50	0.01–0.14	Speight (2014), Central Pollution Control Board, India (2018), International Petroleum Industry Environmental Conservation Association (2010), and Malakar et al. (2015)
	Oily water	150		
	Spent catalyst	50		
	Chemical oxygen demand	600–1200		
Solvent extraction/dewaxing/propane ee deasphalting	Furfural	1–5	0.01–0.35	Central Pollution Control Board, India (2018), International Petroleum Industry Environmental Conservation Association (2010), and Malakar et al. (2015)
	Phenol	1–10		
	Toluene	1–3		
	Methyl-ethyl-ketone	1–3		
	Asphalted propane	4–8		
	n-hexane	1.8–1.85		
Sulphur recovery unit	Amines	<100	0.0001–0.03	World Bank Group, United States (1998) and Malakar et al. (2015)
	Sulphur compounds	<10		
	Ammonia	<100		
	Suspended solids	<10		
	Free hydrocarbons	<10		
Heat exchanger	Oily sludge	100	–	Central Pollution Control Board, India (2018)
Cooling tower	Oily sour water	5–100	0.00001–0.01	Central Pollution Control Board, India (2018), International Petroleum Industry Environmental Conservation Association (2010), and Patwardhan (2008)
	Chemical oxygen demand	150		
	Suspended solids	200		
	Dissolved solids	700		
	Heavy metals	1–100		
Blow-down	Sulphur compounds	50–100	0.0016–0.01	Central Pollution Control Board, India (2018), International Petroleum Industry Environmental Conservation Association (2010), and Patwardhan (2008)
	Organometallic	10–40		
	Compounds	10–40		
	Organic nitrogen	1–10		

8.2.3 Petrochemicals Industries

Petrochemicals mean different chemicals which are produced from petroleum products and natural gas and used for production of valuable market demanding items for consumption. From petrochemical industries, the water is contaminated with either process water or with waste chemicals. There are different types of petrochemical industries, like petrochemical production industry, fertilizers industry, textile industry, polymer and plastic manufacturer industries. Wastes from petrochemical industries are very hazardous and carcinogenic, because they contain benzene, napthenic acid, phenanthrene, benzo[a]pyrene, dye chemicals, phenols, organometallic hydrocarbons, colour pigment and different solvents (Patwardhan 2008; Sharma et al. 2017; Vineta et al. 2014; Sengupta 2019; Porwal 2015; Sher et al. 2013).

Petrochemical Waste

Petrochemical wastes are generally generated due to some accidental discharges and abnormal operation, like naphtha cracking, polyethylene, ethylene oxide, ethylene glycol, polyolefins, propylene plants of the petrochemical complex. The wastewater of the petrochemical complexes is contaminated with large quantities of polycyclic aromatics, polyaromatic hydrocarbons, methanol, acetic acid, cumene, phenols, heavy alcohols, benzene, toluene, xylene, acrylonitrile and other polymeric chemicals. These pollutants may cause environmental hazards as well as health hazards to living beings (Patwardhan 2008; Ghimire and Wang 2018; Balasubramani and Sivarajasekar 2018).

Fertilizer Wastes

Fertilizers are mainly phosphorous-potassium-nitrogen-based chemicals and also bio-organic as well as organic chemicals. Fertilizers are used for healthy growth of plants as well as to improve the soil quality. One of the important fertilizer wastes is phosphogypsum slurry of phosphoric acid and calcium sulphate when phosphate rock is dissolved in sulphuric acid. Coal and naphtha are used as feedstocks of fertilizer. Eventually, surface-water is contaminated with coal dust and naphtha effluents (Environmental Protection Agency, Washington 2017). From fertilizer complex, the main hydrocarbon pollutants are pentyl-pyrone, methyl ethyl amine, methanol, etc. The water is also polluted with suspended and dissolved impurities and some heavy metals (arsenic, vanadium, uranium and polonium) which altogether impose a negative impact on the aquatic environment (Patwardhan 2008; National Programme on Technology Enhanced Learning, India 2014; Sengupta 2019).

Textile Wastes

The textile industries are divided into three categories like cotton, woollen and synthetic fibres. The textile factories consume huge quantities of water and also produce huge volumes of wastewater during different processes. The typical features of wastewater from such industries are that, it is rich in coloured pigments, dyes, printing chemicals and packaging wastes. The pollutants from cotton textiles are carboxyl methyl cellulose, polyvinyl alcohol and mineral acid during sizing and de-sizing of cotton; sodium hypochlorite and hydrogen peroxide during bleaching; naphthol dyes, sulphur dyes, basic dyes, synthetic resins, synthetic waxes during dyeing and finishing operations. Similarly, the woollen textile industry wastes include alkali, soap, soda ash and sulphuric acid during scouring and carbonizing; toxic organic dyes from dyeing; mineral oil during oiling; colour pigments during finishing (Jain et al. 2016). The water is contaminated with organic and polymeric chemicals in synthetic fibre mills during bleaching, mercerizing and dyeing. The coloured wastewater also has high pH, high chemical oxygen demand, high biochemical oxygen demand and contains high level of total suspended solids (Ramesh et al. 2007; Patwardhan 2008).

Polymer and Plastics Wastes

Polymeric materials and plastics are abundantly utilized in our daily life. They are consumed as packaging films, wrapping materials, shopping-garbage bags and boxes, fluid bottles-pouches, toys, industrial products, construction as well as household materials. For this reason, their productions are increasing very fast and production level crosses around 150,000 kg/year worldwide. But polymeric and plastic materials are non-biodegradable and remain on earth for several years; so, these wastes cause adverse effects on the environment, like choking of drains and flooding of localities during monsoon. Total generation of wastes from plastic industries is approximately 5600 kg/year (Central Pollution Control Board, India 2013). The typical hydrocarbon wastes are benzene, 1,3-butadiene, tetra-chloro methane, dioxin, furans, amines, nitrides, styrene, acetaldehyde, etc. Other non-recyclable plastic wastes are low-density polyethylene, high-density polyethylene, some thermoset polymers, etc. So, this wastewater must be treated before being disposed (Datta and Kopczynska 2016).

Paint Wastes

Paint is a useful material in our modern colourful life. The different raw materials of paint industries are resins, drying oil, solvents, pigments, extenders, etc. The wastewater is generated from paint industry during packaging the products and raw materials, cleaning the equipment, washing the floors, cooling water blowdown

Table 8.2 Different effluents from petroleum related industries

Industries	Characteristic of wastewater	Total effluents (litre/day)	References
Petrochemical complex	Phenols, methanol, organic acids, heavy alcohol, biochemical oxygen demand, chemical oxygen demand, acetic acid, benzene, cumene, toluene, xylene, acetonitrile	23×10^6 litre/day	Tehrani et al. (2016)
Fertilizer industries	Urea, methanol, isobutene, pentyl-pyrone, methyl ethyl amine	18×10^6 litre/day	Central Pollution Control Board, India (2017)
Textile industries	Detergents, solvents, colour pigments, grease	20×10^6 litre/day	Jain et al. (2016) and Vineta et al. (2014)
Polymeric industries	Acrylonitrile, terephthalic acid, di-isocyanate, epichlorohydrine, polyesterpolyols	15×10^6 litre/day	Central Pollution Control Board, India (2013)
Paint wastes	Ethyl benzene, di-(2-ethylhexyl) phthalate, tetrachloroethylene, toluene, xylene	10–15 $\times 10^6$ litre/day	Central Pollution Control Board, India (2017)

and spillage. The main water pollutants are spent solvents, caustic solution, adhesives, paints sludge, heavy metals, etc. The wastes and paint spills are washed with xylene and water (Subhasmini 2019). The wastewaters of paint industries also have high biochemical oxygen demand, high chemical oxygen demand, high total suspended solids, high pH, organometallic compounds and high concentration of ethyl benzene, di-(2-ethylhexyl) phthalate, tetra-chloro-ethylene and toluene. The wastewater from stiff and water-based paint industries contain oil-grease mixture, suspended solids and phenolics. Thus, the wastewater generated is quite toxic and hazardous in nature (Aboulhassan et al. 2014). Table 8.2 shows the different effluents from petroleum related industries.

8.2.4 Oil Spillage and Transportation

After production, all marketable products are transported via pipelines, trucks, tanker, ships and rail. During transportation, accidental spillage and leakage of these hazardous chemicals can occur. Spillage means the spread of oil or chemicals above the surface of earth during drilling and transportation. Oil and hazardous chemicals contaminate the surface water affecting human, animal and plant health and aquatic life. The contaminated water from spillage may contain benzene, toluene, xylene, cycloalkanes, isoalkane, polycyclic aromatics, polyaromatic hydrocarbons, liquid fuels, etc. Oceans are being regularly polluted by crude oil due to spillage, run-offs and illegal dumping (Michel 2017; Environmental Protection

Table 8.3 Events of worldwide large oil spills

Tanker	Location	Time of occurrence	Crude oil in tonnes	References
Deepwater horizon	United States, Gulf of Mexico	April 20, 2010–July 15, 2010	560–585	Kanuric (2014) and Fey et al. (2011)
Taylor energy	United States, Gulf of Mexico	September 23, 2004–Present	210–490	Kanuric (2014) and Fey et al. (2011)
Fergana Valley	Uzbekistan	March 2, 1992	285	Doerffer (1991)
ABT summer	Angola	May 28, 1991	260	Coipuram (2006)
Kuwaiti oil fires	Kuwait	January 16, 1991–November 6, 1991	136,000	Al Damkhi (2007)
Kuwaiti Oil Lakes	Kuwait	January 1991–November 1991	3409–6818	Coipuram (2006), Torres et al. (2014), David et al. (1991), and Juhasz (2011)
Gulf war oil spill	Kuwait, Iraq, Persian gulf	January 19, 1991–January 28, 1991	818–1091	Coipuram (2006), Torres et al. (2014), David et al. (1991), and Juhasz (2011)

Agency, United States 2010; Prasad and Anuprakash 2016). Table 8.3 shows the worldwide large oil spills that occurred after the 1990s.

8.3 Adverse Effects of Petroleum-Related Water Pollutants

The water gets contaminated with petroleum-related pollutants by the process water from petroleum industries, oil spillage and leakage during handling, storage and transportation. Water does not dissolve into oil easily. The oil layers are stretched over the water (Environmental Protection Agency, Washington 2003). Oil and oily pollutants on water surface blocks sunlight from reaching the deeper layers, hampering photosynthesis of aquatic plants. They also increase the biochemical oxygen demand and chemical oxygen demand level of surface water. Most hydrocarbons are hazardous, some are even toxic and carcinogenic and above all, they are non-biodegradable in nature. Hence, the water contaminated with these pollutants is unsuitable for use for all life forms (Pathak and Mandalia 2012; Damian 2013; Environmental Update #12, 2003). Table 8.4 shows the undesirable effects of water pollutants from petroleum industries.

Table 8.4 Undesirable effects of water pollutants from petroleum industries

Industries		Pollutants	Adverse effects	References
Drilling/exploration/upstream	Seismic survey	Explosive chemicals	Greater risk of long term effects for children and older people. May damage the hearing ability of various marine species	Damian (2013) and Palaniandy et al. (2017)
	Exploratory drilling	Drilling fluids, hydraulic fluids, lubricants, additives, oil sludge, oil spills	Corrosive and toxic Damage the liver, kidney, brain of living beings Cause cancer, affect the immune system and lead to reproductive failure Decrease the aquatic population	Damian (2013), Environmental Pollution Centers, India (2017), Palaniandy et al. (2017), and Olajire (2014)
	Construction	Lubricants, solvents, paints	May damage the liver, kidneys, heart, blood vessels, vessels, bone marrow and the nervous system. May cause skin disorders and dermatitis	Damian (2013), Palaniandy et al. (2017), and Olajire (2014)
	Production	Production chemicals, sludge bottom	Allergies or asthma problems Adverse effects on the mental, common sense or physical development of children corrosion of equipments and blockage of pipe line	Damian (2013), Palaniandy et al. (2017), and Olajire (2014)
	Maintenance	Lubricants, spent solvents	Irritation and increased risk of infection from even short-term exposure. Poisoning, muscle weakness, intestinal blockage, skin sores and breathing problems.	Patwardhan (2008) and Helmy and Kardena (2015)

(continued)

Table 8.4 (continued)

Industries		Pollutants	Adverse effects	References
Refinery	Desalter	Suspended solids, dissolved hydrocarbons, phenol, benzene, nitrogen compounds, Sulphur compound	Damage the brain and nervous system	Central Pollution Control Board, India (2018), Pathak and Mandalia (2012), Speight (2014), Radelyuk et al. (2019), and Pak and Mohammadi (2008)
			Dizziness and unconsciousness	
			May cause cancer.	
			Corrosion of equipment for the presence of Sulphur, nitrogen compounds and suspended solids.	
	Atmospheric distillation	Mercaptan, hydrogen sulphide, chlorides, suspended hydrocarbons	Irritation of eye skin	Pathak and Mandalia (2012), Speight (2014), Radelyuk et al. (2019), and Pak and Mohammadi (2008)
			Respiratory tract, headache, dizziness, tremors and seizures	
			Nausea and vomiting	
	Vacuum distillation	Phenol, heavy hydrocarbons	Toxic, dangerous for central nervous system	Olajire (2014), Damian (2013), Pathak and Mandalia (2012), and Pak and Mohammadi (2008)
			Blockage of equipment and pipelines	
	Cracking	Suspended solids (fine cokes), phenol, o,m,p-cresol, ammonia, oily sour water, hydrogen cyanide	Breathing problems	International Petroleum Industry Environmental Conservation Association (2010), Environmental Update #12, 2003, and Pathak and Mandalia (2012)
			Headache, dizziness, weakness	
			Seizures, fainting and even rapid death.	
			Irritation and burning of skin, eyes, mouth and throat	
			Abdominal pain and vomiting	
			Heart damage, anaemia, liver and kidney damage, facial paralysis, coma	
	Reforming	Suspended solids, oily water, spent catalyst	Plugging lines	International Petroleum Industry Environmental Conservation Association (2010), Environmental Update #12, 2003, and Patwardhan (2008)

(continued)

Table 8.4 (continued)

Industries		Pollutants	Adverse effects	References
	Solvent extraction/ dewaxing/ propane deasphalting	Furfural, phenol, toluene, methyl-ethyl-ketone, asphalted propane,n-hexane	Harmful for central nervous system. Breathing trouble Irritation of skin Liver damage Adverse reproductive effects such as sperm changes and infertility	Central Pollution Control Board, India (2018)
	Sulphur recovery unit	Amines, Sulphur compounds, ammonia, suspended solids, free hydrocarbons	Irritation and itching of skins. Corrosion of equipment.	International Petroleum Industry Environmental Conservation Association (2010), Environmental Update #12, 2003, and Pathak and Mandalia (2012)
	Heat exchangers	Oily sludge	Scale formation and deposition of sludge The removal of deposited oil sludge from shell side of heat exchanger is very costly.	International Petroleum Industry Environmental Conservation Association (2010) and Environmental Update #12, 2003
	Cooling tower	Oily sour water, suspended solids, dissolved solids, heavy metals	Scaling, fouling and discolouration of apparatus. Decrease the working efficiency of equipment.	International Petroleum Industry Environmental Conservation Association (2010), Patwardhan (2008), and Central Pollution Control Board, India (2018)
	Blow-down	Sulphur compounds, organo-metallic compounds, organic nitrogen compounds, different solvents	Toxic and injurious to health. Harmful effects on aquatic life in ocean Organic solvents are highly toxic and corrosive.	Central Pollution Control Board, India (2018), International Petroleum Industry Environmental Conservation Association (2010), and Crompton (2017)
Petrochemical complex		Phenols, methanol, organic acids, heavy alcohol, acetic acid, benzene, cumene, toluene, xylene, acetonitrile	Global warming Cause acid rain Shortness of breath, eye irritation, dizziness, cough, nose congestion, sore throat and weakness Risk of mortality, lung cancer, chronic respiratory disease and heart disease, damage liver and kidneys.	Tehrani et al. (2016) and Sharma et al. (2017)

(continued)

Table 8.4 (continued)

Industries	Pollutants	Adverse effects	References
Fertilizer industry	Urea, methanol, isobutene, pentyl-pyrone, methyl ethyl amine	Acid rain	Sengupta (2019) and Hunt (2019)
		Soil acidification	
		Burning of crops	
		Fishes die	
		Cause gastric cancer, goitre, birth malformations and hypertension, testicular cancer & stomach cancer	
Textile industry	Detergents, solvents, coloured pigments, grease, dioxin	Highly toxic	Malik et al. (2014) and Vineta et al. (2014)
		DNA damage	
		May cause cancer	
		Aesthetic issues	
		Suppression of human immune system	
Polymeric industry	Acylonitrile, terephthalic acid, di-isocyanate, bisphenol A epi-chlorohydrin, polyesterpolyols,	Toxic for marine mammals	Sher et al. (2013) and Central Pollution Control Board, India (2013)
		Promote endocrine disruption	
		Irritation of nose, mouth and skin.	
		May cause cancer	
		Decrease thyroid hormone receptor (TR) activity	
		Disrupt normal, physiological levels of sex hormones	
Paint industry	Ethyl benzene, di-(2-ethylhexyl) phthalate, tetrachloroethylene, toluene, xylene	Headaches, trigger allergies and asthmatic reactions, irritate skin, eyes	Aboulhassan et al. (2014) and Porwal (2015)
		Risk of certain types of cancer (in particular lung cancer)	

8.4 Treatment of Wastewater in Petroleum Industries

Oily wastewater treatment is essential before being released to the environment due to its high contaminant (mainly hydrocarbons) content that potentially pollutes coastal waters, rivers, ground water, oceans and can cause negative impact on the health of living beings both aquatic and non-aquatic. This effluent is generally discharged to an offsite waste-water treatment plant where the upgradation or cleaning of wastewater is done by applying modern technology. In wastewater plant, the wastewater is accumulated in a separate location and subjected to the different treatment processes. Mainly wastewater is collected in large volumes and treatment processes are held on either continuous or batch basis (International Petroleum Industry Environmental Conservation Association 2010; Central Pollution Control Board, India 2018; Patwardhan 2008; Shahryar 2017).

The wastewater treatment processes depend on certain factors such as (Mareddy 2017)

- Quality and quantity of pollutants
- Availability of space of the treatment area
- Degree of automation of the treatment plant
- Capital and operating costs
- Discharge facility without further pollution
- Specification of effluents to be maintained

The wastewater treatment process is mainly subdivided into physical, chemical and biological processes. The physical process includes sedimentation, screening, filtration; chemical process includes chlorination, neutralization, bleaching; and biological means sludge and aerobic-anaerobic treatment (International Petroleum Industry Environmental Conservation Association 2010; Mareddy 2017).

8.4.1 Physical Treatment Methods

Physical methods are used for improvement and upgradation of wastewater. Removal of large entrained objects is affected through sedimentation and screening. At first, wastewater is collected in a tank and allowed to stand for some time where the suspended solids and large molecules are settled down by centrifugation followed by separation of the clarified effluents. Lighter materials (paper, wood particles, plastics, polymeric materials) and oil, grease that float are removed by screening, trapping and skimming using automated raked bar screens. Sometimes, agitation is required for floatation of these materials which is done either by applying air to the bottom of wastewater lagoon or pond to cause the release of harmful gases such as carbon dioxide, methane, hydrogen sulphide, etc. Another physical step, filtration, is used for wastewater treatment where both suspended and floatable solids are filtered through a filtering media, for example, sand (International Petroleum Industry Environmental Conservation Association 2010; Central Pollution Control Board, India 2018; Patwardhan 2008; Shahryar 2017).

Sometimes, undesirable toxic wastes like slugs occur in wastewater of certain petroleum industries. These unwanted periodic wastes may harm the subsequent biological treatment process. So, these wastes are held in another tank, mixed with other effluents and gradually released. The elimination of these slugs is called equalization (International Petroleum Industry Environmental Conservation Association 2010).

8.4.2 Chemical Treatment Methods

The wastewater is treated by using different chemicals for quality enhancement in chemical treatment process. The most common chemical treatment processes in petroleum industry are chlorination, neutralization, coagulation and adsorption. Chlorination is used for killing the pathogens and bacteria to slow down the decomposition of wastewater. Ozone is also occasionally used as an oxidizing disinfectant (International Petroleum Industry Environmental Conservation Association 2010; Shahryar 2017). The acid or base is used for neutralization of base or acid of wastewater in order to adjust pH level. Another chemical treatment process is coagulation where polyvalent metal salts (alum, ferric chloride) are used as coagulants for treatment of wastewater by removing substances through precipitation. Some treatment processes are both physical and chemical like adsorption. In adsorption, pollutants are attached to the surface of porous solids. The most common industrially used adsorbent is granular activated carbon which is highly porous. Ion exchange is also sometimes applied to wastewater treatment due to its high selectivity. The different metal salts (iron, manganese) and hardness are eliminated by this process (Central Pollution Control Board, India 2018; Mareddy 2017; Shahryar 2017).

8.4.3 Biological Treatment Methods

In biological treatment microorganisms, typically, bacteria are used for biological decomposition of polluted water. In biological treatment process, huge amounts of microorganisms are cultured and they degrade the pollutants, oil sludge and hydrocarbons to form stable products like carbon dioxide, methane, oxygen and nitrogen gas. Mainly there are two types of biological treatment methods – aerobic and anaerobic; these methods are differentiated by the availability of dissolved oxygen.

In aerobic method, solid-liquid organic-inorganic contaminants are destroyed with the help of different microorganisms in presence of oxygen, resulting in the formation of carbon dioxide. The aerobic treatment is done by the following methods (Shahryar 2017; Patwardhan 2008; Alireza 2014).

Activated sludge: In this biological step, the industrial wastewater is digested by microorganisms like bacteria, protozoa in presence of oxygen.

Trickling Filter

Trickling filter is a fixed bed filter of polymeric materials, polyurathanes foam, ceramic, rocks, coke and gravel designed for development of bio-layer using microorganisms. This bio-layer is used for removal of pollutants mainly organic compounds (oil, grease, heavy hydrocarbons) from wastewater by absorption or adsorption in presence of oxygen, releasing carbon dioxide (Environmental Protection Agency, Washington 2000; Environmental Protection Agency, Washington 2011).

Oxidation Ponds

Oxidation ponds or stabilization ponds are designed for reducing the pollutants mostly organic matter from industrial wastewater. This treatment requires several days. In these large and shallow ponds, the wastewater is interacted with sunlight, bacteria and algae. The wastewater is discharged into oxidation ponds where organic pollutants are consumed by living microorganisms for their growth, reproduction, energy generation and converted into carbon dioxide on the surface of pond in presence of sunlight and oxygen which is generated during photosynthesis of algae. In some cases, mechanical agitators are incorporated to increase the dissolved oxygen level (Tharavathy et al. 2014; Environmental Protection Agency, Washington 2011).

Lagoons

Lagoons are artificial aeration ponds or pond like water bodies or basins for treatment of polluted water for a predetermined period of time. These types of ponds are stabilized with clay, artificial liner to avoid any leaks to the groundwater below. Here, the wastes are treated by bacteria, algae in presence of dissolved or supplied oxygen in warm, sunny climate (Tharavathy et al. 2014; Cavaseno 1980).

Aerobic Digestion

In aerobic digestion, organic pollutants are digested by aerobic bacteria (saprotrophic bacteria) in presence of oxygen in a digester tank; it is a batch process. Aerobic bacteria consume organic matter, oil, grease as food and produce carbon dioxide and hydrogen sulphide. This process results in degradation of solids up to a level of 10–20%.

The other biological process is the anaerobic method where the sewage generated by the industrial taskforce is treated in a septic tank in presence of bacteria to reduce biochemical oxygen demand by about 35%–40% in 1–2 days (Alireza 2014; Shahryar 2017).

Anaerobic Digestion

In this wastewater treatment, microorganisms digest the organic matter of sewage in absence of oxygen in a digester chamber. The organic pollutants are consumed by hydrolysis of bacteria and converted into ammonia, hydrogen, organic acid, hydrogen sulphide, bio-methane, etc. (Mareddy 2017; International Petroleum Industry Environmental Conservation Association 2010).

Anaerobic Lagoon

Anaerobic lagoons are mainly used for treatment of organic pollutants devoid of oxygen like a septic tank but not underground. Lagoons should be lined with reinforced material to avoid seepage. The anaerobic bacteria, protozoa digest the organic matter and evolve methane, nitrogen, hydrogen sulphide, carbon dioxide and ammonia gas. This gas may be utilized as biogas (Alireza 2014; Environmental Protection Agency, Washington 2011; Walczyk and Gorny 2018).

After treatment, the purified water (parameters meeting specifications) is recycled, reused and few times, it is discharged to a nearby aquatic body. However, treated water must be analysed before being discharged to ensure that the parameters meet the required specifications (Shahryar 2017; Alireza 2014).

8.4.4 Refinery Wastewater Treatment

A typical petroleum refinery has different wastewater treatment facilities based on effluent quantity and quality. The refinery wastewater treatment consists of preliminary treatment, primary treatment, secondary treatment, tertiary treatment and advanced treatment if required (Mareddy 2017; International Petroleum Industry Environmental Conservation Association 2010; Patwardhan 2008).

Preliminary Treatment

The preliminary treatment is essential for smooth performance of subsequent treatment processes as well as for the protection and maintenance of equipment of the facility. Mainly this process protects the pumps and heat exchangers from getting clogged by eliminating the large suspended solids, heavy hydrocarbons, floating materials, inorganic solids, excessive oils and greases. These wastes are generated during drilling as well as refining of crude (Environmental Protection Agency, Washington 2003; Shahryar 2017). Following devices are used in preliminary treatment -.

Screener

It removes plugging or clogging materials like polymeric materials, large suspended solids, grit which may damage the pipelines, pump, etc. Examples are rack, bar or fine.

Comminuting Device

This device is used to cut or reduce the size of larger materials into smaller ones in order to protect the equipment, lines and channels from clogging or plugging. Examples are grinder, cutters and shredders.

Grit Chamber

This long channel type chamber is used to remove suspended particles, grit to protect subsequent equipment like sedimentation tanks, sludge digesters, pumps from tear, wear, corrosion as well as deposition in pipelines and channels. In these chambers, the flow rate of wastewater is sufficiently reduced so as to allow deposition of the heavy solids.

Pre-aeration Tank

Pre-aeration is a part of wastewater treatment where external air is injected to the tank at the rate of 0.028–0.11 m^3/min for about 20–30 min to achieve the following:

(a) To reduce biochemical oxygen demand and chemical oxygen demand of wastewater
(b) To flocculate lighter floating solids into heavier ones to facilitate settling
(c) To separate oil and grease from wastewater and transfer them to the surface
(d) To maintain aerobic conditions in the septic wastewater

Pre-chlorination

Pre-chlorination may be sometimes used in pre-treatment of industrial wastewater to control odour, prevent wastewater decomposition and accelerate sedimentation.

Sour Water Stripper

Some contaminated water in the refinery cannot be mixed with other wastewater such as sour water from distillation reflux drums containing dissolved hydrogen sulphide, organic sulphur compounds and ammonia, since they are not treatable by conventional methods. For such cases, the sour water stripper is often required in the pre-treatment section before discharging sour water to the wastewater plant for removal of hydrogen sulphide, ammonia, etc. (Speight 2014).

All the preliminary devices should be operated and maintained with care.

Primary Treatment

The main aim of the primary treatment is removal of the suspended solids, organic matter, oily sludge from wastewater by physical means, usually by gravity separation. This treatment of wastewater uses oil-water separator or screener or skimmer where oil, water and suspended solids are segregated from each other. Neither dissolved solids are separated nor oil-water emulsion is broken in this stage. For separation of colloidal materials, some chemicals are used in primary treatment. However, the oil in effluent is recovered at this step itself and is recycled (Patwardhan 2008; Shahryar 2017; Alireza 2014).

In this treatment method, the flow rate of wastewater is reduced sufficiently to allow suspended solids to settle down and light materials to float at the surface of water. There are many devices which are used in primary wastewater treatment such as settling tanks, clarifiers, skimmers, screeners, filters, etc. (International Petroleum Industry Environmental Conservation Association 2010).

The primary treatment of a petroleum refinery consists mainly of two stages for the isolation of oil, water and solids (International Petroleum Industry Environmental Conservation Association 2010; Shahryar 2017).

First Stage

Oil-water separation is achieved using American petroleum institute separators, corrugated plate interceptors or parallel plate interceptors separators or tilted plate interceptor separators or hydrocyclone separators or buffer or equalization tanks. Wastewater is allowed to pass very slowly over the separator, so that demulsified oil floats on the surface and suspended solids settle down at bottom of the separator due to gravity. The free oil is skimmed off, while the settled solids are removed using scrapers or flights to a sludge-collecting hopper. The wastewater flows down the separator towards the outlet through a diffusion barrier. To prevent the oil from flowing to the outlet, baffle plates are employed. However, the American petroleum institute separator has certain limitations. It cannot separate the dissolved or emulsified oil. It can stabilize emulsions at high pH. So, spent caustic must be added to reduce pH of the American petroleum institute separator. In wastewater treatment for separating oil, water and solids, it is an efficient equipment. Some refineries also use corrugated plate interceptors or parallel plate interceptors separators instead of American petroleum institute separator, because these separators are more compact than American petroleum institute separator.

Dissolved solids may cause corrosion, plugging problems in pipelines, heat exchanger, etc. For this reason, secondary oil-water separators are involved for separation of the three-phase mixture.

Second Stage

Oil-water-solid separation is carried out using dissolved air flotation separators or induced air flotation separators or dissolved gas flotation or induced gas flotation or sand filtration. The effluent from the first stage of oil-water separator is sent to the second stage separator for the elimination of dissolved solids. The use of dissolved air flotation and induced air flotation depends on amounts, condition and quality of influent and also specification of effluents.

Dissolved Air Floatation

In this device, the first step is coagulation-flocculation. The scattered components (oil, solids) carry same charge (negative) on their surface and hence repel each other. These similarly charged components do not agglomerate to form flocs, hence do not settle. So, for removal of these dispersed particles, chemical coagulation and flocculation are needed. This is done sequentially by a combination of chemical and physical methods. At first, several coagulants like lime, certain iron-containing compounds (such as ferric chloride or ferric sulphate) and alum (aluminium sulphate) are added to wastewater to assist the suspended solids to form stable bulky particles which can settle down easily and can be removed. A portion of its effluent is pressurized, saturated with dissolved air and added to the inflowing wastewater. When the pressure of the recycle stream is released, the air bubbles liberated cause free oil and solids to float up, which is skimmed off. In this device, the solids that settle down are occasionally scraped off.

Induced Air Floatation

In the induced air floatation, a rotor-disperser system drags the air and combines with the influent wastewater. The wastewater passes through a set of chambers before being discharged from the unit while the float (~ 1–10% of the forward flow) moves over the weir, thus enabling effective removal of free oil. These units operate satisfactorily when the oil and dissolved solids level of the wastewater is less and there is minute variance in flow as well as load. Low capital cost and compact size are the main advantages of this system.

However, dissolved air floatation and dissolved gas floatation devices are more widely used in petroleum and petrochemical industries, since they are more robust, can produce better-quality effluent and can handle greater variances in flow and load.

Clarifiers and filters (sand or dual media) may be used as alternatives to floatation. Sand and anthracite are commonly used as filtering media. Anthracite entraps large particles, whereas sand filter catches the fine solids. Dual media filter means a combination of anthracite and sand filters. These types of filters can separate the oil particles with diameters of 2–5 μm and effluentoil concentration less than equal to 20 mg/L can be achieved. The filter is regularly cleaned up using a backwash cycle to remove the trapped particles and oil by an air scour.

Equalization System

The equalization system aims to minimize fluctuations in flow and composition of wastewater. Reducing flow variations decreases loads on the downstream units, thereby reducing their sizes and costs. On the other hand, composition equalization reduces shock generation in subsequent biological units. The performance of the biological system largely depends on the adaptability of the microorganisms to the changing environment of the wastewater both in terms of quality and quantity. The equalization tank should be cleaned regularly (once or twice in a year) to prevent accumulation of wastes (International Petroleum Industry Environmental Conservation Association 2010; Shahryar 2017; Alireza 2014).

Secondary Treatment

The secondary treatment further handles the effluents from primary treatment in the petroleum refinery. After primary treatment, the residual organics, colloidal organic matters, suspended solids and oily sludge are treated by using cultured microorganisms like bacteria (*Arcobacter)*, fungi (*Aspergillusniger*), algae (*Chlorella)* in presence of oxygen, that is aerobic biological treatment or absence of oxygen, that is anaerobic biological treatment. But, most refineries use the aerobic process, because it is faster, produces no smell and forms stable products (Indus Eco Water, India 2019). In aerobic biological treatment, the aerobic microorganisms such as *Longilinea, Georgenia* metabolize the organic matter, oily sludge, thereby increasing the growth of microorganisms and produce some inorganic compounds like carbon dioxide, ammonia and hydrogen sulphide. The biological treatment process is dependent on the volume of the reactor, growth rate of microorganisms and the oxygen availability. If the reactor volume is small and high concentrations of microorganisms are present, then the rate of the secondary treatment is high and efficiency is also better. In aerobic process, the chemical oxygen demand and biochemical oxygen demand of wastewater is significantly reduced (International Petroleum Industry Environmental Conservation Association 2010; Central Pollution Control Board, India 2018; Shahryar 2017; Alireza 2014).

After wastewater treatment, the used microorganisms are separated from the treated water. These used microorganisms are called biological solids which are combined with the sludge after wastewater treatment (International Petroleum Industry Environmental Conservation Association 2010).

The most important processes involved in the secondary aerobic wastewater treatment are suspended growth process (activated sludge, stabilization pond), attached growth process (trickling filter, rotating biological contactor), nitrification and denitrification (International Petroleum Industry Environmental Conservation Association 2010; Shahryar 2017).

Suspended Growth

In this process, the microorganisms are systematically combined with organic wastes (non-settleable, colloidal particles) to maintain suspended growth of microbes for removal of oil, grease, suspended hydrocarbons in presence of oxygen. There are two types of suspended growth: (1) activated sludge and (2) stabilization pond.

Activated Sludge

The most widely used suspended growth process is the activated sludge process. It is an incessant suspension growth process of aerobic microorganisms in wastewater that may consist of suspended colloidal, dissolved organic-inorganic matter, which is used as food for growth of microbes and evolving carbon dioxide, ammonia and methane gas by oxidation. The whole process is done in a dispersed growth reactor: an aeration tank or basin. Air is constantly injected using a submerged diffuser (aeration device) into the system to control the aerobic sludge in suspension medium. The requirement of oxygen is about 0.6–1.5 kg O_2/kg of biochemical oxygen demand removal in this system. The mixtures that occur in this aeration basin such as wastewater-sludge are called mixed liquor suspended solids. The organic fraction of the mixed liquor is referred to as mixed liquor volatile suspended solids. The mixed liquor suspended solids of a typical refinery wastewater system consists of 70–90% active mixed liquor volatile suspended solids and 10–30% inert solids (International Petroleum Industry Environmental Conservation Association 2010).

From the aeration tank, the mixed liquor suspended solids or mixed liquor volatile suspended solids is passed through a clarifier. Here, the sludge containing the biomass is separated. A portion of the concentrated sludge is recycled to the aeration tank to maintain an adequate microbial mass and is called the return activated sludge. The rest is regularly discharged as waste activated sludge (International Petroleum Industry Environmental Conservation Association 2010).

According to the Environmental Protection Agency, the removal efficiency of activated sludge is 80–99% for biochemical oxygen demand, 50–95% for chemical oxygen demand, 60–85% for suspended solids, 80–99% for oil, 95–99% for phenol, 33–99% for ammonia and 97–100% for sulphides (Shahryar 2017).

Stabilization Pond

The stabilization pond is basically a large pond of low depth where bacteria stabilize the wastewater introduced to this pond under warm weather conditions. Stabilization pond is of two types: aerobic and anaerobic based on biological activity. Normally, refinery biological wastewater treatment involves the aerobic type pond or the oxidation pond (International Petroleum Industry Environmental Conservation Association 2010; Shahryar 2017).

The oxidation ponds have excessive weed growth and normally have a depth of about 1.2 m. Oxygen is supplied to the surface of pond by natural aeration and by the photosynthesis reaction of algae (*Chlamydomonas*, *Chlorella)*. The organic matters are aerobically degraded by the algae, bacteria, fungi, etc., in presence of sunlight.

The efficiency of oxidation ponds is influenced by some factors like temperature, presence of turbidity and emulsions in the pond. The microbial activity in the pond slows down with temperature and when ice forms over the surface of pond due to shortage of oxygen and sunlight, the activity drops abruptly. The emulsion and turbidity in the pond also diminishes the light transmission and during such situation, the photosynthetic action of bacteria is inhibited. However, the oxidation ponds require a sufficiently large space. The advantages of this system are low maintenance cost. A report of the Environmental Protection Agency states that the removal efficiency of oxidation pond is 40–95% for biochemical oxygen demand, 65–85% for chemical oxygen demand, 80–90% for suspended solids and 50–90% for oil (International Petroleum Industry Environmental Conservation Association 2010; Shahryar 2017; Alireza 2014).

Aerated lagoons are artificial aerobic stabilization ponds, where oxygen is supplied usually by mechanical devices like pump, diffuser, and bacteria consume the organic matter, suspended solids in warm weather. It requires less area for wastewater treatment but requires high maintenance of mechanical equipment. According to the Environmental Protection Agency, the removal efficiency of lagoons is 75–95% for biochemical oxygen demand, 60–85% chemical oxygen demand, 60–95% for suspended solids, 70–90% for 90–99% for phenol and 95–100% for sulphides. But the efficiency of lagoons also diminishes in cold weather similar to oxidation ponds, because in absence of sunlight, the bacterial growth reduces, generating bad odour. By incorporating the clarifier, sludge-return pumps and additional aeration equipment aerated lagoons can be stepped up to an activated sludge system (International Petroleum Industry Environmental Conservation Association 2010; Central Pollution Control Board, India 2018; Shahryar 2017; Alireza 2014; Mareddy 2017; Patwardhan 2008).

Attached Growth Process

In the attached growth process, microorganisms are immobilized on inert polymeric materials. The microorganisms digest the oily wastes with the help of oxygen for growth of excess biomass, producing carbon dioxide. When a huge amount of biomass called sloughs are generated, they are immediately cleaned up. There are two types of attached growth equipment like trickling filter and rotary biological contactor (International Petroleum Industry Environmental Conservation Association 2010).

Trickling Filter

Trickling filter or bio-filter is a basin which is supported with permeable media such as shredded polyvinyl chloride, rocks, gravels, tubes, corrugated blocks, etc. The specific surface and diameter of the permeable materials are about 30–900 m^2/m^3 and 7–9 cm, respectively. The microorganisms are attached to these substances for their suspended growth. The microorganisms are added to the wastewatereffluents from primary treatment or equalization system. These microorganisms consume the wastes (oil, grease), producing carbon dioxide, methane, ammonia, etc. Generally, oxygen is introduced either up or down to the bed by natural air flow. Occasionally, air is introduced forcefully by blower, pump and diffuser. The underwater air moves through the void space of the filter bed by inlet draught tubes. After treatment of wastewater in trickling bed, the treated water is drained out through the under drain channel. The trickle filter is cleaned up periodically (once or twice in year) by scraping the dead microorganisms. It may be located upstream of the activated sludge process to reduce organic loads. Sometimes wastes microbes are recycled to the filter for enhancing hydraulic distribution of the wastewater into the filter. The removal efficiency of trickling bed is 60–85% for biochemical oxygen demand, 30–70% for chemical oxygen demand, 60–85% for suspended solids and 50–40% for oil (International Petroleum Industry Environmental Conservation Association 2010; Shahryar 2017; Alireza 2014).

Rotating Biological Contactor

Rotating biological contactors contain rotating discs that are closely placed on a horizontal shaft. The distance between two rotating discs is 2–3 cm, approximate diameter of discs is 3 cm and the speed of the disc is about 1–2 rpm. The rotating discs are made of plastic materials, polyurethane, polyvinyl chloride, polystyrene, etc. These plastic discs are partially immersed (approximately 40–45%) into the wastewater and are continuously rotated along a horizontal shaft using an air-driven machine. Amount of dissolved oxygen in wastewater is increased by surface turbulence (bubbles formation) due to disc rotation. The microorganisms, like oil-degrading bacteria (*Burkholderia cepacia*), protozoa, attach to the discs and digest the organic pollutants as feed and also grow vigorously on this media. Excess biomass generated is cleared off regularly from the disc surface. Some advantages of this contactor are low energy consumption, simple operation and maintenance. Moreover, they do not need addition of aeration devices, because oxygen transfer facility is present in the system by the rotation of discs. According to the Environmental Protection Agency, the removal of efficiency of this equipment is 85% for biochemical oxygen demand and suspended solids. Some industry rotating biological contactors may be incorporated into grit chamber, settling tank and comminutors for better removal of organic pollutants (International Petroleum Industry Environmental Conservation Association 2010; Shahryar 2017; Alireza 2014).

Nitrification and Denitrification

Normally, organic pollutants are treated by secondary biological treatment in most of the refineries. But, nitrogen-containing organic matter and ammonia-based pollutants are removed by nitrification or integrated nitrification-denitrification processes. Nitrification is a biological oxidation treatment where ammonium $\left(NH_4^+\right)$, nitrogen-based compounds are oxidized to nitrite (NO_2^-) in presence of bacteria (*Nitrosomonas*) and then nitrite (NO_2^-) is further oxidized to nitrate $\left(NO_3^-\right)$ with the help of bacteria (*Nitrobacter*). Both reactions are carried out in presence of oxygen in an aeration or oxic tank. Heterotrophic bacteria use the nitrate produced during nitrification to derive oxygen and the available carbon resource (methanol, glycerine and ethanol) for denitrification. In denitrification, nitrate $\left(NO_3^-\right)$ is reduced to nitrite (NO_2^-), nitric oxide (NO), nitrous oxide (N_2O) and nitrogen (N_2) in absence of dissolved oxygen with the help of heterotrophic bacteria (*Pseudomonas*) (Shahryar 2017; The water planet company, New London 2019).

(i) *Nitrification reactions*:

Presence of Nitrosomonas

$$2\mathrm{NH_4^+} + 3\mathrm{O_2} \rightarrow 2\mathrm{NO_2^-} + 2\mathrm{H_2O} + 4\mathrm{H^+} \tag{8.1}$$

Presence of Nitrobacter

$$2\mathrm{NO_2^-} + \mathrm{O_2} \rightarrow 2\mathrm{NO_3^-} \tag{8.2}$$

(ii) *Denitrification reactions*:

Presence of *Pseudomonas*

$$\mathrm{NO_3^-} + 2\mathrm{H^+} + 2\mathrm{e^-} \rightarrow \mathrm{NO_2^-} + \mathrm{H_2O} \tag{8.3}$$

$$\mathrm{NO_2^-} + 2\mathrm{H^+} + \mathrm{e^-} \rightarrow \mathrm{NO} + \mathrm{H_2O} \tag{8.4}$$

$$2\mathrm{NO} + 2\mathrm{H^+} + 2\mathrm{e^-} \rightarrow \mathrm{N_2O} + \mathrm{H_2O} \tag{8.5}$$

$$\mathrm{N_2O} + 2\mathrm{H^+} + 2\mathrm{e^-} \rightarrow \mathrm{N_2} + \mathrm{H_2O} \tag{8.6}$$

So, the overall reaction is

$$2NO_3^- + 12H^+ + 10e^- \rightarrow N_2 + 6H_2O \qquad (8.7)$$

The reaction rate depends on the pH and temperature of wastewater. The effective pH of this reaction is 6.5–7. The wastewater temperature is 30–35 °C to attain maximum rate. However, if temperature is higher than 40 °C, then the nitrification rates fall to near-zero and if the temperature is less than 20 °C, then reaction proceeds slowly but may continue up to 10 °C. In certain cases, when high concentrations of nitrogenous wastes elimination are needed and to meet nitrogen specification in effluents, then combination of nitrification-denitrification reactions need to be applied. To improve the secondary biological treatment process, the nitrification-denitrification reactions can be included into both activated sludge and trickling bed processes. The separation efficiency of wastewater treatment plant is improved using the nitrification-denitrification process. This requires the inclusion of anoxic (non-aerator) tank either before (pre-nitrification) or after (post-denitrification) the oxic tank. During post-denitrification, the anoxic chamber contains a carbon source to improve denitrification. Here in pre-denitrification, the biochemical oxygen demand of wastewater serves as the source of food in the anaeration chamber. The European commission and the joint research centre stated that removal of nitrogen is typically about 10% by activated sludge process, 70–80% by nitrification-denitrification bio-reactor and up to 90% by three-step denitrification system (Shahryar 2017; Alireza 2014).

Tertiary Treatment

Tertiary treatment is the extension of conventional secondary wastewater treatment that is carried in petroleum industry to get stable products and to meet discharge specifications with respect to biochemical oxygen demand, chemical oxygen demand, total dissolved and suspended solids, heavy metals, carcinogenic compounds like benzene, refractory hydrocarbons, nitrogen and phosphorous. Tertiary treatment involves chemical oxidation (disinfection) succeeded by pressure sand filtration and then activated carbon adsorption for sludge treatment and removal of toxic organic contaminants (Shahryar 2017).

Chemical Oxidation

In chemical oxidation, the oxidizing reagents like hydrogen peroxide, chlorine peroxide, ozone and methanol are used for disinfection and neutralization of non-biodegradable pollutants and reduction of residual chemical oxygen demand, total suspended solid, etc. The non-biodegradable pollutants are passed to the oxidizer via a feed tank. The chemical oxidants are freshly prepared to sustain their reactivity and then introduced to the oxidation reactor. After oxidation, the effluents from this reactor are sent to another vessel to maintain the pH. Sometimes, the efficiency of this treatment process can be enhanced by using ultra-violet rays as catalyst. When the refinery wastewater contains high level of toxic materials like aromatic fractions, then secondary biological treatment is unsuitable; however, chemical oxidation can degrade these wastes (International Petroleum Industry Environmental Conservation Association 2010; Shahryar 2017; Alireza 2014).

Disinfection

During disinfection, chlorine solution (bleaching) is injected into the disinfectant tank to destroy the microorganisms including bacteria, viruses and protozoa, like *Salmonella*, *Shigella* and *Vibrio cholera*. Disinfection is also sometimes referred to as chlorination. Chlorine is the most widely used disinfectant, because it controls odour, activated bulk sludge, foaming, removes grease, ammonia and destroys cyanides, phenols. In some refineries, ozone or ultra-violet rays are also used for disinfection to enhance the efficiency.

Nowadays, chlorination is frequently used for wastewater treatment before discharging water to river, streams, local aquatic bodies and ocean. The amount of chlorine solution depends on the quality, quantity and pH of wastewater, contact time and effluent temperature. However, the dosage of chlorine used usually ranges from 5 to 15 mg/L. The chlorine-containing chamber is maze shaped, equipped with baffles to avoid short-circuiting. In the reaction chamber, the contact time usually is about 30 min, but for advanced wastewater treatment, the contact time may be as long as 120 min in order to use the treated water for irrigation (International Petroleum Industry Environmental Conservation Association 2010; Shahryar 2017; Mareddy 2017).

Sand Filtration

After secondary wastewater treatment, typically 25–80 mg/L of total suspended solids, 5–25 mg/L of organic suspended solids in colloidal form are present in the effluent ,depending on the working condition of the clarifier. But some refinery effluents are required to meet low levels of suspended solids (15 mg/L). Hence, the solids of effluents from clarifier should be filtered by sand filter. For better removal of large suspended particles, dual filter is used (described earlier in Section Induced Air Floatation). Filtration can reduce colloidal and suspended solids level to around 3–20 mg/L (International Petroleum Industry Environmental Conservation Association 2010; Shahryar 2017; Mareddy 2017).

Activated Carbon Adsorption

Activated carbon adsorption is applied for eliminating the dissolved and refractory organics from wastewater after secondary treatment process. It is widely used because of its (activated carbon) small pore size, large surface area, bulk density and high adsorption capacity. In this step, the activated carbon in the form of granular activated carbon, bentonite, powdered activated carbon and deposited carbon is used as adsorbent for oil removal from oil-water emulsion by adsorption. The adsorption capability is higher for deposited carbon and bentonite than powdered activated carbon. The activated carbon bed is either fixed or moving in parallel. For moving activated carbon adsorption bed, carbon is moved from adsorbers to regenerator and back continuously. These activated carbon beds are costly. When high-quality effluent is needed, then activated carbon adsorption is used for treatment of wastes. The operating parameters such as flow rate, depth and contact time of an activated carbon adsorption system are 3.42–6.9 × 10^{-3} $m^3/s/m^2$, 3.048 m minimum and 15–38 min, respectively. The biochemical oxygen demand, oil and phenol content of effluents can be reduced to 3–10 mg/L, less than 1 mg/L and approximately ‘0’, respectively, by applying this process. The removal efficiency of the activated bed generally increases with increased contact time and amount of adsorbents and decreases when concentration of adsorbate (effluent) is increased (International Petroleum Industry Environmental Conservation Association 2010; Shahryar 2017; Alireza 2014). Figure 8.2 shows the block diagram of wastewater treatment in petroleum refinery.

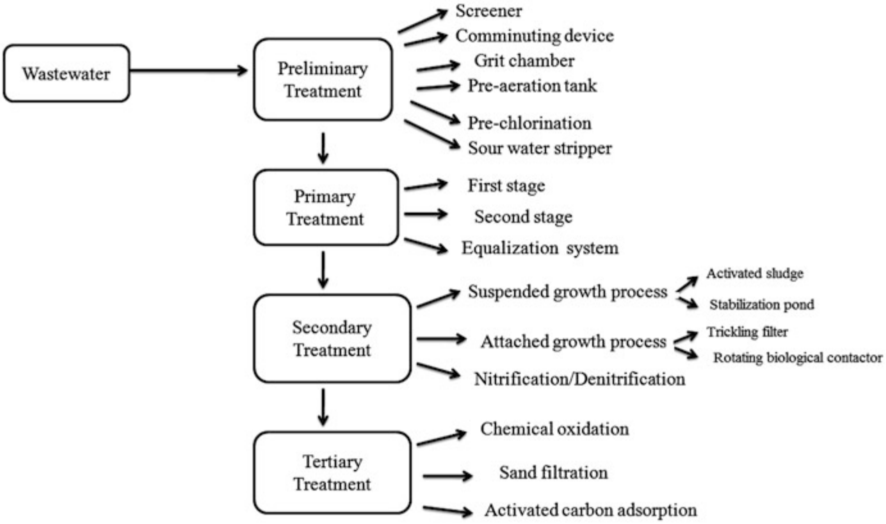


Fig. 8.2 Block diagram of wastewater treatment in petroleum refinery

Advanced Treatment

Most of the suspended solids as well as biochemical oxygen demand of refinery wastewater are removed by primary and secondary treatment processes. However, in most cases, after these treatment processes, the water quality is inadequate to be reused either in industry or for domestic purposes. Hence, advanced treatment processes are further incorporated for better separation efficiency of organic matter, nutrients and harmful chemicals from refinery effluents, with an aim to achieve better water quality. Advanced treatment may be incorporated into primary, secondary and tertiary treatment units. Following are some advanced technologies which are used for wastewater treatment in refineries (International Petroleum Industry Environmental Conservation Association 2010; Central Pollution Control Board, India 2018; Shahryar 2017; Alireza 2014; Mareddy 2017).

A. Activated sludge with powdered activated carbon
B. Sequencing batch reactor
C. Membrane technology
D. Membrane bioreactor

The advanced technology depends on flexibility, operating and maintenance cost, operability, space availability, etc.

Activated Sludge with Powdered Activated Carbon

The conventional activated sludge process is upgraded by introducing powdered activated carbon as adsorbent. The powdered activated carbon technology is a combination of biological oxidation and adsorption. The surface area of adsorption is increased by using powdered activated carbon, thereby enhancing the removal efficiency of organic matter. In most cases, the used powdered activated carbon is recycled with activated sludge, but fresh powdered activated carbon is also required to maintain the efficiency. This technology is normally applied in situations where specific standards are required to be met for definite contaminants of refinery wastewater (International Petroleum Industry Environmental Conservation Association 2010; Shahryar 2017).

Sequencing Batch Reactor

The sequencing semi-batch reactor is a fill-draw biological treatment which consists of aeration, sedimentation and clarification in a single batch reactor. The aeration and sedimentation steps are similar between sequencing batch reactor and activated sludge system. However, these two steps are operated in different chambers in activated sludge process, whereas in sequencing batch reactor, these two steps are processed in the same tank consecutively. However, this technology is applied only in a few refinery wastewater treatment plants. The steps involved in a sequencing batch reactor process are

A. Fill:

It is a simple filling operation where wastewater from equalization tank is charged into the reactor.

B. React:

Here, wastewater is aerated and biological activity starts sequentially.

C. Settle:

Mixed liquor suspended solids settle down after aeration is stopped. No flow is allowed to enter or leave the reactor during settling.

D. Decant:

In this step, the lighter effluent is taken out from the top of the reactor. The settled sludge is periodically retracted from the bottom of the reactor (International Petroleum Industry Environmental Conservation Association 2010; Shahryar 2017; Alireza 2014).

Membrane Technology

Membrane technology is a separation technology (based on particle size) where a selective barrier between two adjacent phases is applied for the separation of submicron suspended and dissolved contaminants such as organic matter, nutrients, turbidity, microorganisms, inorganic metal ions, etc., from wastewater in a modern refinery. The separation efficiency depends on selectivity of membrane. The advantages of membrane technology are their transport selectivity as compared to other processes, no need of any catalyst, additives and provides a clean compact technology. The membrane may be degraded after long-term utilization and fouled due to clogging of pores and gel formation on its surface. So, the membrane efficiency and flux decrease. The fouling can be controlled by using fouling or scaling inhibitors.

There are four types of pressure-driven membrane separation processes such as microfiltration, ultrafiltration, reverse osmosis and nanofiltration. It is noticed that an individual membrane technology is not suitable for oily wastewater treatment. A combination of two or three types like ultrafiltration and reverse osmosis, microfiltration and reverse osmosis, microfiltration and nanofiltration, microfiltration and ultrafiltration, etc., is required (International Petroleum Industry Environmental Conservation Association 2010; Central Pollution Control Board, India 2018; Shahryar 2017).

A. Microfiltration:

Microfiltration is used for the rejection of suspended solids and emulsified oil which have particle size greater than 0.1 μm approximately in refinery. After conventional treatment, microfiltration is used before reverse osmosis as pre-treatment for protection of reverse osmosis membrane life, to reduce fouling as well as operational cost of this process. The microfiltration membrane is porous, isotropic and is usually made of hydrophobic polymers like polysulphone, polyethersulphone, polypropylene, polyvinylidene fluoride. However, recently, ceramic materials and inexpensive clay mixtures, such as ball clay, kaolin, feldspar, quartz, pyrophyllite, calcium carbonate, are also employed for preparation of these membranes. The hydrophobic nature of the membrane renders greater affinity towards organic matter such as oil and grease. This might lead to membrane fouling by oil and grease. Hence, pre-treatment with granular activated carbon is done to limit the oil and grease content to less than 1 mg/L. The membrane module may be either hollow or tubular type. The wastewater is passed through a series of membranes under pressure or vacuum. The wastes accumulate on the upstream side of the membrane. When the thickness of fouling layer on the surface of the membrane increases, the trans-membrane pressure will slowly increase. The accumulated contaminants are eliminated periodically by use of backwash with disinfectants such as sodium hypochlorite, etc. The operating pressure range and hydraulic permeability range are 0.1–2 bar and greater than 1000 L/hr-m^2 –bar, respectively. Scaling, fouling or biofouling may occur on the membrane due to the formation of biological growth and long-term operation; therefore, flux as well as separation factor may diminish. Hence, some biofouling inhibitors such as bioacids (chlorine, chloramine) are added to protect the membrane. However, the accumulated contaminants are removed by using disinfectants like sodium hypochlorite. Spent granular activated carbon or polymeric materials may require regeneration, and it depends on quality and quantity of wastewater. The treated water after microfiltration is not suitable for makeup water in boiler feed water and in cooling towers but may be used as emergency firewater (International Petroleum Industry Environmental Conservation Association 2010; Shahryar 2017).

B. Ultrafiltration:

Ultrafiltration is used for the removal of colloidal proteins, pigments, oils, organics, microparticles from wastewater and the size range of the retained particles is 0.001–1 μm. The operating pressure is about 1–5 bar and the hydraulic permeability is 10–1000 L/m^2 hr-bar. Ultrafiltration like microfiltration may also be used before reverse osmosis process as pre-treatment to maintain the performance of reverse osmosis membrane. In this technology, tubular or hollow ultrafiltration module is equipped with polymeric or inorganic porous asymmetric type membrane. The ultrafiltration operating process is same as microfiltration. Fouling or biofouling may arise on the membrane of ultrafiltration due to long time operation and generation of biological growth which may be removed by using bioacids as in microfiltration membrane (International Petroleum Industry Environmental Conservation Association 2010; Shahryar 2017). However, both microfiltration and ultrafiltration are not suitable for removal of heavy metals and dissolved salts (Shahryar 2017).

C. Nanofiltration:

Nano filtration is mainly utilized for removal of selective dissolved organic-hydrocarbon pollutants and hardness at moderate pressure: 3–20 bar. Some features like design and operation, as well as physical dimensions of membrane elements of nanofiltration are almost same as reverse osmosis. Hence, nanofiltration membranes can be accommodated in reverse osmosis modules. But main difference between these two filtrations is that salt and metal abandonment is higher with higher operating pressures. The particle size of the retentate ranges from 0.001 to 0.01 μm and the hydraulic permeability is 1.5 to 30 L/m^2 hr-bar in nanofiltration. This membrane may be composite or porous asymmetric. Commercial nanofiltration membranes possess a fixed charge that causes ions to be separated based on size, electrical effects and ion interactions. However, it can replace reverse osmosis in wastewater treatment due to its less energy requirement and higher flux. Nanofiltration membranes usually exhibit greater efficiency in rejecting hydrophilic compounds than the hydrophobic ones. Around 90–95% pollutant rejection can be achieved by this process (International Petroleum Industry Environmental Conservation Association 2010; Shahryar 2017).

D. Reverse Osmosis:

Reverse osmosis uses a semipermeable membrane where dissolved solids, ions, pyrogens, nitrate, etc., are removed from wastewater and the retained particle size varies from 0.0001 to 0.001 μm. Reverse osmosis is operated when the pressure difference is higher than the osmotic pressure (5–120 bar). It is a most commonly used process for desalting of oily wastewater. The reverse osmosis membrane is nonporous, asymmetric or composite and has a hydraulic permeability of 0.05–1.5 L/m^2 hr-bar. After reverse osmosis, the water may be reused in the petroleum industry. The reverse osmosis membranes require pre-treatment by microfiltration or ultrafiltration, because they have very fine pores which are easily plugged by suspended solids. The concentration of oil and grease in the reverse osmosis feed water is recommended to be less than 0.1 mg/L. The salt rejection capacity using this technology may be as high as 99%. It is successfully used worldwide for wastewater treatment but requires high-energy consumption in terms of pressure (International Petroleum Industry Environmental Conservation Association 2010; Shahryar 2017).

Membrane Bio-reactor

Membrane bio-reactor is a membrane-based biological treatment where a membrane process (microfiltration) combines with a suspended growth process (activated sludge) to improve secondary clarification in activated sludge system. The microfiltration membrane is placed in a membrane tank (steel) at a low vacuum to draw water through the membrane as well as pump out the filtered water while the solids are retained in the bio-reactor. The air is compressed and inserted into the reactor to polish the outer surface of the membrane. The membrane bio-reactor is used when the mixed liquor suspended solids level is higher (15,000–20,000 mg/L) than the conventional activated sludge process. In general, membrane bio-reactor is not used in refineries, because it is expensive. But when conventional activated sludge requires tertiary filtration, it can be a better option, since it acts as an effluent filter (International Petroleum Industry Environmental Conservation Association 2010). Where reverse osmosis is used for wastewater treatment, membrane bio-reactor may be an attractive alternative to microfiltration or media filtration after biological treatment (International Petroleum Industry Environmental Conservation Association 2010; Shahryar 2017; Mareddy 2017).

All advanced technologies are still undergoing research and development.

8.4.5 Wastewater Treatment in Petrochemical Complex

The petrochemical complexes produce valuable products, but its effluent may cause harmful effects to the environment. The wastewater from the petrochemical complex contains hazardous compounds, some of which are carcinogenic. Hence, the wastewater treatment requires modern technology to minimize the concentration of pollutants as per the environment laws. In the petrochemical complex, the wastewater treatment technology is more or less same as in a petroleum refinery. Here also the wastewater is subjected to preliminary treatment (skimmer, comminuting device, grit chamber), primary treatment (different separators), secondary treatment (suspended growth, attached growth process, nitrification and denitrification), tertiary treatment (sand filtration, activated carbon adsorption) and advanced treatment (powdered activated carbon, sequencing batch reactor, membrane technology, membrane bio-reactor). These have already been discussed in the refinerywastewater treatment section. However, petrochemical effluents are treated mainly by secondary biological processes (Patwardhan 2008; Ghimire and Wang 2018; Balasubramani and Sivarajasekar 2018).

Additionally, new or better wastewater treatment technologies have been developed to convert the complex refractory substances into more simple substances for improving water quality. Some new technologies are the following (Balasubramani and Sivarajasekar 2018):

A. Anaerobic treatment:

When aerobic treatment is not sufficient for wastewater treatment adequately, then anaerobic treatment can be involved.

B. Autotrophic denitrification:

In this process, the nitrogenous as well as sulphur pollutants are removed by denitrification process followed by biological anaerobic processes.

C. Clean electrochemical technology:

Using clean electrochemical technology, chemical oxygen demand, turbidity, phenol, grease and petrochemicals as well as other hydrocarbon effluents are removed by the combination of electro-flotation and electro-coagulation.

D. Advanced biodegradation using ozone and biological activated carbon:

For the growth of bio-film and degradation of bio-refractory, the pre-ozonation and lifted moving bed biological activated carbon are used.

E. Coagulation-flocculation process:

It is used for specific petrochemical wastewater treatment containing high aromatic content (benzoic acid, phthalic acid, terephthalic acid), purified terephthalic production unit wastewater, etc. In coagulation-flocculation process, some coagulants like ferric chloride and alum are used. The efficiency of this process is 75.5% for removal of chemical oxygen demand. In this process, some cationic compounds (polyacrylamide) are added to improve the sludge filtration. For better removal of suspended solids, coagulation-flocculation process may be used for pre-treatment prior to microfiltration and ultrafiltration membrane technologies (Ghimire and Wang 2018).

8.4.6 Wastewater Treatment in Fertilizer Industry

The water effluent from the fertilizer industries contain nitrogenous, phosphorous-based fertilizers like urea, diammonium phosphate, isobutylidenediurea and dicyandiamide which are hazardous. So, there is an urgent need to treat these wastewaters before reuse. The effluent is accumulated in a holding tank and time to time the level is recorded. The effluent is segregated based on the nature and concentration of pollutants they contain. Suspended solids in effluents with minimum concentration of 100 mg/L should be combined together. Oil-based effluents must be separated; also urea-bearing effluents should be separated from nitrogen-bearing effluents. Highly acidic, alkaline effluents and ash slurry should be separated from the rest of the effluent streams. The cooling tower purge water contains chromate, phosphate and bioacids; hence, they should be segregated from the rest of the effluents. Carbon-, arsenic- and cyanide-containing effluents should be stored separately. These segregated effluents, however, can be combined, depending on their properties and the type of treatment required, such that one can be utilized for the treatment of the other. This type of judicious combination can reduce the operating cost and increase the efficiency of the treatment process. Mainly two types of processes are involved in fertilizer wastewater treatment plant; physico-chemical and biological process (Sengupta 2019; Elela and Elkamah 1995).

Physico-chemical Process

The ammoniacal effluents are removed with the help of physico-chemical processes (air stripping, steam stripping and ion exchange). These effluents are not hydrocarbon based. The suspended solids and oil-grease bearing effluents are removed from fertilizer wastewater by physical process. Generally, the suspended solids are settled down by gravity, but when particle size is small enough, then mechanical clarifiers with proper dosing of coagulants or poly-electrolytes is used for quick settling. The sludge is then discharged from the bottom of the clarifier by either dewatering or mechanically.

The oil-grease based effluents are discharged from fertilizer wastewater in non-emulsified form. The lighter oil-grease floats over the water in an oil-water separator and then easily separated by using skimmer. This type of effluent may be regularly skimmed out mechanically. Usually, by this process, 50 mg/L of oil-grease effluents are removed. But, if high degree of efficiency is required, then the effluents pass through the activated carbon or porous coke bed as in refinery's activated carbon adsorption process. Then oil-grease concentration in effluents as low as 2–10 mg/L can be achieved (Sengupta 2019; Elela and Elkamah 1995).

Biological Process

The oil-bearing or hydrocarbon-based wastes are treated by biological processes. The biological treatment of wastewater in fertilizer industry is almost similar to that of a petroleum refinery.

8.4.7 Wastewater Treatment in Textile Industry

The textile wastewater contains colour pigments, dying materials, organic compounds, etc. The textile effluents are much polluted, since they contain reactive dyes which are not easily treated by biological processes. The reactive dyes and colour organic matter are very harmful for the growth of aquatic organisms and imbalance the environment. Hence, the wastewater from textile industry should be treated by chemical, biological, physical and hybrid treatment processes before discharge. It can also be treated using membrane technology which is similar to refinery wastewater membrane technology such as microfiltration, ultrafiltration, nanofiltration and reverse osmosis processes (Jain et al. 2016; Vineta et al. 2014).

Physical Treatment

Physical treatment is used for the de-colouration of wastewater and reduction of azo dyes by coagulation, flocculation, etc. But these processes have low de-colouration efficiency and large production of sludge, because textile wastewater contains large amount of highly reactive dyes. The attractive physical process is adsorption which is utilized for the de-colouration of wastewater with high efficiency. Its efficiency depends on the adsorption and regeneration capability of adsorbent. The common and useful adsorbent is activated carbon, but it is costly and it has regeneration problems for decolouration (Navin et al. 2018).

Chemical Treatment

The chemical treatment of wastewater in textile industry can be categorized into two processes viz. advanced oxidation and chemical oxidation. The toxic materials and their by-products are degraded by using these processes. In advanced oxidation process, hydroxyl radicals are generated that vigorously react with dyes, because they are strong oxidizing agents as compared to hydrogen peroxide, potassium permanganate, etc. In chemical oxidation, ozone and hydrogen peroxide are used as oxidizing agents, because these compounds generate strong non-selective hydroxyl radicals. These hydroxyl radicals have high oxidation potential to break conjugated double bonds of dye chromophores and functional groups that reduces colour of effluents. The rate of degradation in chemical oxidation is lower than advanced oxidation process, because in the former, few number of hydroxyl radicals are produced.

The other chemical process is ozonation where ozone is used as the oxidizing agent for treatment of wastewater. But, in this process, some toxic by-products are generated.

Another type of degradation of dyes is the combination of ultra-violet light and hydrogen peroxide which again generates high concentrations of hydroxyl radicals. This process is advantageous, since there is no sludge formation and at the same time odour is reduced. The factors affecting the rate of oxidation are the intensity of ultra-violet radiation, the pH of wastewater, structure and composition of dyes (Navin et al. 2018).

Biological Treatment

The biological method is utilized for the removal of dissolved organic matter in the textile wastewater. The removal efficiency of this method depends on the ratio of organic or dye load to microorganism load, enzyme activity, flexibility of the selected microbes, temperature of wastewater and dissolved oxygen concentration. This process is classified as aerobic, anaerobic and a combination of both, depending on the presence of oxygen. The advantages associated with this process are: eco-friendly, cost-effectiveness, less sludge production, production of non-hazardous metabolites, less requirement of water as compared to chemical-physical process, etc. Here common microorganisms like bacteria, fungi and algae are used for wastewater treatment. This treatment process is somewhat similar to that followed in petroleum refineries. Bacteria, fungi, algae digest the dyes or organic matter in presence of intra- or extracellular enzymes such lignin peroxidase, manganese peroxidase and laccase. Usually, the rot white fungi are cultured for removing azo dyes (Navin et al. 2018).

8.4.8 Wastewater Treatment in Paint Industry

Paint industry uses various raw materials like resins, solvents, extenders, pigments, oil and grease. Wastewater from paint industry is also detrimental to human beings and may disturb aquatic life. The wastewater treatment system in paint industry consists of primary, secondary followed by biological treatment. By this treatment process, 90–95% pollutants are removed (Silva and Barbosa 2016; Porwal 2015).

Primary Treatment

A. Oil and grease removal: At first, effluents from all processes except stiff paint unit and caustic cleaning unit pass through an oil and grease disposal device.
B. Equalisation and neutralization: The effluents from stiff paint and caustic washing section are sent to the equalization or neutralization pond. In this pond, the effluents mix with coagulants and next go to the flash mixer.
C. Clariflocculation: After equalization, the effluents are clarified in the clariflocculator tank followed by biological treatment.

Secondary Treatment

A. Secondary clariflocculation: In first clariflocculator, the sludge generated is passed through the secondary clariflocculator for biological treatment followed by sludge drying bed for dewatering. Here, the biological treatment is same as the biological treatment of textile and refinery wastewater.

8.4.9 Wastewater Treatment in Polymeric Industry

The effluents from polymeric industries consist of suspended solids, organic materials and residual polymers. These effluents look like a milky waste liquid with some solid particles dispersed into the wastewater: colloids. This type of effluent is not separated by conventional physical separation process. It requires some chemicals for neutralization of colloidal particles and some new separation technology like chemical coagulation-flocculation, membrane filtration, adsorption on activated carbon, oxidation, advanced oxidation, bio-degradation, etc. (Sher et al. 2013).

Coagulation-flocculation is described in the petrochemical wastewater treatment section. Membrane filtration, adsorption on activated carbon and biodegradation are also described in the refinery wastewater treatment section. Oxidation or advanced oxidation is described in the textile wastewater treatment section.

8.5 Effluent Specifications for Petroleum Industries

The environmental, health and safety guidelines of the World Bank group are scientific and technical documents of good international industry practice to be followed by industries. All industries should obey these guidelines to ensure safe and healthy work environment by practicing safe operating procedures, prospective development as well as prevent pollution and protect the environment. These guidelines provide performance levels and steps that are considered to be feasible in new facilities at reasonable costs (World Bank Group, United States 2016).

According to the World Bank Group and the Environmental Protection Agency, the specifications of hydrocarbon based wastewater that can be discharged from petroleum industries are listed in Table 8.5.

8.6 Conclusion

The petroleum industries generate fuel and many valuable products, but at the same time, they exert unfavourable effects on environment, due to emission of hazardous waste materials. The factors affecting water pollution are the processing technology, the scale of processing, handling and transportation. The petroleum wastewater mainly consists of suspended solids, emulsified oil, hydrocarbons, aromatics, polyaromatic hydrocarbons and heavy metals, some of which may be carcinogenic. These pollutants or hazardous compounds adversely affect the water circle when discharged into the environment. The water pollution can be controlled by following the three ‘r’s – reduce, recycle and reuse. The effluents from petroleum industries should be treated by physical, chemical and biological treatment processes as per the effluent specifications prescribed by the Environmental Protection Agency. The oil pollution act of 1990 deals with pollution of water bodies by crude oil or related products. This act imposes strict liability on owners, vendors and operators for oil spills at both onshore and offshore. The treatment technology depends on the characteristic, source as well as amount of wastewater. The treatment of petroleum

Table 8.5 Specifications of effluents from petroleum industries

Industries	Pollutants	Effluent level (mg/L)
Petroleum refinery	pH	6–9 S.U
	Temperature	<40 °C
	Biochemical oxygen demand	30
	Chemical oxygen demand	125
	Total suspended solids	30
	Oil and grease	10
	Phenol	0.2
	Benzene	0.05
	Benzo(a)pyrene	0.05
	Total sulphides	0.2
	Total nitrogen	10
Petrochemical industry	pH	6–9 S.U
	Temperature	35–38 °C
	Biochemical oxygen demand	30
	Chemical oxygen demand	100–160
	Total suspended solids	30
	Benzene	0.05
	Phenol	0.2
	Cyanides	1.0
	Methyl mercury	0.000005
	Formaldehyde	3.0
	True colour	550
	Total sulphides	1
	Surfactants	10
	Organo-phosphorous	0.5

wastewater consists mainly of such as preliminary, primary, secondary and tertiary, sometimes followed by advanced treatment methods. In preliminary and primary treatment, the oil-grease, suspended solids are skimmed off by physical methods. The organic compounds are removed in secondary step by biological treatment. The emulsified oils are separated by chemical oxidation in tertiary treatment. The fine particles or organic matters are eliminated in advanced treatment process by membrane technology. After treatment, the treated water may be directly released to surface waters under a national pollution discharge elimination system permit.

Sometimes, many technologies are not suitable for removal of stubborn and persistent compounds. Day by day, advanced technologies are being introduced like improved bioreactors, advanced oxidation that offer high efficiency of performance. Hence, effective combined technology should be chosen with proper knowledge like design, process control, systematic integration, process simulation, operation optimization for removal of strong concentrated pollutants from wastewater in petroleum industry. However, this progressive technology depends on capital and operating cost, land availability, operational procedure, discharge specifications and adaptability to industry's circumstances (workers or engineers or operator).

The water may be also polluted during transportation due to leakage of equipment (tankers, vessels) as well as pipelines. Such pollution can be reduced by proper monitoring and maintenance. Awareness and knowledge regarding the adverse effects of the hydrocarbons and related pollutants and their means of abatement is absolutely necessary to curb this problem.

References

Aboulhassan MA, Souabi S, Yaacoubi A, Baudu M (2014) Treatment of paint manufacturing wastewater by the combination of chemical and biological processes. Int J Sci Environ Technol 3(5):1747–1758

Al-Damkhi AM (2007) Kuwait's oil well fires, 1991: environmental crime and war. Int J Environ Stud 64(1). https://doi.org/10.1080/00207230601125036

Alireza B (2014) Waste management in the chemical and petroleum industries. Wiley, Hoboken

Balasubramani K, Sivarajasekar N (2018) A short account on petrochemical industry effluent treatment. Int J Petrochem Sci Eng 3(1):12–13

Cavaseno V and the Staff of Chemical Engineering (eds) (1980) Industrial wastewater and solid waste engineering. McCraw-Hill Publications Co., New York

Comprehensive Industry Document On Petroleum Oil Refinery (Central Pollution Control Board Ministry of Environment and Forests Parivesh Bhawan, Delhi, India, 2018). https://www.cpcb.nic.in. Accessed 15 May 2019

Coipuram T (2006) Iraq: United Nations and humanitarian aid organizations. https://fas.org/sgp/crs/mideast/RL31766.pdf. Accessed 20 May 2019

Crompton TR (2017) Occurrence, toxicity and analysis of toxic compounds in oceanic biota. CRC press, Boca Raton

Damian C (2013) Environmental pollution in the petroleum refining industry. Versita 24 (2):109–114

Datta J, Kopczynska P (2016) From polymer waste to potential main industrial products: actual state of recycling and recovering. Crit Rev Environ Sci Technol 46(10):905–946

David DE, Madrzykowski D, Gerald AH (1991) Flame heights and heat release rates of 1991 Kuwait oil field fires. http://iafss.org/publications/fss/4/1279/view/fss_4-1279.pdf. Accessed 19 May 2019

Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the petroleum refining (United States Environmental Protection Agency, Washington, 1974). https://www.epa.gov/sites/production/files/2015-10/documents/petrorefining_dd_1974.pdf. Accessed on 28 Mar 2019

Doerffer JW (1991) Oil spill response in the marine environment. Pergam on press, Oxford

Effluent standards (United States Environmental Protection Agency, Washington 2014). http://extwprlegs1.fao.org/docs/pdf/tw164144.pdf. Accessed 26 June 2019

Elela SA, Elkamah EM (1995) Management of wastewater from the fertilizer industry. Water Sci Technol 32(11):45–54

Energy and Environmental Profile of the U.S. Petroleum Refining Industry (Department Of Energy, United States, 1998). http://www.oit.doe.gov/petroleum/pdfs/profile.pdf. Accessed 23 Mar 2019

Environmental effects of oil spill (Environmental Pollution Centers, India, 2017). https://www.environmentalpollutioncenters.org/oil-spill/effects/. Accessed 10 May 2019

Environmental, health, and safety guidelines for petroleum refining (World Bank Group, United States, 2016). https://www.ifc.org/ehsguidelines. Accessed 20 June 2019

Environmental Impact of the Fertilizer Industry (National Programme on Technology Enhanced Learning, Indian Institute of Technology, India, 2014). https://nptel.ac.in/courses/103107086/module6/lecture3/lecture3.pdf. Accessed 12 May 2019

Environmental Impact of the Petroleum Industry (Environmental Update #12, Hazardous Substance Research Centers, South and Southwest Outreach Program, 2003). https://cfpub.epa.gov/ncer_abstracts/index.cfm/fuseaction/display.files/fil/1452. Accessed 23 Mar 2019

Fey T, Lane A, Jill et al (2011) Hope is the thing with feathers, reporter at large the Gulf War. The New Yorker Magazine, New York

Ghimire N, Wang S (2018) Biological treatment of petrochemical wastewater. Intech Open. https://doi.org/10.5772/intechopen.79655

Helmy Q, Kardena E (2015) Petroleum oil and gas industry waste treatment; common practice in Indonesia. J Pet Environ Biotechnol 6(241). https://doi.org/10.4172/2157-7463.1000241

Hunt J (2019) Harmful effects of chemical fertilizers. https://www.hunker.com/13406892/properties-of-alluvial-soils. Accessed 10 May 2019

Industry effluent standards (Central Pollution Control Board Ministry of Environment and Forests Parivesh Bhawan, Delhi, India, 2017). https://cpcb.nic.in/industry-effluent-standards/. Accessed 21 May 2019

Jain N, Sethi T, Goyal N (2016) Review paper on various techniques used in effluent treatment of textile industry. SSRG Int J Civil Eng 3(5):262–265

Juhasz A (2011) BLACK TIDE the devastating impact of the Gulf oil spill. Wiley, Hoboken

Kanuric J (2014) Oil spill accidents in the media. Erasmus University, Rotterdam

Malakar et al (2015) Estimation of VOC emission in petroleum refinery ETP and comparative analysis with measured VOC emission rate. Int J Eng Sci 4(10):20–29

Malik A et al (2014) Environmental deterioration and human health. Springer, Berlin

Mareddy AR (2017) Environmental impact assessment. Theory and practice, 1st edn. Butterworth-Heinemann, Oxford, pp 421–490

Michel J (2017) Oil spills: causes, consequences, prevention, and countermeasures. University of Singapore

Navin PK, Kumar S, Mathur M (2018) Textile wastewater treatment: a critical review. Int J Eng Res Technol 6(11):1–7

Nitrification and Denitrification (The water planet company, Huntington Street, New London, 2019). http://kisi.deu.edu.tr/orhan.gunduz/turkce/dersler/Nitrification_and_Denitrification.pdf. Accessed 24 May 2019

Olajire AA (2014) The petroleum industry and environmental challenges. J Pet Environ Biotechnol 5(4). https://doi.org/10.4172/2157-7463.1000186

Overview of Plastic Waste Management (Central Pollution Control Board, Delhi, India, 2013). https://cpcb.nic.in. Accessed 18 May 2019

Pak A, Mohammadi T (2008) Wastewater treatment of desalting units/Afshin. Desalination 222:249–254

Palaniandy P, Abdul Aziz HB et al (2017) Treatment of petroleum wastewater by conventional and new technologies – a review. Global NEST J 19(3):439–452

Pathak C, Mandalia HC (2012) Petroleum industries: environmental pollution effects, management and treatment methods. Int J Sep Environ Sci 1(1):55–62

Patwardhan AD (2008) Industrial waste water treatment. PHI learning Private Ltd, Delhi

Petroleum refining water/wastewater use and management (International Petroleum Industry Environmental Conservation Association Operations Best Practice Series 2010). http://www.ipieca.org. Accessed 22 Mar 2019

Porwal T (2015) Paint pollution harmful effects on environment. Int J Res – Granthaalayah 3(9):1–4

Prasad RG, Anuprakash MVVS (2016) Pollution due to oil spills in marine environment and control measures. IOSR J Environ Sci Toxic Food Technol 10(9):1–8

Preliminary Treatment (United States Environmental Protection Agency, Washington, 2003). http://web.deu.edu.tr/atiksu/ana52/ani405.html. Accessed 12 May

Principles of Design and Operations of Wastewater Treatment Pond Systems for Plant Operators, Engineers, and Manager (United States Environmental Protection Agency, Washington, 2011). www.epa.gov/nrml. Accessed 18 May 2019

Radelyuk I, Tussupova K et al (2019) Pitfalls of wastewater treatment in oil refinery enterprises in Kazakhstan – a system approach. Sustainability. https://doi.org/10.3390/su11061618

Ramesh Babu B, Parande AK, Raghu S et al (2007) Textile technology-cotton textile processing: waste generation and effluent treatment. J Cotton Sci 11:141–153

Sengupta A (2019) Treatment of effluents of fertilizer industry. http://www.engineeringenotes.com/environmental-engineering/treatment. Accessed on 30 May 2019

Shahryar J (2017) Petroleum waste treatment and pollution control. Elsevier, Amsterdam

Sharma A, Sharma P et al (2017) Hazardous effects of petrochemical industries: a review. Recent Adv Petrochem Sci 3(2). https://doi.org/10.19080/RAPSCI.2017.03.555607

Sher F, Malik A, Liu H (2013) Industrial polymer effluent treatment by chemical coagulation and flocculation. J Environ Chem Eng 1:684–689

Silva LF, Barbosa A (2016) Treatment of paint manufacturing wastewater by coagulation/electrochemical methods: proposals for disposal and/or reuse of treated water. Water Res 10:467–475

Speight JG (2014) The chemistry and technology of petroleum. CRC press, Boca Raton

Spill Prevention, Control, and Countermeasure (Spcc) Regulation (Environmental Protection Agency, United States, 2010). https://www.epa.gov/sites/production/files/documents/spccbluebroch.pdf. Accessed 20 July 2019

Subhasmini S (2019) How to treat wastewater from paint industry-waste management. http://www.environmentalpollution.in/water-pollution/wastewater-treatment/how-to-treat-wastewater-from-paint-industry-waste-management/7424. Accessed 23 May 2019

Summary of the Clean Water Act (Environmental Protection Agency, United States, 2017). https://www.epa.gov/laws-regulations/summary-clean-water-act. Accessed 25 June 2019

Tehrani GM, Hashim R et al (2016) Predictive environmental impact assessment of total petroleum hydrocarbons in petrochemical wastewater effluent and surface sediment. Environ Earth Sci 75:177.https://doi.org/10.1007/s12665-015-4918-1. Accessed 24 Apr 2019

TENORM: Fertilizer and fertilizer production wastes (United States Environmental Protection Agency, Washington, 2017). https://www.epa.gov/radiation/tenorm-fertilizer-and-fertilizer-production-wastes. Accessed 24 Apr 2019

Tharavathy NC, Krishnamoorthy M, Hosetti BB (2014) Oxidation pond: a tool for wastewater treatment. J Ecol Environ 2(1):1–4

The World Bank Group in collaboration with the United Nations Environment Programme and the United Nations Industrial Development Organization (1998) Pollution prevention and abatement handbook. The World Bank Group, Washington, United States

Torres O, Bhartia PK, Larko D (2014) Space view of the 1991 Gulf War Kuwaiti oil fires, http://adsabs.harvard.edu/abs/2014AGUFM.U31A..02T. Accessed 12 May 2019

Types of Waste Water Treatment Plant- Aerobic and Anaerobic (Indus Eco Water, Bangalore, India, 2019). http://www.modernstp.com/methods-treating-sewage.php. Accessed 23 May 2019

Understanding the Safe Drinking Water Act (Environmental Protection Agency, United States, 2004). https://www.epa.gov/sites/production/files/2015-04/documents/epa816f04030.pdf. Accessed 25 May 2019

Vineta S, Silvana Z, Sanja R, Golomeova S (2014) Methods for waste waters treatment in textile industry. In: Paper presented at the 3rd international scientific conference on Unitech – Gabrovo, University Goce Delcev, 21–22 November 2014

Wastewater Technology Fact Sheet Trickling Filters (United States Environmental Protection Agency, Washington, 2000). https://www3.epa.gov/npdes/pubs/trickling_filter.pdf. Accessed 25 May 2019

Walczyk AL, Gorny RL (2018) Anaerobic bacteria in wastewater treatment plant. Int Arch Occup Environ Health 91(5):571–579. https://doi.org/10.1007/s00420-018-1307-6

Chapter 9
Fate of Pharmaceutical Drugs and Metabolites in the Environment

Aliru Olajide Mustapha

Contents

Abstract

1. Issues/Problems

In recent years, there have been global concerns about the emerging levels of abused drugs (cocaine, opioid, cannabinoid, amphetamine, lysergic diethylamide and hallucinogen) apart from pharmaceuticals, dyes, solvents, pesticides, heavy metals and chemicals from industrial wastes and direct dumping of other contaminants to the aquatic environment. The escalating levels of these pollutants have prompted the need for proper monitoring of their prevalence in order to stem its

---

A. O. Mustapha (✉)
Department of Chemical, Geological and Physical Sciences, Faculty of Pure and Applied Sciences, Kwara State University Malete, Ilorin, Kwara State, Nigeria
e-mail: aliru.mustapha@kwasu.edu.ng

Inamuddin et al. (eds.), *Water Pollution and Remediation: Organic Pollutants*, Environmental Chemistry for a Sustainable World 54,
https://doi.org/10.1007/978-3-030-52395-4_9

social and environmental impacts. New drugs are daily being introduced as the number of patents keeps increasing, and the pharmaceutical products for numerous therapeutic and commercial purposes keep escalating accordingly, reaching already the increasingly polluted environment. The inadvertent and purposeful discharges of pharmacologically active compounds via excreta remain underappreciated, yet their toxicological potency on the ecosystem has become a global issue. Environmental monitoring and risk assessments have shown the sewage treatment works as one of the potential routes through which the levels of consumption by a local population can be estimated. The exposure data of trends in their distribution, biodegradability, fate, toxicity and environmental assessment can safeguard aquatic and human environment by letting the appropriate authorities involved in fighting and controlling drug menace develop the desired approaches in controlling and effective monitoring of emerging pollution challenges.

2. Major Advances

We reviewed the occurrence of bioactive metabolites, metabolism, measurement, transport routes in the aquatic environment and treatment processes with the available analytical methodologies in the literature.

The major points are:

1. The literature showed the distribution of the plethora of trace drugs include abused drugs, which were as follows: cocaine, opioid, cannabinoid, amphetamine, lysergic diethylamide, hallucinogen and pharmaceuticals of many therapeutic classes of drugs: antibiotics, anti-inflammatory, anti-epileptics, antineoplastics, antidepressants, beta-blockers, β_2-sympathomimetics, contraceptives, diagnostic contrast media, lipid regulators, preservatives, sunscreen agents and tranquilizers in the environment. They occurred in varying concentration and range from 10 to 8700 ng L^{-1} in sewage treatment works and 10–410 ng L^{-1} and stream at different locations.
2. The environmental analyses have shown that significant routes which the pharmaceutical drugs enter the aquatic environment are some domestic sewage systems from Italy, Belgium, Spain, Germany, the United States and the United Kingdom with 15 compounds detected from biweekly samplings from Nottingham sewage treatment work effluents, including ibuprofen, caffeine, lidocaine, cocaine, codeine, amphetamine, ecgonine methyl ester, benzoylecgonine, ephedrine, methadone, nicotine, 6-acetylmorphine, diacetylmorphine, diazepam and procaine. The mean concentrations, 19.2 ± 5.8, 15.2 ± 4.3, 13.6 ± 5.7, 9.1 ± 3.5, 8.2 ± 3.1, 5.1 ± 2.8, 4.7 ± 1.7 and 4.2 ± 1.7 ng L^{-1}, were found, respectively. In Spain, 225 and 2307 ng L^{-1} of cocaine and benzoylecgonine in 5 sewage treatment work influents were higher compared to 47 ng L^{-1} of cocaine concentrations in effluent. The toxicity and extent of persistence may have potential effects on the environment after the sewage-sludge disposal to surface waters or landfills.
3. The reported hydrophilicity/lipophilicity properties of compounds allowed the chemical partitioning onto suspension in solution and biosolids with microbial degradation. The degradation possibilities of compounds include partial/complete

degradation, mineralization or sorption to sludge, which is a repository of microorganism during sewage treatment work degradation processes.

4. The reported multistep extraction protocols reduced the matrix influences and improved recovery under stability of pH. The delivered extracts were very clean using several solid-phase extraction adsorbents as recent advances. The effluent concentrations ranged from 0.3 to 30.2 ng L^{-1} with percentage recoveries from 78.6 to 97.8%, using solid-phase extraction-gas chromatography-mass spectrometry in many studies.
5. The observed degree of removal of drugs from the influent and its relative concentrations were higher when compared to the effluent drug concentrations where about 10 times higher in the influent compared to the effluent were found. However, improved sampling strategies and recovery, new detection methodologies and reduction of matrix influences employed at the determination of most effluents have added new trends that will further improve the treatment capability and assessments of sewage treatment plants.

Keywords Drugs · Pharmaceuticals · Wastewater · Analysis · Environment

9.1 Introduction

Human activities impact the environment through occurrence of pollutants and the interconnectedness of their metabolites in a myriad of ways. Chemical pollution is caused by the presence of dyes, solvents, pesticides, heavy metals and chemicals from industrial wastes and direct dumping to the aquatic environment. Disrupting chemicals such as natural hormones from humans and animals and phytoestrogen as well as agricultural herbicides and fertilizers are in the environment. Other sources such as mining, deforestation and release of semi-volatile organics have worldwide significant consequences. For example, nitrates are found from fertilizers; industrial effluents have bisphenol A, nonylphenol, polycyclic aromatic hydrocarbons and phthalates (Rogers 1996).

Pharmaceutical substances are ever-increasing at the risks to our lives as a result of high consumption and deposition of many of these therapeutic classes of drugs harbouring potential consequences for the environment. Despite the continuous discharge and rapid rise of some of these chemicals that are mutagenic, reproductive, toxic and carcinogenic in the environment, the assessment of occurrence and metabolism of pharmaceuticaldrugs and associated metabolites would continue to generate concerns due to the underappreciated levels of inadvertent and purposeful discharges of these toxicological substances (Mustapha 2013).

In recent years, there have been global concerns about the emerging levels of abused pharmaceuticals (illicit drugs) apart from drugs used for therapeutic purposes. The escalating levels of these drugs have prompted the need for proper monitoring of their prevalence in order to stem its social and environmental impacts.

Table 9.1 Contaminants in wastewaters

Pollutants	Sources/usages	Analytes
Acrylamide monomer	Coagulants	Polyacrylamide
Alkylphenols	Detergents, surfactants	4-Alkylphenol; polyethoxylates; 4-nonylphenol; monoethoxylates
Chlorophenols and chlorophenoxy acids	Herbicides	4-Chlorophenol, 2-chlorophenol
Lipids	Petroleum hydrocarbon	Phosphatidylserine, Phosphatidylethanolamine, Phosphatidylcholine
Mineral oils	Engine oils, paints	Paraffin, alkylbenzene cycloparaffin
Nitrosamines and nitroaromatics	Control nematodes	Dimethylnitrosamine
Organochlorine pesticides	Agricultural control of pests, transformer fluids, plasticizers and artificial rubbers	Aldrin, endrin, dieldrin
Organophosphorus compounds	Pesticides	Residues
Organotin compounds	Stabilizers in biocides, foams	Tributyltin oxide
Phthalates esters	Plasticizers	Bis(2-ethylhexyl)phthalate
Polychlorinated dibenzodioxins	Pulp bleaching	Congener group
Polycyclic aromatic hydrocarbons	Pyrolysis of organic materials	Naphthalenes
Surfactants and related residues	Detergents	Linear alkylbenzene
Chlorobenzenes	Paint removers	Chlorobenzenes

Environmental monitoring and risk assessments have shown the sewage treatment works as one of the potential routes through which the levels of consumption by a local population can be estimated. Studies revealed a plethora of illicit drugs and their common classes include cocaine, opioid, cannabinoid, amphetamine, lysergic diethylamide and hallucinogen (Baker and Kasprzyk-Hordern 2011; Harman et al. 2011; Karolak et al. 2010).

The biodegradability and non-biodegradability or resistance to degradation has increased the environmental risk factors of the ecosystem due to the hydrophobicity/lipophobicity properties of these drugs. In Table 9.1, the myriads of chemicals are shown coupled with the menace of use and abuse of illicit drugs having necessitated the establishment of many international agencies saddled with the responsibilities to monitor the production, transport, unlawful possession and usage of the ‘controlled’ substances. The substances considered risky for human health and social well-being of the society have different legislation in many countries with the hope to curb the menace, but the concerted efforts have not been fully achieved for their purpose.

Regardless, the nefarious activities of the consumers are on the increase, and the hidden natures of the business have helped its purported widespread and escalating consumption.

Until the idea of Daughton and Ternes (1999) and Daughton (2004), using intrusive approach to provide information on the community consumption of illicit drugs of whose idea was later demonstrated by Zuccato et al. (2005), nearly nothing was in the public domain about the estimation and levels of abused drugs in the environment. Today, the abused drugs are similarly surviving like other pharmaceuticals and medicinal drugs as reported by several studies, but the extent and spread differ from one location to another. The levels of abused drugs and abused pharmaceuticals in the effluents to receiving waters can generate exposure data to indicate potential threats; it constitutes to the environment as well to the appropriate authorities involved in fighting and controlling drug menace.

Therefore, we must provide updates on the fate and removal of these pharmacologically active contaminants from effluents to safeguard aquatic and human environment. The highlight of pharmaceutical occurrence, metabolism, transport routes, stability, analysis and current development in monitoring their fate is of great interest to humans and the environment.

9.2 Pharmaceutical Occurrence in Aqueous Environment

Pharmaceutical products produce active ingredients from parent drugs after metabolism; the biotransformation of these drugs generates associated metabolites that are excreted after intended use by dose users and pass on to the sewage system. In the sewage system, there exist increased possibilities of risks of environmental effects as more polar degradation products are produced in complex biochemical pathways that are very complicated to follow. The concerns for environmental sustainability and safety have led increasing attention to the large production of pharmaceuticals and their corresponding metabolites including those that are normally procured illegally (without approval/prescription) for illicit purposes. Yet, new pharmaceuticaldrugs of varying chemical classes enter the aquatic environment through sewage system and run-off.

The drug residue (unmetabolized) from excreta and urine and associated active metabolites are flushed in the toilets, and unwanted drugs are directly dumped to the surface river or disposed via drains; this constitutes a major source of pollution. The distributions of therapeutic classes of drugs in the environment are antibiotics, anti-inflammatory, anti-epileptics, antineoplastics, antidepressants, beta-blockers, β_2-sympathomimetics, contraceptives, diagnostic contrast media, lipid regulators, preservatives, sunscreen agents and tranquilizers (Hedgespeth et al. 2012). Selected different classes of pharmaceuticals are in Tables 9.2, 9.3 and 9.4.

Detectable levels of different classes of pharmaceuticals ranging from ng L^{-1} to μg L^{-1} were found in rivers, seas, lakes and surface and underground waters due to incomplete removal from the sewage system.

Table 9.2 Classes of pharmaceuticals in wastewaters

Groups of pharmaceuticals	Drugs
Acidic pharmaceuticals Antiphlogistics, analgesics and phenolic antiseptics	Salicylic acid, bezafibrate (lipid regulator, antiseptic biphenylol, antiphlogistic ibuprofen, ibuprofen, diclofenac, clofibric acid, naproxen, bezafibrate, fenoprofen, mefenamic acid, paracetamol)
Antibiotics	Penicillin, tetracyclines, sulphonamides and macrolides
Beta-blocker and β_2-sympathomimetics	Atenolol, sotalol, metoprolol and β_2-sympathomimetics (salbutamol)
Oestrogens	Oestrone, oestradiol, ethinyloestradiol
Iodinated contrast media	Iopamidol, iomeprol, iopromide, iohexol, diatrizoate, ioxitalamic acid, adsorbable organic iodine
Neutral pharmaceuticals	Antiphlogistics, anti-epileptic agents, lipid regulators, vasodilators
Nitrosamines	Morpholine, N-nitrosodimethylamine, diethylamine, di-n-propylamine, di-n-butylamine, diphenylamine, methylethylamine, pyrrolidine, piperidine
Other micro-pollutants	Benzotriazole, 4-tolyltriazole, 5-tolyltriazole, bisphenol A

Table 9.3 Psychoactive drugs and beta-blockers from wastewaters

	Influent [ng L^{-1}]			Effluent [ng L^{-1}]		
Substances	LOQ	No of samples	Max	LOQ	No of samples	Max
Anti-epileptics						
Carbamazepine	200	9	1000	100	9	1200
Primidone	200	9	420	10	9	250
Antidepressants						
Doxepin	200	9	100	10	9	190
Opioids						
Codeine	200	9	160	10	9	30
Dihydrocodeine	200	9	140	10	9	70
Methadone	100	9	130	5	9	120
Morphine	200	9	440	10	9	29
Oxycodon	200	0	–	10	0	–
Tramadol	200	6	470	10	6	370
Tranquilizers						
Diazepam	200	0	–	10	0	–
Nordiazepam	200	0	–	10	0	–
Oxazepam	200	6	190	10	6	180
Beta-blockers						
Atenolol	100	9	910	5	9	370
Sotalol	100	9	1300	5	9	1200
Metoprolol	100	9	1200	5	9	1100
Propranolol	5	9	70	3	9	60
Bisoprolol	100	9	380	5	9	270
Celiprolol	100	9	160	5	9	160
Betaxolol	5	4	10	3	1	–

Note: LOQ = limit of quantification; Max = maximum

Table 9.4 Pharmaceuticals in effluents, rivers and streams

	STWs (ng L^{-1})			Rivers/streams (ng L^{-1})	
Analyte	LOQ	Number STWs	Maximum	LOQ	Maximum
Lipid regulator					
Bezafibrate	250	49	4600	25	3100
Gemfibrozil	50	49	1500	10	510
Clofibric acid	50	49	1600	10	550
Fenofibric acid	50	49	1200	10	280
Antiphlogistics					
Acetylsalicylic acid	100	49	1500	20	340
Diclofenac	50	49	2100	10	1200
Ibuprofen	50	49	3400	10	530
Indomethacin	50	49	600	10	200
Ketoprofen	50	49	380	10	120
Naproxen	50	10	520	10	390
Phenazon	100	30	410	20	950
Salicylic acid	50	36	140	10	4100
Beta-blocker					
Betaxolol	25	29	190	10	30
Bisoprolol	25	29	370	10	2900
Metoprolol	25	29	2200	10	2200
Propranolol	25	29	290	10	590
β_2-Sympathomimetics					
Salbutamol	50	29	170	10	35
Terbutaline	50	29	120	10	<LOQ
Psychiatric drug					
Diazepam	30	20	40	30	<LOQ
Anti-epileptic					
Carbamazepine	50	30	6300	30	1100
Antibiotics					
Clarithromycin	20	8	260	20	260
Roxithromycin	20	10	1000	20	560
Chloramphenicol	20	10	560	20	60
Sulphamethoxazole	20	10	2000	20	480
Trimethoprim	20	10	660	20	200
Dehydrato-erythromycin	20	10	6000	20	1700
X-ray contrast media					
Diatrizoate	10	25	8700	10	ca.100
Iomeprol	10	12	3800	10	890
Iopamidol	10	25	15,000	10	2800
Iopromide	10	24	11,000	10	910
Oestrogens					
Oestrone	1	38	70	0.5	1.6
17β-oestradiol	1	38	3	0.5	<LOQ
17β-oestradiol-17-valerate	4	38	<LOQ	2	<LOQ
17α-Ethinyloestradiol	1	38	15	0.5	<LOQ
16α-Hydroxyestrone	1	15	5	0.5	<LOQ

Note: LOQ = limit of quantification

9.3 Abused Pharmaceuticals (Illicit Drugs) in Aqueous Environment

Cocaine, amphetamine, opioid, lysergic acid diethylamide, hallucinogen and cannabinoid are common classes of abused drugs. They are often referred to as 'hidden drug', and the users' hidden activities have given rise to their purported widespread and escalation. Until recently, limited information in the literature was known about illicit drugs and whether they similarly exist as pharmaceuticals in the environment. The emerging trends in the spread and usage of these drugs have prompted many international agencies to conduct risks assessment to ascertain the levels of impacts to the environment. The sewage treatment plants were identified as routes through which the drugs enter the environment, while direct dumping of expired drugs by end-users and drug manufacturing companies is another source.

Some drug users do divert prescription drugs for medical purposes in many ways to supplement their personal nefarious activities. The continuing practice has affected people, environment and societies in many ways as their active bioactive metabolites are continuously being discharged through the sewage disposal (e.g. to landfills, grassland, incineration and land reclamation) to the environment in complex mixtures of reactions that are very difficult to understand.

Table 9.5 therefore illustrates and compares the drug levels from different sewage treatment locations so as to appreciate the distribution and potential threats as reported in the literature. The observed degree of removal of drugs from the influent and its relative concentrations were higher when compared to the effluent drug concentrations. For example, 225 and 2307 ng L^{-1} cocaine and benzoylecgonine in 5 sewage treatment work influents in Spain were higher compared to 47 ng L^{-1} of cocaine concentrations in effluent**.** The benzoylecgonine relative concentration is about 10 times higher in the influent compared to the effluent.

The urination and faeces are products of metabolism through which unmetabolized drugs and associated metabolites get to the sewage systems. The fluctuation pattern in the use of lavatory, periods of work and resident population vary from individuals and locations which invariably would similarly affect the illicit load pattern. Active researches are ongoing on the detection of abused drugs; their fate through human metabolism and environmental degradation processes are needed to fully understand their myriad of pathways and behaviour.

Human metabolism of drugs in the body is associated with the biotransformation of drugs into metabolites with the unchanged parent drug being eliminated in the body. A degree of metabolism has been associated with a number of parameters such as ethnicity, gender, age, patient and the drug administration time.

The conjugation reaction occurs when polar molecules transfer metabolites such as the glucuronic acid transfer to hydroxyls, phenols, thiols, carboxyls, hydroxyl amino and amines groups (Mustapha 2013). The interests are the metabolites that may pass to the sewage, retain in the STWs and pass on to the environment through effluents or biosolids. The following are the metabolisms of major illicit drugs detected in wastewaters.

Table 9.5 Abused pharmaceuticals in wastewaters

Analytes	Matrix	Influent (ng L^{-1})	Effluent (ng L^{-1})	Surface water (ng L^{-1})
Cocaine	5 STPs, Spain	225.0	47	10
	5 STPs, Belgium	22–678	–	1.2–26
	37 STPs, Belgium	32–753	–	–
	3 rivers, Italy	–	–	0.3–44
	5 STPs, Ireland	489 ± 117	25–248 ± 20	0–33 ± 11
	Eastern Spain	370–1000.24	30–560	–
	30 STPs, Belgium	09–683	–	–
	2 STPs, Italy	218.4–421.4	0.9–10.7 ± 3.2	–
	4 STPs; River Po	42–120	–	–
	42 STPs, NE Spain	04–4700	01–100	–
	Barcelona, Spain	2.40	–	–
Benzoylecgonine	5 STPs, Spain	2307.0	–	111
	5 STPs, Belgium	82–1898	928	44–191
	37 STPs, Belgium	46–2258	–	–
	3 rivers, Italy	2.2–183	–	–
	5 STPs, Ireland, UK	290 ± 11	22	–
	Eastern Spain	150–1000.5	22 ± 4–31 ± 18	–
	30 STPs, Belgium	37–1550	6.0–7.9	–
	2 STPs, Italy	547.4–197.2	–	–
	4 STPs; River Po	420–750	0.92–100.3 ± 28.6	–
	42 STPs, NE Spain	09–7500	–	–
	Barcelona, Spain	5.24	01–1500	–
	12 STPs, Germany	65 ± 5	77 ± 9	71

Note: STPs = sewage treatment plants

9.3.1 Cocaine Metabolism

Cocaine is a powerful stimulant and addictive drug that has smoking, intranasal and intravenous routes of administration. The addicts usually mix street cocaine with diluents which sometimes cause poisoning. The cocaine is metabolized spontaneously in the presence of hepatic esterase and pseudocholinesterase to produce ecgonine methyl ester. Cocaine under non-enzymatic hydrolysis at pH 6 demethylates and converts to its main metabolite, benzoylecgonine (and this is detected in urine). The most toxic norcaine is produced through N-demethylation;

Analytes	Matrix	Influent	Effluent	SW
Nor- BE	3 rivers, Italy	–	–	0.2–8.4
	Eastern Spain	150–430	30–170	–
	2 STPs, Italy	18.8 ± 5.6–36.6 ± 7.8	<LOQ – 7.5 ± 2.9	–
Cocaethylene	2 STPs, Italy	5.9 ± 2.6–11.5 ± 5.1	0.2 ± 0.5	–
	Barcelona, Spain	77.5–78.5 ± 33.2	1.71–4.2 ± 1.2	4.63
	3 rivers, Italy	–	–	0.07–0.2
Norcocaine	3 rivers, Italy	–	–	0.15–3.6
	Eastern Spain	0.15–0.43	0.03–0.17	–
	2 STPs, Italy	4.3 ± 0.9–13.7 ± 5.3	0.7 ± 0.5	–
Amphetamines	3 rivers, Italy	–	–	<0.65
	Eastern Spain	1400	110–210	–
	2 STPs, Italy	5.4–14.7 ± 10.6	2.8	–
	42 STPs, Spain	Mar-80	Apr-00	–
	Barcelona, Spain	20.8–41.1 ± 9.1	0.45–2.2 ± 0.1	2.84
	5 STPs, Spain	15	<1.0	<0.8
Methamphetamines	5 STPs, Nebraska	1.3 ± 0.1–1.4	35.0 ± 7.3	–
	3 rivers, Italy	0.1–62.6 ± 13	–	<0.41–1.7
	Eastern Spain	–	<100–540	–
	2 STPs, Italy	<500	<1.11–3.5 ± 2	–
	42 STPs, Spain	3–277	Mar-90	–
	3 STPs, America	15 ± 2–66 ± 14	0.8–1.3	–
	Barcelona, Spain	4.8–18.2 ± 5.8	2.1–6.3 ± 0.6	2.87
	Murray, America	6.0–34	03-Jul	–

(continued)

Analytes	Matrix	Influent	Effluent	SW
MDA	42 STPs, Spain	03–266	01–200	–
	3 Rivers, Italy	–	–	3 ± 0.3–4
	Eastern Spain	500–1400	41.0–68.0	–
	2 STPs, Italy	4.6 ± 7.3–8.7	0.9 ± 1.9–1.1 ± 1.5	–
	5 STPs, Spain	03–266	1–200	–

Note: STPs = sewage treatment plants; Nor-BE = Nor-benzoylecgonine; MDA = methylenedioxyamphetamine

Analytes	Matrix	Influent	Effluent	SW
MDMA	3 rivers, Italy	–	–	1.1–4.0
	Eastern Spain	326–2700.5	100–210.2	–
	2 STPs, Italy	13.6–14.2	4.4 ± 3.7–5.1 ± 3	–
	5 STPs, Spain	91	67	3.5
	STP, Italy	2–598	2–267	–
	Barcelona, Spain	133–135.13 ± 29.8	8.2–14.8 ± 2.2	129
	Murray, America	<1.0–10.0	–	–
	42 STPs, Spain	2–598	2–267	–
MDEA	5 STPs, Spain	27	<2.1	–
	2 STPs, Italy	4.19–1.5 ± 3.8	<1.64	–
	STP, Italy	6–114	12	–
	STP, Spain	<500	<100	–
	42 STPs, NE Spain	06–114	12	–
Opiates				
Heroin	Barcelona Spain	2.4	1.2	–
	STP, Italy	20	<20.0	<1.5
Morphine	5 STPs, Spain	25.9–96.7	20.9–81.1	–
	3 rivers, Italy	–	–	3.5–38
	5 STPs, Ireland	874 ± 86	452	–
	2 STPs, Italy	83.3–204.4	5.5 ± 11.1	1-2 L
	Barcelona, Spain	68.1–162.9 ± 20.0	21.8 ± 3.0	3.25
	12 STPs, Germany	123 ± 6	9.0 ± 1.2	83
	STP, Italy	7.1–96.7	0.1–8.1.	4.8–6.3
Nor-morphine	5 STPs, Spain	30.7	–	–
	1 STP, Italy	<25	<2.5–3.7	<12.0.5
6 ACM	3 rivers, Italy	–	–	0.93
	2 STPs, Italy	10.4 ± 4.8–11.8 ± 8.5	–	–
	Barcelona, Spain	8.4–12.8 ± 3.1	2.5–3.6 ± 0.5	–

MDMA = methylenedioxymethamphetamine; MDEA = methylenedioxyethyamphetamine; 6 ACM = 6-monoacetylmorphine; STPs = sewage treatment plants

Analytes	Matrix	Influent	Effluent	SW
	12 STPs, Germany	8.4–12.8 ± 3.1	0.9 ± 1.2	83
	STP, Italy	102 ± 14	<3.1	<0.9–3.4
M3G	2 STPs, Italy	2.5 ± 7.1–18.1 ± 30	<0.48	–
Methadone	5 STPs, Spain	4.0–239	4.0–24.7	–
	3 rivers, Italy	–	–	4.9–10.1
	2 STPs, Italy	11.6 ± 1.7–49.7 ± 9.6	9.1 ± 0.5–36.2 ± 2.8	–
	12 STPs, Germany	123 ± 6	9.0 ± 12	83
	STP, Italy	4–23.9	2–2.7	4.9–10.1
Codeine	5 STPs, Spain	18.1–119.7	3.1–397	–
	3 rivers, Italy	–	–	1.0–51
	12 STPs, Germany	80 ± 5	7.7 ± 8	90
Norcodeine	5 STPs, Spain	5–68.0	15.5–22.9	–
6 Acetyl codeine	3 rivers, Italy	–	–	<0.31
EDDP	3 rivers, Italy	–	–	9.9–18.0
	5 STPs, Ireland	9.0–206 ± 10	–	–
	2 ST1 STP, Italy	19.8 ± 3.1–91.3 ± 19.2	22.6 ± 0.6–72.1 ± 8.7	–
	STP, Italy	4.5–41.3	4.9–56.7	9.61–17.5
THC	5 STPs, Spain	11.3–31.5	–	–
	2 STP, Italy	62.7 ± 5–91.2 ± 24.7	<0.94–7.2 ± 3.7	–
	Barcelona, Spain	4.3–21.03 ± 7.8	8.4 ± 3.8–11. 23	2.65
	STP, Italy	8.3–31.5	<8.3	<7.0–13.6
THC-COOH	3 rivers, Italy	–	–	0.48–3.7
	STP, Italy	12.5–96.2	12.5	16.4–34.1
	5 STPs, Spain	37.8–96.2	14.8–48.1	–
OH- THC	Barcelona, Spain	8.4–46.3	4.8–15.3	10.7

STPs = sewage treatment plants; M3G = morphine-3-glucuronide; **THC =** tetrahydrocannabinol; THC-COOH = 11-nor-9-carboxy-Δ^9-tetrahydrocannabinol; OH-THC = 11-hydroxy-Δ^9-tetrahydrocannabinol; EDDP = 2-ethylidene-1,5-dimethyl-3,3-diphenylpyrrolidine

other metabolites are anhydroecgonine, cocaethylene, ecgonidine, *p*-hydroxyl-benzoylecgonine, *m*-hydroxyl-benzoylecgonine and norecgonidine methyl ester.

9.3.2 Amphetamine Metabolism

Amphetamine classifications are amphetamines, methamphetamines (‘speed’) and methylenedioxymethamphetamine (‘ecstasy or Adam’). The addictive drugs can be taken orally or by snorting, smoking or injecting. Among other risks, the stimulant drugs give risks of abuse and dependence that cause harm to the central nervous system.

9.3.3 Opiate Metabolism

Opium poppy (*Papaver somniferum*) is an ingredient in morphine, thebaine and codeine. Most popular illegal drugs from opium poppy are morphine and heroin, while morphine and 6-monoacetylmorphine are related metabolites. The positions 3 and 6 of phenolic hydroxyl and alcoholic hydroxyl with the nitrogen atom typifies morphine metabolism. The degradation of heroin (diacetylmorphine) pathways produces main metabolites with different morphine conjugates; different enzyme actions emphasize the morphine metabolism complexity. Approximately 90% of an administered dose of morphine is excreted in the urine; only about 10% is excreted as unchanged parent morphine. The major metabolite is morphine-3-glucuronide, while minor metabolite is morphine-6-glucuronide. Others are codeine (3-O-methylmorphine), normorphine-6-glucuronide and morphine-N-oxide found in human urine and in wastewaters.

9.3.4 Lysergic Acid Diethylamide Metabolism

The drug is quickly dispersed in the body after metabolism, with smaller dose of the original eliminated in the human urine. The lysergic acid diethylamide metabolites in human biological fluids include 2-oxo-lysergic acid diethylamide, 2-oxo-3-hydroxy-lysergic acid diethylamide, N-demethyl-lysergic acid diethylamide, 14-hydroxy-lysergic acid diethylamide and 13-hydroxy-lysergic acid diethylamide. The 13- and 14- hydroxyl-lysergic acid diethylamide and 2-oxo-3-hydroxy-lysergic acid diethylamide are found in urine as glucuronide conjugates.

9.3.5 Cannabinoid Metabolism

One of the important cannabinoids is tetrahydrocannabinol, and C*annabis sativa L* is the active chemical, and cannabinol and cannabidiol are other constituents. On ingestion, the cannabinoids are metabolized by cytochrome P45 oxidase in the liver. The Δ^9-tetrahydrocannabinol metabolism leads to 11-hydro-Δ^9-tetrahydrocannabinol, which turned to 9-carboxy-tetrahydrocannabinol. The tetrahydrocannabinol metabolism is yet to be properly understood.

9.4 Sewage Treatment Works as Transport Routes of Pollutants

The significant routes which the pharmaceuticaldrugs enter the aquatic environment are domestic sewage systems. The faeces and urine are excreted along with its ingested chemicals and metabolites. Other major sources are discharges from commercial, domestic, drug manufacturers and run-off areas. The residues were found in varying concentrations in wastewaters reported in Italy, Belgium, Spain, Germany, the United State and the United Kingdom (Ai Jia et al. 2012; Ashfaq et al. 2016, 2017; Baena-Nogueras et al. 2017; Kasprzyk-Hordern and Baker 2012a; Kasprzyk-Hordern and Baker 2012b). Apart from the percolating filters, active sludge processes, nitrification and denitrification facilities, ozonation and membrane bioreactors as biological removal methods of trace pollutants from wastewaters, microbial degradation is the most effective removal process in sewage works. Studies of transformation of organics in mammals and humans, persistence of chemicals and microbial biodegradations involve complex interplay of biochemical, physical and transformational reactions of pollutants, and their nature determines the quality of effluent.

Apart from biodegradation, volatilization and hydrolysis, adsorption onto the biosolid surfaces through physico-chemical interactions also occurs. The removal extent due to the interaction of polar compounds is most times determined by the adsorption coefficient, with low adsorption coefficient compounds easily released to the receiving waters as effluents. The incomplete removal of these organic compounds from municipal sewage treatment works often leads to soil leaching and damaged ecosystem. This practice constitutes primary routes for chemicals to enter the aquatic environment.

Apart from the chemical degradation, sorption processes and biodegradation, typical sewage treatment work details of complex mixtures in the removal processes are not understood during the wastewater treatment. The toxicity and extent of persistence have potential effects on the environment after the sewage-sludge disposal to seas or agricultural landfills.

9.5 Microbial Degradation of Compounds in the Environment

The hydrophilicity/lipophilicity properties of compounds allow the chemical partitioning onto suspension in solution and biosolids. Understanding the degradation possibilities of compounds includes partial/complete degradation, mineralization or sorption to sludge which is a repository of microorganism during sewage treatment work degradation processes. Organic contaminants are located with the fraction of biomass determining the degree of contamination. Sewage contains mixtures of human excreta in complex association of fats, protein, sugars, cellulose, lignin, fatty acids, humid materials and amino acids. The drugs and their metabolites found in both aquatic environments and human fluids are given in Tables 9.6 and 9.7.

The metabolites of cocaine are norecgonidine methyl ester, ecgonidine, *m*-hydroxyl-benzoylecgonine and *p*-hydroxyl-benzoylecgonine, and methamphetamine conjugates. Degradation studies have been carried out on the degradation of

Table 9.6 Human drug metabolites found in the aquatic environment

Compound	Human metabolites identified
Amphetamine	Amphetamine
	3, 4-Methylenedioxyamphetamine
	Methylenedioxymethamphetamine
	Methylenedioxyethylamphetamine
	Methylbenzodioxolylbutanamine
	Methamphetamine
	p-Hydroxy-methamphetamine
Cannabinoids	Δ^9-Tetrahydrocannabinol
	Hydroxyl-tetrahydrocannabinol – conjugate
	Nor-9-carboxy-Δ9-tetrahydrocannabinol – glucuronide
	Δ^9-Tetrahydrocannabinol-9-carboxylic acid
Cocaine	Benzoylecgonine
	Cocaethylene
	Cocaine
	Ecgonidine
	Ecgonidine methyl ester
	Ecgonine
	Ecgonine methyl ester
	m-OH-benzoylecgonine
	Norecgonine methyl ester
	Norcocaine
	Norecgonidine
LSD	2-Oxo-3-hydroxy-lysergic diethylamide
	Hydroxyl lysergic diethylamide
	Iso-lysergic diethylamide
	Lysergic diethylamide
	Nor-lysergic diethylamide
Opiates	6-Monoacetylmorphine
	Heroin
	Morphine
	Normorphine
	Morphine-3-glucuronide
	Methadone
	2-Ethylene-1,5-dimethyl-1-3,3-diphenylpyrrolidine
	Ethyl morphine

Table 9.7 Biodegradability test of some pharmaceuticals

Compound tests		
Non-biodegradable	Biodegradable	Readily biodegradable
Chlorhexidine	Ampicillin	Aspirin
Clofibrate	Ibuprofen	Caffeine
Codeine phosphate		Ephedrine
Dextropropoxyphene		Menthol
Amitriptyline		Paracetamol
Erythromycin		Phenylpropanolamine
Meprobamate		Theobromine
Methyldopa		Theophylline
Metronidazole		
Naproxen		
Sulphamethoxazole		
Sulphasalazine		
Tetracycline		
Tolbutamide		

16α-hydoxyestrone, antitumor cisplatin, diatrizoate, trimethoprim, cyclophosphamide, X-ray contrast agents, cytarabine and iopromide, but details of metabolites were not identified or reported (Azaria et al. 2017; Mustapha 2013;)

9.6 Analytical Methodologies for Pharmaceuticals Residues in Wastewaters

Important advances in the detection and quantitative measurement of pharmaceuticaldrugs and their metabolites using various chromatographic and mass spectrometric methods have been developed. In gas chromatography-mass spectrometry and liquid chromatography-mass spectrometry techniques, liquid chromatography-mass spectrometry is most popular due to its measurement ability of chemicals at low concentration. Several alternative methods such as immunochemical techniques are good and inexpensive for pharmaceuticalanalyses (Mustapha 2013).The literatures have reported multistep extraction protocols, to reduce the matrix influences (Boruszko 2017; Gómez-Acata et al. 2017; Kasprzyk-Hordern et al. 2007; Ledjeri et al. 2016; Lepik and Tenn 2017; Madikizela et al. 2017; Martín et al. 2012; Mendoza et al. 2015; Olajire et al. 2005). Improved recovery after matrix effect under stability of pH delivers extracts that are very clean using several SPE adsorbent. Suitable parameters depend on application needs, the reason why several SPE adsorbents have been used with GC-MS^2 or LC-MS^2 for the determination of drugs and metabolites at low concentrations (ng L^{-1} levels) in aquatic media (Patrolecco et al. 2015; Paz et al. 2016; Song et al. 2016; Tang et al.

Table 9.8 Types of cartridges and adsorbent materials

Types	Sorbent materials
Isolute, pH® (1000 mg/6 mL)	Silica treated with phenyl groups in which silanol group is end-capped
Bond Elut Certify® (300 mg/6 mL)	Lipophilic and strongly cationic properties
Oasis, MCX® (500 mg/6 mL)	Polymeric sorbent with strong cation-exchange sulphonic group located on surface of polydivinyl. High selectivity for basic compounds. Benzene-co-N-vinyl pyrrolidone) copolymer
Phenomenex Strata-X™ (200 mg/6 mL)	–
Chrolut, ENV® (500 mg/6 mL)	Hyper-cross-linked polystyrene-divinylbenzene polymer based
Chromabond, Easy (500 mg/6 mL)	Bifunctional polystyrene-divinylbenzene copolymer
Isolute,C_{18} (EC)® (500 mg/6 mL)	Strongly apolar and lipophilic based on octadecyl silica with end capping of free silanol group
Isolute, ENV® (500 mg/6 mL)	Hydrophobic sorbent with hydroxylated polystyrene-divinylbenzene copolymer
Oasis, HLB® (500 mg/6 mL)	Divinylbenzene/N-vinyl pyrrolidone copolymer with hydrophilic/lipophilic properties. Application: all compounds and polar metabolites
Oasis, MAX (60 mg)	Strong anion-exchange mixed mode polymeric sorbent built upon HLB copolymer. Application: acidic compounds
Chromabond, C_{18} (200 mg).	Silica-based, end-capped sorbent. Application: non-polar compounds
Isolute, HCX (200 mg)	Weak anion-exchange mixed mode. Application: non-polar and basic analyte
Oasis, WAX (60 mg)	Weak anion-exchange mixed mode polymeric sorbent built upon HLB copolymer. Application: strong acids (e.g. sulphonates)
Oasis, WCX (60 mg)	Weak cation-exchange mixed mode polymeric sorbent built upon HLB copolymer. Application: strong bases e.g. quaternary amines)

2017; Tiwari et al. 2016; Xiang et al. 2017; Xu et al. 2016; Zhong et al. 2017). The different types of cartridges and adsorbent materials in multistep extraction procedures reported in the literature are shown in Table 9.8.

9.7 Pharmaceuticals and Metabolites Detected in Nottingham Sewage Treatment Work Effluent

The Nottingham sewage treatment work is located at Stoke Bardolph in the East Midlands; it treats the sewage of about 170 million litres per day using activated sludge. It serves over 500,000 people. A total of 16 h is used for wastewater treatment stages from influent wastewater to effluent including recycling before discharging it to River Trent. The sewage treatment work further removes 330 tonnes of plastics and paper as well as 2000 tonnes of grit per year (Mustapha 2013).

Systematic samplings for the biweekly collections of samples were adopted to obtain representative samples. To avoid effluent dilution due to distance from the discharge point to the receiving waters, efforts were made to ensure that collections were made at the same distance close to the effluent discharge points to minimize uncertainties in analyte concentrations. The varying amounts of analytes at the receiving waters further confirmed the major routes of sewage treatment plants by which pharmaceutical compounds enter the aquatic environment. The new challenges are introduction of abused pharmaceuticals making treatability at sewage treatment plants very difficult due to dearth of information of removal techniques.

In Table 9.9, there are 15 compounds that were detected from biweekly samplings from Nottingham sewage treatment work effluents including ibuprofen, caffeine, lidocaine, cocaine, codeine, amphetamine, ecgonine methyl ester, benzoylecgonine, ephedrine, methadone, nicotine, 6-acetylmorphine, diacetylmorphine, diazepam and procaine with their corresponding concentrations as presented. This study confirms necessary analytical capabilities for the determination of drugs in wastewaters using solid-phase extraction-gas chromatography-mass spectrometry. The presence of 15 different compounds, ibuprofen, caffeine, lidocaine, cocaine, codeine, amphetamine, ecgonine methyl ester, benzoylecgonine, ephedrine, methadone, nicotine, 6-acetylmorphine, diacetylmorphine, diazepam and procaine, was found. The compounds detected in effluents ranged from 0.3 to 30.2 ng L^{-1} with percentage recoveries from 78.6 to 97.8%, using solid-phase extraction-gas chromatography-mass spectrometry. The instrumental limits of detection ranged from 0.1 to 1.5 ng L^{-1} and standard deviation values of 1.1–21.4%. The most abundant compounds found in the final effluents were nicotine, ibuprofen, codeine, ephedrine, procaine, benzoylecgonine, lidocaine and caffeine, with mean concentrations of 19.2 ± 5.8, 15.2 ± 4.3, 13.6 ± 5.7, 9.1 ± 3.5, 8.2 ± 3.1, 5.1 ± 2.8, 4.7 ± 1.7 and 4.2 ± 1.7 ngL^{-1}, respectively.

However, improved sampling strategies employed at the determination of effluents at Stoke Bardolph Sewage Treatment Plant in Nottingham have added new trends that will further improve the treatment capability and assessments of the sewage treatment plant (Mustapha 2013).

9.8 Conclusions

With the different aspects of drug's occurrence, fate, treatability and transformations in the aquatic environment in the literature, the pharmaceutical markets for numerous therapeutic and commercial purposes will keep escalating. The desired approaches at safeguarding the environment in controlling and effective monitoring of chemical discharges into the environment are the new pollution challenges. This work examines aspects of some pharmaceuticals' fate, transport routes,

Table 9.9 Concentration of compounds from Nottingham sewage treatment work effluents

Compound	Biweekly sampling periods of Nottingham effluents (ng L^{-1})								Mean ± STD	LOD (ng/L)	Major ions for substance identification (m/z)		
	1ST SMP	2ND SMP	3RD SMP	4TH SMP	5TH SMP	6TH SMP	7TH SMP	8TH SMP			Molecular ions	Precursor ions	Product ions
6-Acetylmorphine	1.4	2.1	3.6	8.2	3.9	1.0	1.2	–	3.3 ± 2.5	0.8	341	282	229
Amphetamine	3.9	4.6	4.8	6.6	2.5	3.0	3.5	5.6	4.3 ± 1.4	0.3	206	116	73
Benzoylecgonine	4.9	4.9	4.7	3.5	2.4	11.0	4.1	–	5.1 ± 2.8	1.4	290	168	150
Caffeine	7.7	4.9	6.5	3.9	4.1	5.0	3.4	2.2	4.7 ± 1.7	0.5	194	109	67
Cocaine	1.7	1.4	1.1	1.4	1.4	–	–	–	1.4 ± 1.3	0.7	303	182	82
Codeine	10.1	11.0	10.8	14.2	11.3	13.0	10.9	27.2	13.6 ± 5.7	0.4	299	178	73
Diacetylmorphine	–	–	3.4	2.6	1.1	–	–	1.4	2.1 ± 1.1	0.8	369	310	268
Diazepam	3.5	8.9	1.2	4.2	5.3	4.7	1.4	2.6	4.0 ± 2.5	1.2	285	256	221
Ecgonine ME	0.6	–	1.7	1.4	0.8	0.8	–	0.3	0.9 ± 1.3	0.3	199	99	82
Ephedrine	3.7	13.8	14.2	8.0	6.9	9.1	10.0	7.3	9.1 ± 3.5	0.1	230	179	58
Ibuprofen	14.3	13.4	8.0	16.7	15.2	13.5	17.3	23.3	15.2 ± 4.3	0.8	278	160	73
Lidocaine	15.7	5.8	1.4	2.4	2.0	5.2	2.3	3.2	4.7 ± 1.7	1.4	234	86	58
Methadone	3.8	3.2	4.1	2.3	4.1	1.3	–	–	3.1 ± 1.2	1.2	283	197	180
Nicotine	20.4	16.8	17.0	11.4	14.5	30.2	20.4	23.0	19.2 ± 5.8	1.5	162	133	84
Procaine	15.2	6.5	8.4	7.1	7.4	4.7	8.3	8.3	8.2 ± 3.1	1.1	235	99	88

Note: SMP = sampling period; n = triplicate determinations; STD = standard deviation; STW = sewage treatment work; - (<LOD = limit of detection); Ecgonine ME = ecgonine methyl ester; m/z = mass/ions ratio

environmental distribution and bioactive metabolites. The inadvertent and purposeful discharges of pharmacologically active compounds via excreta remain underappreciated, yet their toxicological potency on the ecosystem has become a global issue. The persistent influxes of these pollutants with new and emerging contaminants have shown potential effects based on several studies reported on the plethora of compounds in the aquatic realms.

Highlights of current developments in drug monitoring, measurements of distribution and the extent at which sewage treatment plants allow the transport of chemicals (through different environment media) into the environment are reviewed. Preferred removal methods and measurements of trace drugs depend largely on sludge types, influents, effluents and sediments from sewage treatment plants. The capability to furthering the understanding of overall issues of pharmaceuticals' fate and other contaminants is now made available with exposure data on pollutant trend in the aquatic environment.

References

Ai Jia, Wan Y, Yang X, Hu J (2012) Occurrence and fate of quinolone and fluoroquinolone antibiotics in a municipal sewage treatment plant. Water Res 46:387–394. https://doi.org/10.1016/j.watres.2011.10.055

Ashfaq M, Khan KN, Rasool S, Mustafa G, Saif-Ur-Rehman M, Nazar MF (2016) Occurrence and ecological risk assessment of fluoroquinolone antibiotics in hospital waste of Lahore, Pakistan. Environ Toxicol Pharmacol 42:16–22. https://doi.org/10.1016/j.etap.2015.12.015

Ashfaq M, Nawaz KK, Saif Ur Rehman M, Mustafa G, Faizan Nazar M, Sun Q (2017) Ecological risk assessment of pharmaceuticals in the receiving environment of pharmaceutical wastewater in Pakistan. Ecotoxicol Environ Saf 136:31–39. https://doi.org/10.1016/j.ecoenv.2016.10.029

Azaria S, Nir S, van Rijn J (2017) Combined adsorption and degradation of the off-flavor compound 2-methylisoborneol in sludge derived from a recirculating aquaculture system. Chemosphere 169:69–71. https://doi.org/10.1016/j.chemosphere.2016.11.051

Baena-Nogueras RM, González-Mazo E, Lara-Martín PA (2017) Degradation kinetics of pharmaceuticals and personal care products in surface waters: photolysis vs biodegradation. Sci Total Environ 590–591:643–654. https://doi.org/10.1016/j.scitotenv.2017.03.015

Baker DR, Kasprzyk-Hordern B (2011) Multi-residue analysis of drugs of abuse in wastewater and surface water by solid-phase extraction and liquid chromatography–positive electrospray ionisation tandem mass spectrometry. J Chromatogr A 1218(12):1620–1631. https://doi.org/10.1016/j.chroma.2011.01.060

Boruszko D (2017) Research on the influence of anaerobic stabilization of various dairy sewage sludge on biodegradation of polycyclic aromatic hydrocarbons PAHs with the use of effective microorganisms. Environ Res 155:344–352. https://doi.org/10.1016/j.envres.2017.02.019

Daughton CG (2004) Non-regulated water contaminants: emerging research. Environ Impact Assess Rev 24(7–8):711–732. https://doi.org/10.1016/j.eiar.2004.06.003

Daughton CG, Ternes TA (1999) Pharmaceuticals and personal care products in the environment: agents of subtle change? Environ Health Perspect 107(Suppl 6):907–938. https://doi.org/10.1289/ehp.99107s6907

Gómez-Acata S, Esquivel-Ríos I, Pérez-Sandoval MV, Navarro-Noya Y, Rojas-Valdez A, Thalasso F (2017) Bacterial community structure within an activated sludge reactor added with phenolic compounds. Appl Microbiol Biotechnol 101(8):3405–3414. https://doi.org/10.1007/s00253-016-8000-z

Harman C, Reid M, Thomas KV (2011) In situ calibration of a passive sampling device for selected illicit drugs and their metabolites in wastewater, and subsequent year-long assessment of community drug usage. Environ Sci Technol 45(13):5676–5682. https://doi.org/10.1021/es201124j

Hedgespeth ML, Sapozhnikova Y, Pennington P, Clum A, Fairey A, Wirth E (2012) Pharmaceuticals and personal care products (PPCPs) in treated wastewater discharges into Charleston Harbor, South Carolina. Sci Total Environ 437(0):1–9. https://doi.org/10.1016/j.scitotenv.2012.07.076

Karolak S, Nefau T, Bailly E, Solgadi A, Levi Y (2010) Estimation of illicit drugs consumption by wastewater analysis in Paris area (France). Forensic Sci Int 200(1–3):153–160. https://doi.org/10.1016/j.forsciint.2010.04.007

Kasprzyk-Hordern B, Baker DR (2012a) Estimation of community-wide drugs use via stereoselective profiling of sewage. Sci Total Environ 423(0):142–150. https://doi.org/10.1016/j.scitotenv.2012.02.019

Kasprzyk-Hordern B, Baker DR (2012b) Enantiomeric profiling of chiral drugs in wastewater and receiving waters. Environ Sci Technol 46(3):1681–1691. https://doi.org/10.1021/es203113y

Kasprzyk-Hordern B, Dinsdale RM, Guwy AJ (2007) Multi-residue method for the determination of basic/neutral pharmaceuticals and illicit drugs in surface water by solid-phase extraction and ultra-performance liquid chromatography–positive electrospray ionisation tandem mass spectrometry. J Chromatogr A 1161(1–2):132–145. https://doi.org/10.1016/j.chroma.2007.05.074

Ledjeri A, Yahiaoui I, Aissani-Benissad F (2016) The electro/Fe3+/peroxydisulfate (PDS) process coupled to activated sludge culture for the degradation of tetracycline. J Environ Manag 184(Pt 2):249–254. https://doi.org/10.1016/j.jenvman.2016.09.086

Lepik R, Tenn T (2017) Determination of biodegradability of phenolic compounds, characteristic to wastewater of the oil-shale chemical industry, on activated sludge by oxygen uptake measurement. Environ Technol 33(1–3):329–339. https://doi.org/10.1080/09593330.2011.572923

Madikizela LM, Tavengwa NT, Chimuka L (2017) Status of pharmaceuticals in African water bodies: occurrence, removal and analytical methods. J Environ Manag 193:211. https://doi.org/10.1016/j.jenvman.2017.02.022

Martín J, Camacho-Muñoz D, Santos JL, Aparicio I, Alonso E (2012) Occurrence of pharmaceutical compounds in wastewater and sludge from wastewater treatment plants: removal and ecotoxicological impact of wastewater discharges and sludge disposal. J Hazard Mater 239–240:40–47. https://doi.org/10.1016/j.jhazmat.2012.04.068

Mendoza A, Aceña J, Pérez S, López de Alda M, Barceló D, Gil A (2015) Pharmaceuticals and iodinated contrast media in a hospital wastewater: a case study to analyse their presence and characterise their environmental risk and hazard. Environ Res 140:225–241. https://doi.org/10.1016/j.envres.2015.04.003

Mustapha AO (2013) Fate and behavior of drugs in the environment; PhD Thesis. Nottingham Trent University, UK. P

Olajire AA, Altenburger R, Kuester E (2005) Chemical and ecotoxicological assessment of polycyclic aromatic hydrocarbon-contaminated sediments of the Niger Delta. Sci Total Environ 340:123–136. https://doi.org/10.1016/j.scitotenv.2004.08.014

Patrolecco L, Capri S, Ademollo N (2015) Occurrence of selected pharmaceuticals in the principal sewage treatment plants in Rome (Italy) and in the receiving surface waters. Environ Sci Pollut Res Int 22(8):5864–5876. https://doi.org/10.1007/s11356-014-3765-z

Paz A, Tadmor G, Malchi T, Blotevogel J, Borch T, Polubesova T (2016) Fate of carbamazepine, its metabolites, and lamotrigine in soils irrigated with reclaimed wastewater: Sorption, leaching and plant uptake. Chemosphere 160:22–29. https://doi.org/10.1016/j.chemosphere.2016.06.048

Rogers HR (1996) Sources, behaviour and fate of organic contaminants during sewage treatment and in sewage sludges. Sci Total Environ 185(1–3):3–26. https://doi.org/10.1016/0048-9697(96)05039-5

Song X, McDonald J, Price WE, Khan SJ, Hai FI, Ngo HH (2016) Effects of salinity build-up on the performance of an anaerobic membrane bioreactor regarding basic water quality parameters and removal of trace organic contaminants. Bioresour Technol 216:399–405. https://doi.org/10.1016/j.biortech.2016.05.075

Tang K, Escola Casas M, Ooi GT, Kaarsholm KM, Bester K, Andersen HR (2017) Influence of humic acid addition on the degradation of pharmaceuticals by biofilms in effluent wastewater. Int J Hyg Environ Health pii: S1438-4639(16):30250–30254. https://doi.org/10.1016/j.ijheh.2017.01.003

Tiwari M, Sahu SK, Pandit GG (2016) Distribution and ecotoxicological concerns of persistent organic pollutants in sediment from creek ecosystem. J Environ Sci Health B 51(9):616–621. https://doi.org/10.1080/03601234.2016.1181907

Xiang X, Chen X, Dai R, Luo Y, Ma P, Ni S (2017) Anaerobic digestion of recalcitrant textile dyeing sludge with alternative pretreatment strategies. Bioresour Technol 222:252. https://doi.org/10.1016/j.biortech.2016.09.098

Xu J, He W, Wang Z, Zhang D, Sun J, Zhou J (2016) Comparison of molecular biology mechanism of Shewanella putrefaciens between fresh and terrestrial sewage wastewater. Front Bioeng Biotechnol 4:86. https://doi.org/10.3389/fbioe.2016.00086

Zhong HY, Wang H, Liu X, Liu C, Liu GY, Tian Y (2017) Degradation and characteristic changes of organic matter in sewage sludge using Vermi-biofilter system. Chemosphere 180:57–64. https://doi.org/10.1016/j.chemosphere.2017.03.121

Zuccato E, Chiabrando C, Castiglioni S, Calamari D, Bagnati R, Schiarea S, Fanelli R (2005) Cocaine in surface waters: a new evidence-based tool to monitor community drug abuse. Environ Health: Glob Access Sci Sour 4:14. https://doi.org/10.1186/1476-069X-4-14

Chapter 10
Pharmaceutical and Personal Care Products in the Aquatic Environment and Wastewater Treatment by Advanced Oxidation Processes

Enrico Mendes Saggioro

Contents

Abstract The massive consumption of different organic substances and their release through various pathways into the environment constitute an emerging environmental problem that poses serious threats to public health. Micropollutants discharged in domestic wastewaters, which pharmaceuticals and personal care products have been received scientific interest potentially dangerous to environment. Current wastewater treatment plants are not designed to remove pharmaceuticals compounds, since they are not treatment targets. Advanced oxidation processes are efficient methodology for the degradation of organic compounds in the environmental matrices. We reviewed more than 100 papers about heterogeneous and homogenous advanced oxidation processes for the removal personal care products and pharmaceuticals compounds. Advanced oxidation processes have been an alternative to remove micropollutants from wastewater. Ozonation is the most appropriate for the treatment of different kinds of wastewater (42% of papers). Chlorine with

---

E. M. Saggioro (✉)
Department of Sanitation and Environmental Health, National School of Public Health,
Oswaldo Cruz Foundation, Rio de Janeiro, Brazil
e-mail: enrico.saggioro@ensp.fiocruz.br

Inamuddin et al. (eds.), *Water Pollution and Remediation: Organic Pollutants*,
Environmental Chemistry for a Sustainable World 54,
https://doi.org/10.1007/978-3-030-52395-4_10

ultraviolet is the less studied (6.4%) however is the fastest process to remove the compounds. Toxicity evaluation during the oxidation process is an important tool to assess possible effects of by-product to human and environment health.

Keywords Advanced oxidation processes · Personal care products · Pharmaceutical compounds · Wastewater treatment

10.1 Introduction

Industries, agriculture, and the general population use water daily and release many compounds in wastewaters. These activities play an important role regarding the presence of micropollutants in waters and wastewaters (Deblonde et al. 2011). Micropollutants have increasingly become of concern in nowadays, due to their occurrence in the environment. As well as being described as emergent contaminants, they consist of a broad and expanding range of substances. These include pharmaceuticals and personal care products, endocrine-disrupting compounds, illicit drugs, pesticides, and several other compounds that are not included in environmental monitoring programs (Luo et al. 2014).

The presence of micropollutants in the environment has frequently been associated with many adverse effects in wild organisms, e.g., chronic toxicity, endocrine disrupting, and antibiotic resistance (Fent et al. 2006; Pruden et al. 2006). According to the US Environmental Protection Agency 2001, endocrine-disrupting compounds are, by definition, "exogenous agents that interfere with the synthesis, secretion, transport, binding, action and elimination of natural hormones in the body," thus promoting the breakdown of hormonal homeostasis. Endocrine-disrupting compounds include a broad spectrum of compounds which have natural and synthetic steroid hormones representing one of the main examples of endocrine-disrupting compounds found in wastewaters. Li et al. 2013 collected samples from a rural wastewater treatment plant in the United States where they found estrone (16.9 ng/L), estriol (126 ng/L), and estrone 3-sulfate (21.2 ng/L). Bartelt-Hunt et al. 2011investigated endocrine-disrupting compounds and their metabolites in US aqueous matrices. Several hormones and metabolites from human excretion were found in wastewater ranging from 30 to 3600 ng L^{-1}; these substances are linked to several disorders in reproductive systems such as imposex, decrease of fertility, hermaphroditism, and hormone-dependent cancers (Gültekin and Ince 2007). Pharmaceuticals and personal care products comprise a diverse groups of organic compounds. The pharmaceutical compounds include antibiotics agents, anti-inflammatory, anti-hypertensives, and anxiolytic drugs. Personal care products are represented to antimicrobial agents, insect repellents, synthetic musks, preservatives, and sunscreen filters (Liu and Wong 2013). Montagner et al. 2014 studied the personal care producttriclosan in several rivers in Brazil, for 1 year, and detected triclosan in 32, from a total of 71 analyzed samples (ranging from 2.2 to 66 ng L^{-1}). An extensive study performed by Kosma et al. 2014investigated the presence of 18 pharmaceuticals and personal care products in 8 wastewater treatment plant in Greece. Anti-inflammatory drugs such as paracetamol, diclofenac, and salicylic acid were the predominant compounds at concentrations up to 96.65 μg L^{-1}.

Most pharmaceuticals andpersonal care products are considered as pseudo-persistent pollutant, since is constantly come into the environmental compartments from wastewater treatment plant, as consequence are commonly present in low concentrations in waters, ranging from a few ng L^{-1} to several μg L^{-1} (Saggioro et al. 2014b). Most pharmaceuticals and personal care products are discharged from conventional wastewater treatment plant through the sewage system that is not designed for pharmaceuticals and personal care products removal (Daughton and Ternes 1999). Incomplete human metabolism is also an important source of emerging contaminants to aquatic environments (Kümmerer 2009). The conjugated metabolized arrive in the sewage system that is not able to remove and promotes a conjugate release in the aqueous being able to bind the receptors of the organisms (Li 2014). The domestic sewage treatment plants has been the main source of introduction pharmaceuticals and personal care products compounds (Ternes 1998). The use of sewage sludge in land surface fertilization is another substantial diffusion source of pharmaceuticals and personal care products to aquatic and terrestrial resources (Lapworth et al. 2012). Sewage sludge, or biosolid, is a wastewater treatment residue commonly used for soil fertilizer, since it contains nutrients that improve agriculture production (Kinney et al. 2008).

Current municipal wastewater treatment plant are designed to control a several kinds of substances e.g., nitrogen, phosphates, organic matter, and pathogens. While these substances can be efficiently removed, many pharmaceuticals and personal care products can pass through wastewater treatment processes unaltered, since they are not treatment targets (Bolong et al. 2009).

Hence, the evaluation of pharmaceuticals and personal care products removal in the conventional wastewater treatment plant is now necessary for the optimization of treatments, to prevent the release of these compounds, that are recognized hazardous compounds into the environment (Luo et al. 2014).

Advanced oxidation processes are powerful methodology for the degradation of persistent pollutants (Gil Maia et al. 2014; Jiménez et al. 2015; Saggioro et al. 2014a). Advanced oxidation processes produce of high oxidant and non-selective $^{\bullet}OH$, which can react to the different class of organic compounds, including pharmaceuticals and personal care products, promoting to their mineralization or the formation of simple intermediate structures that are more biodegradable (Amat et al. 2009).

Thus, the objective of this study is to review and compare published research about advanced oxidation processes that improve the biodegradability of most detected pharmaceuticals and personal care products in aqueous environment, namely, pharmaceuticals and personal care products.

10.2 Pharmaceutical and Personal Care Products Overview

Among the miscellaneous micropollutants discharged in domestic wastewaters, the three top classes that have received scientific interest as displaying the most potentially dangerous effects are pharmaceuticals and personal care products. All possess as common feature the fact that they are produced and consumed in large quantities and a considerable is discharged into the environment after their use.

10.2.1 Personal Care Products

Personal care products are a class of micropollutants represented by disinfectants, fragrances, preservatives, and sunscreen filters. Therefore, many personal care products residues have often been detected at low concentrations in wastewater treatment plant effluents and downstream surface waters. Triclosan and triclocarban are among the most frequently compounds determined in aqueous matrices. (Brausch and Rand 2011; Liu and Wong 2013). Triclosan and triclocarban are cytostatic agents incorporated in the formula (around 0.1–2% w/v) of products to prevent the growth of microorganisms in the detergents, toothpaste, and medical disinfectants and cosmetic products (Singer et al. 2002).

Triclosan is produced worldwide at large amount per year (1500 of triclosan) (Gao et al. 2014) and is a nonvolatile compound with lipophilic characteristic (log Kow of 4.8), which makes it persistent and bioaccumulative (Zhao et al. 2010, 2013). In water, triclosan can be slowly transformed into dioxin-like compounds by photolysis, according to the amount of sunlight, pH, and the presence of metal ions and organic matter (Montagner et al. 2014). Triclosan was developed as a bactericide inhibiting the enzyme enoylacyl protein reductase (Heath et al. 1999). Triclosan and its metabolites can cause hazardous non-target organisms, for example, green algae (Yang et al. 2008), crustaceans (Orvos et al. 2002) and fish (Chalew and Halden 2009), and display endocrine-disrupting implications humans, for example, promoting of human breast cancer (Gee et al. 2008; Raut and Angus 2010).

Triclocarban has been incorporated to detergents and cosmetics since 1957 to prevent spoilage and microbial infections (Halden and Paull 2005). It has an annual production around 227,000–454,000 kg in the United States (Halden and Paull 2005). The chemical fate of triclocarban in the aquatic environment is governed by its physicochemical properties, as log K_{ow} 4.9 and log K_{oc} 4.5, exhibiting a moderate lipophilic character (Ying et al. 2009). Almost 100% of triclocarban is released into sewage system during their normal use (Gao et al. 2014); the wastewater treatment plant is not able to remove triclocarban by activated sludge systems (Heidler and Halden 2007). Moreover, triclocarban is considered toxic (Nolen and Dierckman 1979), persistent (Gledhill 1975), and able to be incorporated into the food chain (Dimitrov et al. 2003).

The chemical structures of triclosan and triclocarban display similarities with several toxic compounds such as bisphenol A, dioxins, polybrominated compounds, and polychlorinated biphenyls that have already demonstrated endocrine activity in humans (Feng et al. 2016). Estrogenic and anti-androgenic effects have been reported in in vivo studies. For example, estrogenic effects in female rats, such as increases in uterine weight, resulting in an earlier-onset vaginal opening, have been reported (Jung et al. 2012) and the production of vitellogenin in male fish (Ishibashi et al. 2004). Reduction in serum testosterone, sperm production, and gland weights were reported as anti-androgenic activity in male rats (*Rattus norvegicus*) (Kumar et al. 2009). Moreover, the production of thyroid hormones has also been postulated as being negatively affected by personal care products (Rodríguez and Sanchez 2010).

10.2.2 Pharmaceuticals

Among emerging contaminants, pharmaceuticals are an important group of substances considering their possible effect on the aquatic environment, due to their massive use and incomplete elimination after wastewater depuration (Heberer 2002). Hundred thousand tons of pharmaceutical substances are consumed and used per year in the world (Zenker et al. 2014). Particularly, diclofenac and ibuprofen and an antiepileptic drug carbamazepine were chosen for inclusion in this review due to their high annual consumption, occurrence in aqueous systems, less 10% elimination during conventional biological treatments, and possible effects on human and aquatic organisms.

Ibuprofen is anti-inflammatory drug widely used as an analgesic, treatment of fever, and rheumatic disorders (Hutt and Caldwell 1983). It is the third-most popular drug in the world, an essential nonprescription drug, and is often used at high therapeutic doses (600–1200 mg/d) and has a high excretion urine doses (Buser et al. 1999). Because of its wide usage, ibuprofen has been detected worldwide in the aquatic environment, frequently reported in rivers and streams across Japan (Nakada et al. 2006), Europe (Buser et al. 1999), North America (Kolpin et al. 2002), Taiwan (Lin and Tsai 2009), and North Korea (Kim et al. 2007). Ibuprofen has been designed to inhibit the synthesis of bioactive fatty acids, inflammatory response (e.g., prostaglandins and leukotrienes) from the second carbon groups of glycerol synthetized by phospholipase A2, which in mammals and invertebrates function as paracrine signalers relationship with reproduction and ion transport (Hayashi et al. 2008); (Paíga et al. 2013).

Diclofenac is a highly consumed and used in ambulatory care, as an analgesic, antiarthritic, antirheumatic proposes. Diclofenac was developed to inhibit cyclooxygenase, both cyclooxygenase-1 and cyclooxygenase-2, since its enzyme isoforms are responsible for the inflammatory effects of prostaglandin production (Moncada et al. 1976). Diclofenac is primarily metabolized to hydroxylated or methoxylated derivatives (phase I) and after conjugated to phase II reactions in the liver, which produce glucuronides metabolites (Stülten et al. 2008). Diclofenac hydroxylated metabolites have been reported to damage vital organ functions in fish (O ‘connor et al. 2003; Schwaiger et al. 2004). These compounds have been detected in several environmental aquatic samples, such as drinking, surface, and wastewater (Andreozzi et al. 2003; Jux et al. 2002; Ternes 1998; Vieno et al. 2007).

Carbamazepine belongs to a class of medications with anticonvulsant action, used to therapeutic of different kinds of seizures (Mohapatra et al. 2014). Carbamazepine is also used to restore episodes of mania or mixed episodes in patients with bipolar disorder, and it is estimated that around 1014 tons of carbamazepine are annually prescribed and used by population (Zhang et al. 2008; Mohapatra et al. 2014). The greatest concern regarding carbamazepine is that its extensive detection in the environment can be assigned to the its extensive use in day-to-day life and to the low efficiencies of the biological methods employed in wastewater treatment plant (e.g., only less than 10% of this compound are removed) (Calisto et al. 2011). Carbamazepine has been commonly found in surface (Tixier et al. 2003), ground (Focazio et al. 2008), wastewater treatment plant (Bahlmann et al. 2009), and even treated drinking water (Heberer et al. 2002).

10.3 Assessment of Advanced Oxidation Processes for Pharmaceuticals and Personal Care Product Removal

Some conventional wastewater treatment processes have been researched and applied. However, these technologies are inefficient regarding total removal of most pharmaceuticals and personal care products from contaminated municipal waters and wastewaters. Advanced oxidation processes are important chemical oxidation technologies capable of completely mineralizing organic pollutants by generation of reactive species, mainly the $^{\bullet}OH$ that has a high oxidation potential of 2.80 V (Deng and Zhao 2015; Mohapatra et al. 2014). The $^{\bullet}OH$ is non-selective and can destroy a broad set of compounds, including several pharmaceuticals and personal care products, with subsequent conversion of the pollutants to CO_2, H_2O, and mineral acids (Miralles-Cuevas et al. 2013). Advanced oxidation processes include heterogeneous and homogeneous systems (Table 10.1) based on the systems with ultraviolet or solar-driven systems and without radiation (e.g., Fenton’s reaction). Depending on the proprieties of the waste to be treated, advanced oxidation processes may be used alone or coupled with primary and/or secondary conventional treatment, as a pretreatment or as a posttreatment step (Miralles-Cuevas et al. 2013). Thus, this review focuses on (i) heterogeneous advanced oxidation processes involving TiO_2; (ii) homogenous advanced oxidation processes focused on ozone, ultraviolet light, hydrogen peroxide, Fenton’s reaction, and their combined process; and (iii) coupling advanced oxidation processes with other treatment processes for pharmaceuticals and personal care products removal from municipal wastewaters.

Table 10.1 Homogeneous and heterogeneous AOPs systems most common for water and wastewater treatment

Advanced oxidation processes			
Homogeneous systems		Heterogeneous systems	
UV light	In the dark	UV light	In the dark
UV/H_2O_2	Ozonation	Photocatalysis (TiO_2/UV)	Eletrochemical oxidation
UV/O_3	O_3/ H_2O_2	TiO_2/O_3/UV	Electron-Fenton
UV/H_2O_2/O_3	Fenton	TiO_2/ H_2O_2/UV	
UV/Ultrasound (US)	Ultrasound (US)	Sonophotocatalysis	
Photo-Fenton	US/H_2O_2, US/O_3, US/Fenton		
Vacuum UV (VUV)	Microwave		

10.3.1 Degradation of Personal Care Products

Heterogeneous Photocatalysis

Photocatalytic degradation via photo-generated TiO_2 has been extensively studied for wastewater treatment. Under near ultraviolet or sunlight irradiation, aqueous TiO_2 solutions are photoexcited to promote electron transfer to generate valence band holes (e.g., valence band holes) and conduction band electrons (e.g., conduction band electrons) (Klavarioti et al. 2009). Valence band holes can react with water and the hydrogen ion to form reactive oxygen species. On the other hand, electrons react with oxygen, reducing it to the superoxide radical anion that, in turn, reacts with protons to form peroxide radicals (Mohapatra et al. 2014), as displayed in Fig. 10.1. Some heterogeneous photocatalysis studies involving personal care products are listed in Table 10.2.

Operational photocatalysis parameter evaluations are a crucial step in obtaining satisfactory results. The pH medium is essential for catalyst and pollutant adsorption. For example, regarding triclosan photodegradation by TiO_2, a neutral pH range (6.5–7.5) is the optimum condition, due to higher adsorption of undissociated triclosan to the TiO_2 surface (Stamatis et al. 2014). Triclosan is resistant to ionization, since its pKa ranges from 7.9 to 8.1 and can be formed into the triclosan anion at $pH > 8$. On the other hand, at acidic media, the catalyst is positively charged, whereas it is negatively charged under alkaline medium (Pemberton and Hart 1999). Thus, at $pH > 8$, a repulsive force exists between triclosan and TiO_2, while acidic conditions significantly inhibit the generation of the hydroxyl radical (Son et al. 2004). Son et al. (2009) evaluated the optimal operational parameters such as pH, triclosan amount, and presence of scavenger under photolysis and TiO_2 photocatalysis employing ultraviolet radiation. The authors found that the best condition for triclosan adsorption was a neutral pH, where photocatalysis decreased as the initial triclosan concentration increased and the triclosan degradation rate was

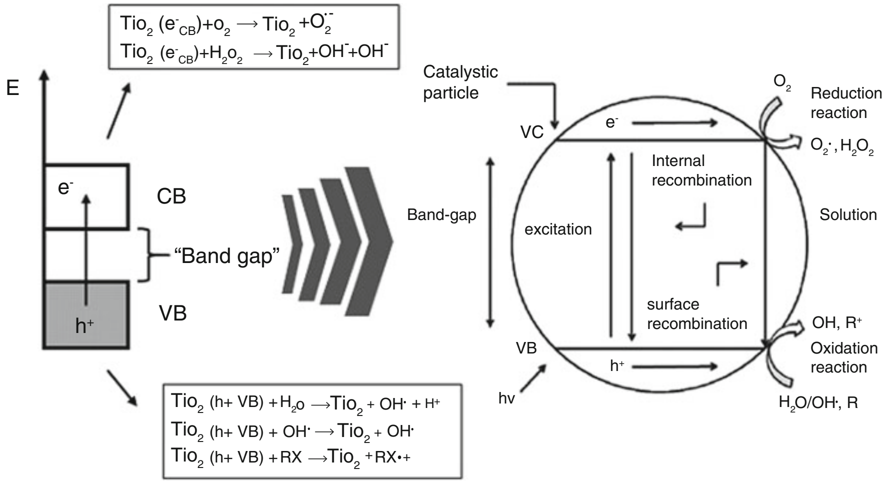


Fig. 10.1 Mechanism and reactions of semiconductor (TiO_2) particle surface. Valence band (VB), conduction band (CB), and band gap are represented to be necessary for hydroxyl radical formation. (Author)

decreased during the photolysis and photocatalytic processes in the presence of scavenger. The use of 2-propanol during the photocatalytic process are important to investigate detailed mechanisms to evaluate the contribution of reactive species such as $^\bullet$OH, $O_2^{-\bullet}$, positive holes. Stamatis et al. (2014) evaluated the contribution of reactive species on triclosan degradation and found that the hydroxyl radical was the main reactive species acting on triclosan degradation, while positive holes contribute indirectly to produce $^\bullet$OH. The hydroxyl radical species is, thus, vital to prevent *p*-dioxin derivatives during triclosan photocatalysis. Son et al. (2009) detected dibenzo-dichloro-*p*-dioxin when $^\bullet$OH scavenger (e.g., 2-propanol) was employed in TiO_2 photocatalyis, while *p*-dioxin intermediates were not found during photocatalysis without 2-propanol, as displayed in Fig. 10.2.

Triclosan oxidation by ultraviolet light produce a highly toxic compounds, such as *p*-dioxin derivatives such as 2,8-dichloro-dibenzo *p*-dioxin, since their anionic form is involved a ring closure process (Rafqah et al. 2006). These harmful derivate compounds are exclusively formed below 300 nm of ultraviolet irradiation (Latch et al. 2003). According to the triclocarban structure, several chlorine atoms are present, and the dechlorination process promotes the formation of several isomer products. The first step is by a hydroxyl radical attack of the carbons atoms with the highest electron density, preferentially in the *ortho* and *para* positions in the chlorophenol ring. The homolytic scission of the carbon–oxygen bond promotes OH-adduct formation (Rafqah et al. 2006). An unstable semi-quinone radical is then formed, where its deprotonation generates *p*-hydroquinone and *p*-quinone from triclosan (Yu et al. 2006). Therefore, 2,4-dichlorophenol is the major detected intermediary and the dechlorination reaction is not a major step during triclocarban photodegradation, as observed in Fig. 10.3 (Behar and Behar 1991). Rafqah et al.

Table 10.2 Summary of reaction conditions for triclosan (TCS) and triclocarban (TCC) removal from water by heterogeneous and homogeneous processes and combined AOPs with other treatment processes

References	Target compound/ initial concentration	Water matrix	Process conditions parameters	Scale	Measure of degradability	Summary results
Heterogeneous photocatalysis						
Rafqah et al. (2006)	Triclosan at 1.55×10^{-5} mol/L	Natural water	Suspended TiO_2 P25, PC50 and PC500: 1.0 g/L/ Fluorescence lamp 15 W	Bench	Triclosan and intermediated products, TOC, ammonium, and sulfate ions	Total disappearance of TCS was obtained within 1 h. Process leads to the formation of 2,4-dichlorophenol which represents 25% of triclosan conversion
Yu et al. (2006)	Triclosan at 9 mg/L	Deionized water	TiO_2 P25 suspensions:100 mg/L/15 W UV lamp-365 and 254 nm	Bench	Specific pollutant, 2,4-dichlorphenol, 2,8-dichlorodibenop-Dioxina, [a]TOC	95% degradation within 6 h by UV at 365 nm. Intermediated products were phenol, quinone, and hydroquinone
Son et al. (2009)	Triclosan at 1.73×10^{-2} mM	Distilled water	Suspended TiO_2 P25: 0.1 g/L/Hg-vapor UV-A lamp Effect of parameters (pH, isopropanol, initial TCS concentration)	Bench	Triclosan, intermediated products and TOC	75 and 82% of degradation by photolysis and photocatalysis, respectively Dioxin-type intermediates were produced
Klamerth et al. (2009)	9 emerging contaminants including Triclosan at 100 μg/L	Distilled water	Comparison of TiO_2 P25 (5 mg/L) suspensions with photo-Fenton/solar irradiation	Pilot plant	Specific contaminants and TOC	The TiO_2 experiment showed almost complete degradation of the 9 compounds except atrazine after 200 min under illumination

(continued)

Table 10.2 (continued)

References	Target compound/ initial concentration	Water matrix	Process conditions parameters	Scale	Measure of degradability	Summary results
Miranda-García et al. (2011)	15 emerging contaminants including triclosan at 100 μg/L	Simulated and real municipal wastewater	Immobilized TiO_2 on glass spheres/sunlight	Pilot plant	Specific contaminants and TOC	85% of the compounds were degraded within 120 min of irradiation time. The results show the potential application of immobilized TiO_2 to suspensions systems for the treatment of polluted water
Song et al. (2012)	Triclosan at 10 mg/L	Distilled water	H_2O_2 only; ^{b}EDTA–H_2O_2; H_2O_2–$BiFeO_3$ and EDTA–$BiFeO_3$–H_2O_2 $[H_2O_2] = 10$ mmol/L $[BiFeO_3] = 0.5$ g/L $[EDTA] = 0.5$ mmol/L	Bench	Triclosan and degradation intermediates, evolution of chloride ions dissolved iron and $^{\bullet}OH$ generation	The alone addition of H_2O_2 induced little degradation of the TCS, while the use of $BiFeO_3$ ^{c}MNPs increased the TCS removal to 82.7% in the presence of H_2O_2
Ding et al. (2013)	Triclocarban at 5 mg/L	Distilled water	TiO_2 P25 suspensions: 0.05–1.0 mg/L/UV and Xe lamp 300 W /effect of parameters (pH, anions, humic acid, initial TCC concentration)	Bench	Triclocarban and intermediated products	A higher TCC degradation rate was observed by direct photolysis than TiO_2 photocatalysis. Four main degradation products were identified
Stamatis et al. (2014)	Triclosan at 1 mg/L	Ultrapure water	TiO_2 P25: Suntest solar simulation $[TCS] = 1–3$ mg/L, $[TiO_2] = 200–600$ mg/L irradiation intensity = 500–700 W/m	Bench	Target compounds, intermediated products, TOC, and toxicity	Transformation of TCS involved reactions of mono- and di- hydroxylation, dechlorination, and cleavage of the ether bond

Homogeneous processes						
Suarez et al. (2007)	Triclosan at 0.5 μM	Municipal wastewater	O_3 dose range 0.1–6 mg/L, anionic, and neutral TCS	Bench	Triclosan rate constants, antibacterial activity	TCS-O_3 reaction increase with increasing pH. Biological assay indicated that reaction with O_3 eliminated of TCS antibacterial activity
Wert et al. (2009)	31 organic trace contaminants (TCS: 21–76 ng/L)	Three different real tertiary-treated wastewatereffluents	O_3, O_3/H_2O_2; dose normalized based upon TOC and nitrite	Bench and pilot scale	Specific contaminants, ozone decomposition, $^{\bullet}OH$ exposure, effluent organic matter (EfOM)	O_3/H_2O_2 did not increase the net production of $^{\bullet}OH$ compared to O_3. Trace contaminants including CBZ, DFC, naproxen, sulfamethoxazole and TCS were removed independent of water
Klamerth et al. (2010a)	15 mixed contaminants at 5 and 100 μg/L, including TCS	Real wastewater	Solar photo-Fenton (5 and 20 mg/L of Fe; pH ~3; 50 mg/L of H_2O_2)/treatment with each contaminant spiked and unspiked wastewater	Pilot plant	Target contaminants, TOC, iron and H_2O_2 determination	All experiments showed successful degradation in real effluents at low iron concentration and $^{\bullet}OH$ without substantial competition with organic content of the real effluent
Klamerth et al. (2010b)	15 mixed contaminants at 100 μg/L, including TCS	Synthetic water, simulated and real effluent wastewater	Solar photo-Fenton (Fe = 5 mg/L; unchanged pH; H_2O_2 = 50 mg/L)	Pilot plant	Target contaminants, [d]DOC, [e]TIC, iron and H_2O_2 determination, and toxicity test with *Vibrio fisheri*	The degradation of those 15 compounds was found to depend on the presence of CO_3^{2-} and $HCO^{3-}$and on the type of water. Toxicity showed that degradation of the compounds in real effluent led to toxicity increase

(continued)

Table 10.2 (continued)

References	Target compound/ initial concentration	Water matrix	Process conditions parameters	Scale	Measure of degradability	Summary results
Son et al. (2010)	Triclosan at 1.73×10^{-2} mM	Deionized water	Photolysis by Hg-vapor lamp UVC and UVA/Fenton: 2 mM Fe^{+2}, pH = 3, 5 mM H_2O_2/combined reaction (photo-Fenton)	Bench	TCS, chloride, TOC, Fe^{+2} and total iron concentration	The production of chloride in the Fenton, UVC, and combined reactions were 54, 62, and 78%, respectively, after 150 min
Giri et al. (2011)	16 mixed contaminants at 100 μg/L, including TCS	Ultrapure water	UV and UV/H_2O_2 (0–1.47 mM of H_2O_2 concentration)	Bench	Target contaminants and residual H_2O_2	Clofibric acid, diclofenac, fenoprofen, isopropylantipyrine, ketoprofen, phenytoin and TCS were removed very efficiently (> 96%) by UV photolysis alone
Wu et al. (2012)	8 mixed contaminants ranged from 1 at 20 μg/L, including TCS at 4.96 μg/L	Deionized and natural water	1 mg/L of free chlorine and permanganate, 2 mg/L of ozone, and 3 mg/L of monochloramine	Bench	Target compounds and the oxidants	Free chlorine, permanganate, and ozone treatments were all highly effective at the elimination of TCS and estrone. The pH also played an important role in the removal efficiency of target compounds
Chen et al. (2012)	Triclosan at 1.4, 2.9 and 4.5 mg/L	Ultrapure water	Ozonation: Molar ratio of TCS:O_3 in 1:1, 1:3, and 1:5	Bench	Triclosan and its degradation intermediates, and toxicity tests (cytotoxicity and genotoxicity)	2,4-dichlorophenol, chlorocatecol, mono-hydroxy-TCS and di-hydroxy-TCS were identified. Reduced genotoxic effects after ozonation was demonstrated

Munoz et al. (2012)	Triclosan at 10 mg/L	Deionized water	Fenton (20–50 °C) $[H_2O_2] = 20–100\%$ of the theoretical stoichiometric (2.5 mg H_2O_2/mg TCS) $[Fe] = 1$ mg/L pH = 3	Bench	Triclosan, main aromatic byproducts, short-chain acids, chloride ion and ecotoxicity test	Several aromatic intermediates (mainly, *p*- hydroquinone of TCS and 2,4dichlorophenol). Dramatic decrease of ecotoxicity was achieved in a relatively short time (more than 95% in 15 min)
Tizaoui et al. (2011)	Triclocarban at 100 mg/L	Acetonitrile/ ultrapure water (70:30)	Ozonation at 3.7, 7.5 and 22.4 mg min^{-1}/ pH at 2, 7 and 8, T = 10, 20 and 30 °C	Bench	Target compound	O_3 degraded TCC effectively and the reaction rates increased substantially with O_3 concentration, pH and temperature
Ben et al. (2016)	Triclosan at 20 μM	Deionized water	Low pressure UV lamp (4 W) and chlorination Irradiation time: 60 min $[Cl_2] = 7.1; 2.8; 1.4$ mg/L	Bench	Target compound, intermediated, chloroform, residual chlorine	Combined UV/chlorine can notably enhance the chloroform formation from triclosan comparing to chlorination alone
Peng et al. (2016)	Triclosan at 0.01 mM	Deionized water	Fenton-system Cu^{+2}/H_2O_2 Effect of parameters: pH, temperature, Cu^{+2} and H_2O_2 concentrations	Bench	Target compound and quantitative structure activity relationship (QSAR) model	TCS was effectively oxidized with Cu^{2+}/ H_2O_2 under mild conditions and their degradation rate constants followed pseudo-first-order kinetics
Yang et al. (2016)	Triclosan 100 ng/L	Natural water	UV/chlorine and UV/H_2O_2 Low-pressure mercury lamp (10 W) $[Cl_2] = 3$ or 5 mg/L $[H_2O_2] = 5$ mg/L	Bench	Target compound and disinfection byproducts	UV/chlorine treatment enhanced the formation chloral hydrate, haloketone and trichloronitromethane

(continued)

Table 10.2 (continued)

References	Target compound/ initial concentration	Water matrix	Process conditions parameters	Scale	Measure of degradability	Summary results
Coupling AOPs with other treatment processes						
Wert et al. (2011)	13 trace organic contaminants, including TCS from range 68 at 170 ng/L	Three secondary treated effluent	[h]EC pretreatment ($FeCl_3$ at 0–30 mg/L; 1.5 and 0.70 μm filter)/ozonation – O_3:DOC ratio 1 Bench		Organic contaminants, DOC, O_3 demand and decay rates and $^{\bullet}OH$ exposure	EC pretreatment removed between 10 and 47% of the DOC from the three wastewaters. EC was ineffective at removing any of the contaminants, while O_3 oxidation reduced the concentration of compounds
Hernández-Leal et al. (2011)	16 micropollutants from range 10 at 100 μg/L, including TCS	Gray water	Anaerobic treatment (retention time of 12 h and 25 °C) Ozonation: Flow rate at 20 h/L; dose rate at 1.22 mg/L min^{-1})	Bench	Target compound, [i]COD and TOC	O_3 of aerobically treated grey water at an applied O_3 dose of 15 mg/L reduced the concentrations of five micropollutants and TCS to below limits of quantification, with removal efficiencies of at least 79%

[a]*TOC* total organic carbon, [b]*EDTA* ethylenediaminetetraaceticacid, [c]*MNP*magnetic nanoparticles, [d]*DOC* dissolved organic carbon, [e]*TIC* total inorganic carbon, [f]*BDD* boron-doped diamond, [g]*HCN* acetonitrile, [h]*EC* enhanced coagulation, [i]*COD*chemical oxygen demand

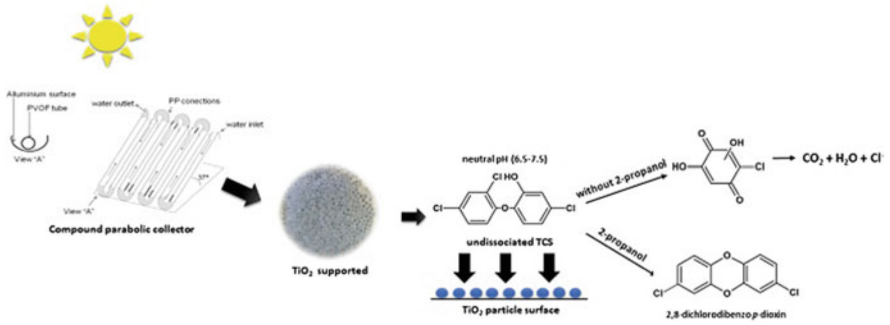


Fig. 10.2 Solar compound parabolic collector photocatalytic degradation of triclosan at supported TiO_2. Triclosan is more absorbed in TiO_2 particle at neutral pH. (Modified from Miranda-García et al. 2011; Son et al. 2009; Stamatis et al. 2014)

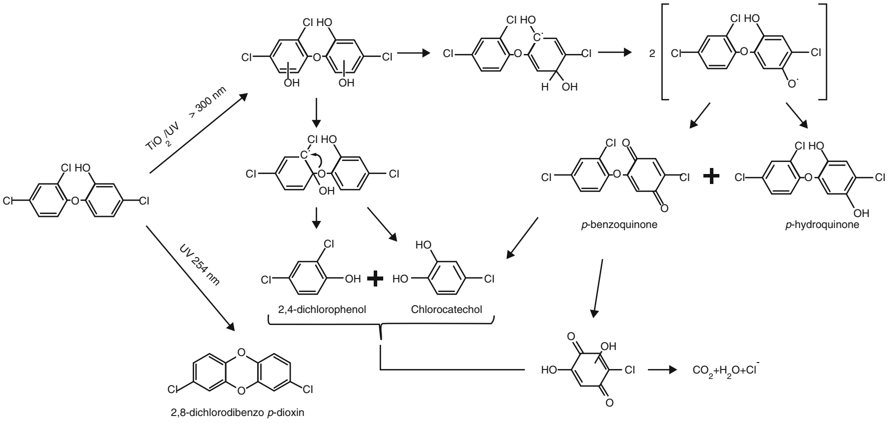


Fig. 10.3 Pathways of mains byproducts of triclosan at ultraviolet photolysis (254 nm) and TiO_2 photocatalysis (>300 nm). Dioxin byproducts are formed at photolysis of triclosan. (Modified from Rafqah et al. 2006; Stamatis et al. 2014; Yu et al. 2006)

(2006) studied triclosan degradation under fluorescence light-mediated TiO_2 P25, PC50, and PC500. The results revealed that TiO_2 P25 promote the total triclosan degradation after 60 min, with 90% mineralization after 10 h, while experiments with TiO_2 PC500 and PC50 indicated a decrease of degradation efficiency since the mixture of crystalline phase anatase and rutile present in TiO_2 P25 favors the photocatalysis. Furthermore, two majority intermediate products were determined as chlorocatechol and 2,4-dichlorophenol, representing 10% and 25% of triclosan conversion, respectively. Yu et al. (2006) used TiO_2 suspensions with ultraviolet artificial irradiation to degrade triclosan and 2,4-dichlorophenol, its main intermediary, as one of the dioxin precursors, to evaluate whether the other transformation products resulted directly from triclosan or dichlorophenol. The findings indicate that direct photolysis removed 8.1% of triclosan after 1 h ultraviolet irradiation, while triclosan concentrations rapidly decreased in 44.2% in the photocatalytic process during the same time. The 2,4-dichlorophenol photocatalysis indicated 34.6% degradation after 1 h. The intermediates identified in that study were 2,8-dichlorodibenzo-*p*-dioxin, quinone, and the hydroquinone structure of triclosan.

In addition to analytical instruments for intermediate product determination after photocatalysis, toxicity evaluations can also be used as a powerful tool. Organisms display either positive or negative responses when in contact with different compounds during photodegradation. In this way, Stamatis et al. (2014) identified intermediate products and performed toxicity assays using *Vibrio fischeri*. Six intermediate compounds were identified, mainly hydroxyl-triclosan derivatives via single or multiple $HO^{\bullet}$ radical electrophilic attacks. The luminescent marine bacteria showed low toxicity at an initial concentration (6% inhibition), while at 5-min irradiation, toxicity increased inhibition in 20%, due the simultaneous generation of photocatalysis transformation products. After this period, toxicity quickly decreased (5% at 10 min of reaction) and reached nontoxicity in 30 min.

In order to enhance degradation, the Fenton-like process can be applied as a heterogeneous photocatalysis. In this context, Song et al. (2012) investigated triclosan oxidation using magnetic BiFeOzone nanoparticles as a catalyst at pH 6.0. It demonstrated that the hydrogen peroxide-BiFeOzone system removed 82.7% of triclosan within 180 min, whereas the addition of ethylenediamine tetracetic acid not only accelerated triclosan degradation (96.1% at 30 min) but also significantly promoted the degradation of the toxic 2,4-dichlorophenol transformation products. This fact is due to formation of the large cave at the BiFe-Ozone surface by ethylenediamine tetracetic acid absorbed. Consequently, the local hydrogen peroxide concentrations are improved with $^{\bullet}OH$ radical generation. Klamerth et al. (2009) compared the degradation of nine different pharmaceuticals and personal care products through two different approaches as mild solar Photo-Fenton and TiO_2 photocatalysis at solar compound parabolic collector pilot plant. The Photo-Fenton process was more effective than TiO_2 regarding several pharmaceuticals and personal care products employed (i.e., triclosan, acetaminophen, caffeine, diclofenac, progesterone, sulfamethoxazole).

Furthermore, a major challenge regarding photocatalysis when using the catalyst in slurry form is that this process requires a further treatment step to remove the catalyst from aqueous solution. In this sense, Miranda-García et al. (2011) explored heterogeneous photocatalysis employing immobilized-TiO_2 on glass spheres (Fig. 10.2) for 15 micropollutants removal, including triclosan, in a solar compound parabolic collector pilot plant (10 L). The authors investigated different water matrices, and the stability and activity on catalyst were evaluated after five times with the same immobilized photocatalyst. The results indicate that diclofenac, ibuprofen, progesterone, triclosan, acetaminophen, and caffeine were degraded in the first cycle in the first 60 min reaction time, while the fifth degradation cycle of the compounds was slower.

Ding et al. (2013) wrote the only research article about photocatalysis involving triclocarban, applying photodegradation under two different artificial irradiation sources such as ultraviolet and xenon light source, varying pH, initial triclocarban concentration, the presence of anions and humic acid, and several concentrations of TiO_2 suspensions. The findings demonstrated that the initial triclocarban concentration and the presence of anions and humic acid negatively affect the degradation rate, while increases in pH produce a substantial improvement in the photocatalysis process. Unexpectedly, higher triclocarban degradation rates were observed by direct photolysis compared to TiO_2 photocatalysis. This fact was assigned to the negative effect of light scattering that was more pronounced than the hydroxyl radical reaction. Moreover, triclocarban molecule has a chlorine atom that hinders electrophilic attack of the $^\bullet OH$ to the benzene ring. Finally, the main degradation products, as 4-chloroisocyanatobenzene, 3,4-dichloroaniline, 4-chloronitrobenzene, and 4-chloroaniline, were detected and identified.

Homogeneous Oxidation Processes

A homogeneous advanced oxidation processes are a system in which both the compound and oxidation factor are located in the same phase. Schematic reactions of the main homogeneous advanced oxidation processes reported are displayed in Fig. 10.4. This section showed (Table 10.2) some of the research performed using either single or combined systems to degrade pharmaceuticals and personal care products. Suarez et al. (2007) demonstrated the use of the ozone oxidation technique in the investigation of the degradation of the disinfectant triclosan in real wastewater. Antibacterial activity, reaction kinetics, and initial responses between triclosan and ozone were monitored. The outcome of the study revealed that second-order rate constant is a kinect order to anionic triclosan degradation, since this compound is highly reactive toward ozone. Thus, ozone attacks triclosan for direct electrophilic interaction of the phenol ring (Fig. 10.5). Experiments with real effluents samples indicate that dissolved organic carbon could compete between ozone and the target

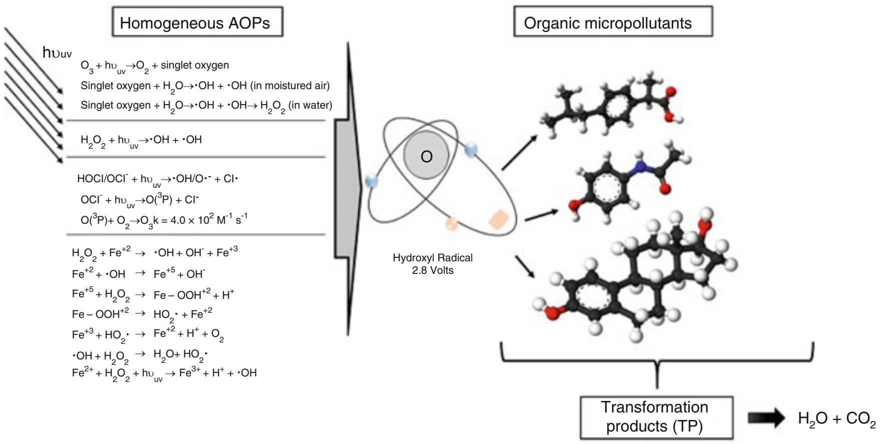


Fig. 10.4 Main reactions of homogeneous advanced oxidation process. (Author)

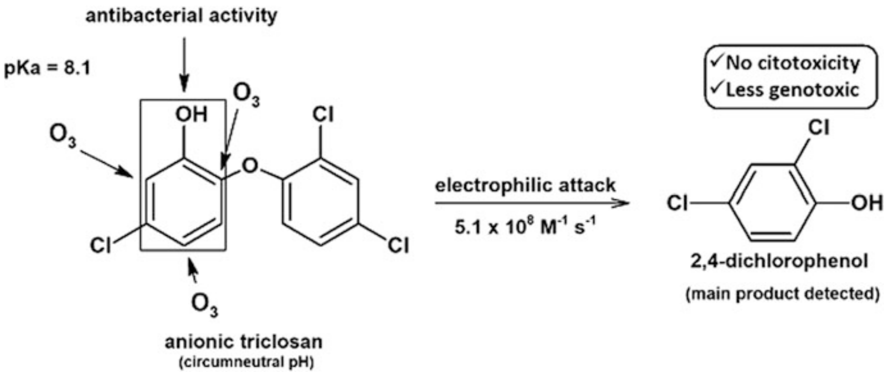


Fig. 10.5 Mechanism of ozonation electrophilic attack of triclosan at antibacterial moiety. By-products formed showed no toxicity. (Modified from Chen et al. 2012; Suarez et al. 2007)

compound, as well as for the generated •OH species. Chen et al. (2012) investigated triclosan ozonation and its degradation products formed, as well as the cytotoxicity and genotoxicity of the system. Triclosan was completely mineralized at a molar ratio of triclosan/ozone dose = 1:5. The active metabolite 2,4-dichlorophenolwas verified as the major metabolite during ozone process. However, the genotoxicity assay indicated that 2,4-dichlorophenol is less genotoxic than triclosan (Fig. 10.5), while any cytotoxicity effect was revealed to both triclosan and 2,4-dichlorophenol. On the other hand, the European Union prioritizes 2,4-dichlorophenol as "harmful to aquatic organisms," according to directive 76/464/EC (The Council of the European Communities 1976).

Tizaoui et al. (2011) studied ozone triclocarban oxidation under various conditions in acetonitrile/water. The results indicate that triclocarban degradation increased at high temperature and ozone gas amount and basic pH, and since at acidic pH occur deactivation of ozone's electrophilic attack, which leads to decreased ozone reactivity. Wu et al. (2012) applied different homogeneous oxidation technologies, under various pH conditions, for the removal of eight selected pharmaceuticals and personal care products. In particular, triclosan was very reactive against ozone and demonstrated higher oxidation percentages at pH of 6.6 compared to pH 8.6. Moreover, performance is enhanced at the combination of hydrogen peroxide, such as ozone/hydrogen peroxide (Wert et al. 2009) or ultraviolet/hydrogen peroxide (Giri et al. 2011).

Homogeneous oxidation with the Fenton reagent is a versatile and simple methodology to improve the •OH producing, since iron is abundant and hydrogen peroxide is easy to handle. Munoz et al. (2012) developed a Fenton-like oxidation process and proposed a reaction pathway for triclosan degradation, as summarized in Fig. 10.6. The authors concluded that primordially •OH attacks the *ortho-* and *para-* positions promoting the cleavage of aromatic ring and formation of 2,4-dichlorophenoland and 4-chlorocathecol. Moreover, *p*-hydroquinone triclosan is produced when *para-* position is attacked. Additionally, Fenton oxidation allowed at the first 15 times of reaction the reduction of toxicity at below 5%, directly related

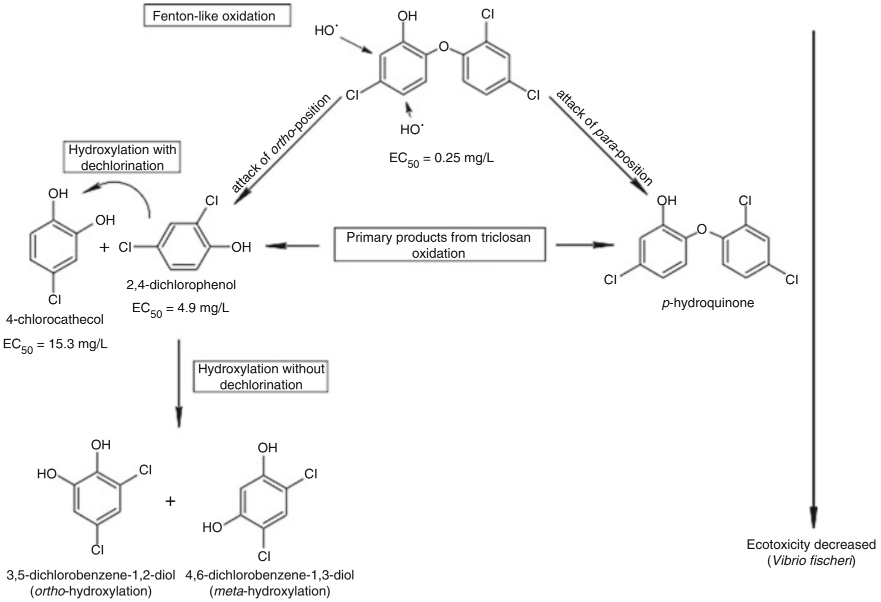


Fig. 10.6 Fenton-like oxidation process and reaction pathway of triclosan degradation. Toxicity decreased after hydroxylation without dechlorination. (Modified from Munoz et al. 2012)

to the disappearance of triclosan. Using the same approach, Peng et al. (2016) evaluated the optimum parameters such as temperature, pH, and hydrogen peroxide and Cu^{2+} concentrations of a Fenton-like Cu^{2+}/hydrogen peroxide system. Triclosan degradation rate constants follow pseudo-first-order kinetics, and quantitative structure-activity relationship predicts the degradation of other chlorinated compounds containing a benzene ring structure.

Furthermore, the Fenton process, when applied irradiation at wavelengths higher than 300 nm, is known as the photo-Fenton process. The degradation rate of organic compounds using Fenton reagents is strongly accelerated by irradiation (e.g., photolysis of Fe^{+3} allowing for Fe^{+2} regeneration). Son et al. (2010) investigated triclosan degradation under the Fenton reaction using only ultraviolet-C and a combined Fenton/ultraviolet-C system. The results revealed that triclosan was completely degraded after 90 min under ultraviolet-C and after 30 min in the Fe^{+2}/ultraviolet-C system. The use of ultraviolet-C instead of hydrogen peroxide displays advantages, as it is not necessary to adjust the system to low pH and there is no use of expensive reagents, such as hydrogen peroxide. Klamerth et al. (2010a,b) conducted 2 studies with 15 mixed contaminants at low concentrations in a solar pilot plant Photo-Fenton reaction. First, the authors used a real wastewater effluent with total volume of 250 L under several Photo-Fenton conditions. Subsequently, they conducted a second study using three different water matrices, with a total volume of 35 L under mild Photo-Fenton conditions, and performed toxicity testing using *Vibrio fischeri*. The authors concluded that pharmaceuticals and personal care products can be successfully degraded by applying the Photo-Fenton process at a low iron concentrations and moderate hydrogen peroxide doses (iron/hydrogen peroxide ratio 5:50 mg L^{-1}). At the other hand, the toxicity increased during phodegradation process in wastewater, demonstrating several toxic intermediates. Thus, the authors stressed the importance to perform toxicity evaluation during photodegradation process as an alternative tool to evaluate the potential reuse of wastewater treated.

Recently, studies have applied ultraviolet/chlorine as advanced oxidation processes, exploring the production of $^{\bullet}OH$ radicals from the photolysis of free chlorine. In this context, Ben et al. (2016) investigated the effects of an ultraviolet-C lamp and free chlorination treatment to remove triclosan. They determined the formation of disinfection byproducts, as chloroform, which is dependent on the residual amounts of free chlorine. Moreover, the UV/Cl process was responsible for chloroform formation in amounts higher than ultraviolet and chlorine process when applied alone. The 4,6-Cl-triclosan intermediate was an important intermediate in chloroform formation, as demonstrated in Fig. 10.7. Another study, conducted by

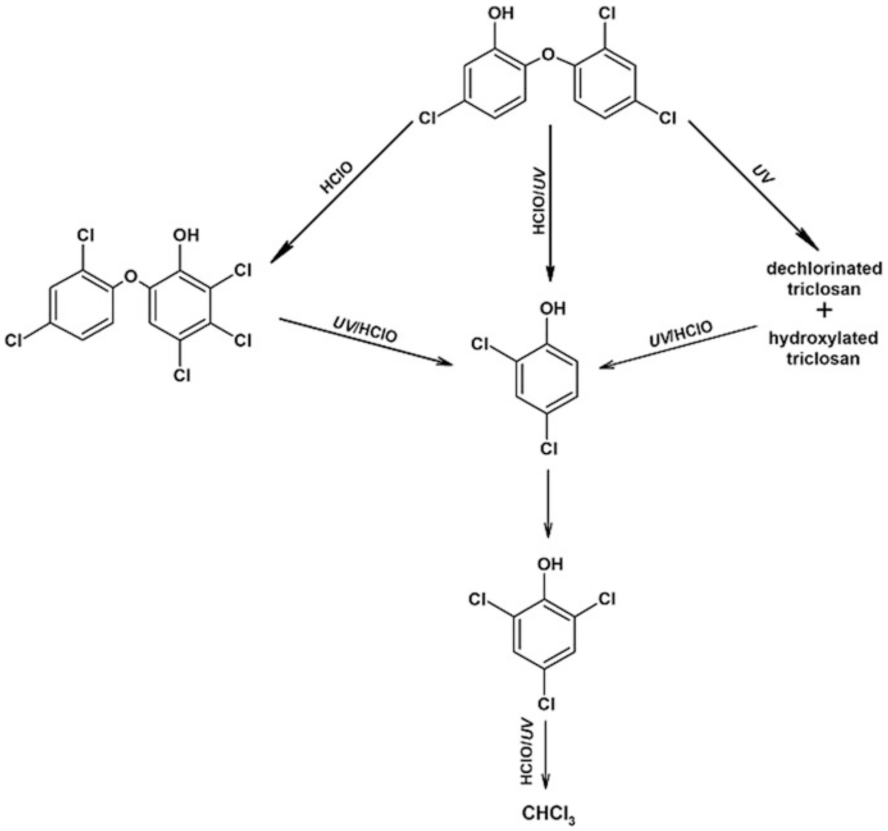


Fig. 10.7 Pathways of chloroform by-product formation at ultraviolet chlorine process. (Modified from Ben et al. 2016)

Yang et al. (2016) evaluated the efficiency of pharmaceuticals and personal care products degradation through ultraviolet/chlorine treatment using natural water samples and compared the results with an ultraviolet/hydrogen peroxide system. The combined ultraviolet/chlorine notably enhanced triclosan degradation. However, by-product formations are always a concern when chlorine is used, and some studies indicate the formation of toxic chlorinated by-products, such as chloroform, trichloronitromethane, haloketone, and chloral hydrate (Yang et al. 2016).

Coupling with Other Treatment Processes

The most studied cases in the literature reveal that conventional wastewater treatment plants are not designed for pharmaceuticals and personal care products removal. Thus, the application of physical and biological technologies (Table 10.2) is required in order to remove large insoluble particles, improving the aqueous matrix, and, consequently, the degradation efficiency of combined advanced oxidation processes (Oller et al. 2011). Wert et al. (2011) improved the pharmaceuticals and personal care products ozonation applying coagulation with ferric chloride as pretreatment. Enhanced coagulation using $FeCl_3$ reduced dissolved organic carbon concentrations (10–47%) in the wastewater. However, the results of the contaminant determination showed a low removal efficiency by this methodology. On the other hand, during the ozonation reactions, the most of pharmaceuticals and personal care products were completely removed, including triclosan. Hernández-Leal et al. (2011) studied ozonation and adsorption onto activated carbon processes for pharmaceuticals and personal care products removal from aerobiological treated graywater. The authors indicate that the contaminants were effectively removed from biologically treated graywater by ozone. Particularly, triclosan was present at 48 ng L^{-1} and was removed to below the limit of quantification of 7 ng L^{-1} at an applied ozone concentration of 10 mg L^{-1}.

10.3.2 Pharmaceutical Compounds Degradation

Published literature on the removal of pharmaceuticals compounds from water by advanced oxidation processes has been extensively reported, in particular for each selected compound separately, such as reviews on carbamazepine (Mohapatra et al. 2014), ibuprofen (Boreen et al. 2003), and diclofenac (Ziylan and Ince 2011) degradation. Additionally, real wastewaters are complex matrices contaminated with several pharmaceuticals compounds. Thus, this section focuses on a thorough research regarding advanced oxidation processes degradation for mixed selected pharmaceutical compounds in these polluted waters (Table 10.3).

Table 10.3 Summary of reaction conditions for mixed contaminated water by carbamazepine (CBZ), ibuprofen (IBP), and diclofenac (DCF) removal from water by heterogeneous and homogeneous processes, and combined AOPs with other treatment processes

References	Target compound/initial concentration	Water matrix	Process conditions parameters	Scale	Measure of degradability	Summary results
Heterogeneous photocatalysis						
Méndez-Arriaga et al. (2008)	[a]IBP and [b]DCF at 200 mg/L	Distilled water	TiO_2 P25 at artificial irradiation by the Xe-OP lamp Influence of parameters such as catalyst load, temperature and dissolved oxygen concentration	Bench	Target compounds, intermediates products, [c]TOC, [d]BOD_5, [e]COD, [f]DOC and microtox tests by *Vibrio fischeri*	The optimum amount of TiO_2, to achieve maximum degradation, of IBP was 1 g/L and 0.1 g/L for DCF. Dissolved oxygen concentration was an important parameter to increase the degradation
Rizzo et al. (2009)	[g]CBZ at 5 mg/L and DCF at 2.5 mg/L	Distilled water and urban wastewater	TiO_2 P25 in the range from 0.2 at 0.8 mg/L 125 W black light fluorescent lamp ($\lambda_{max} = 350$ nm)	Bench	UV–vis, TOC and ecotoxicity testes using *D. magna*, *P. subcapitata*, and *L. sativum*	The TOC rate of the wastewater contaminated was found to be slow ($t_{1/2} = 86.6$ min) compared to that of the same pharmaceuticals spiked in distilled water ($t_{1/2} = 46.5$ min)
Prieto-Rodriguez et al. (2012)	52 emerging contaminants, including CBZ at 100 μg/L and 114 ng/L; DCF at 4425 ng/L; IBP at 726 ng/L	Real wastewater	P-25 slurry TiO_2 (20 or 50 mg/L Suntest solar simulator with a Xe lamp and sunlight irradiation	Bench and pilot plant	Target compounds, DOC, and [i]TIC	Low concentrations of TiO_2 of the order of tens of milligrams per liter were found to be insufficient for the degradation of the compounds in photoreactors with a short light-path length

Sun et al. (2013)	CBZ and IBP at 15 mg/L	Deionized water	Nano-magnetite (Fe_3O_4) Fenton-like Montmorillonite clay = 4.0 g/L $Fe_3O_4 = 0–2$ g/L $[H_2O_2] = 0–600$ mM	Bench	Organic compounds, intermediates products	The degradation rate constants (k) for CBZ and IBP were 0.182 and 0.121 h^{-1}, respectively
Michael et al. (2014)	IBP and DCF at 10 mg/L	Ultrapure water	TiO_2 P25 at 500 mg/L by UV-A or simulated solar irradiation and UV-A sonophotocatalysis	Bench	IBP, DCF and its degradation intermediates, DOC and toxicity analysis by *Daphnia magna*	A higher degradation rate was observed for sonophotocatalysis. Seven transformation products of IBP and ten of DCF were identified
Miranda-García et al. (2014)	IBP, CBZ and DCF at 100 μg/L	Distilled water	TiO_2 immobilized on glass beads (regeneration approaches) Sunlight and Xe lamp	Bench and pilot plant	Organic compounds	Photo efficiencies higher than 90% even after the fourth consecutive cycles were attained moving to longer reaction times
Rioja et al. (2014)	IBP, CBZ and DCF at 500 μg/L	Tap, sea, surface, and wastewater	Combined powdered activated carbons and TiO_2 UVA, UVB, and UVC source lamps $[TiO_2] = 500$ mg/L	Bench	Organic compounds	Presence of activated carbon improved drug removal efficiencies and UV-C light was the most effective source for removal of selected drugs
Sarkar et al. (2015)	IBP and CBZ at 10 mg/L	Deionized water	TiO_2nanoparticlessupported on alginate beads UVA artificial irradiation Packed bed photo reactor (PBPR)	Bench	Organic compounds	Alginate beads immobilization showed lower degradation efficiency when compared with suspensions but PBPR improve the degradation system

(continued)

Table 10.3 (continued)

References	Target compound/initial concentration	Water matrix	Process conditions parameters	Scale	Measure of degradability	Summary results
He et al. (2016)	IBP, CBZ and DCF at 5 mg/L	Real wastewater	Immobilized TiO_2 on quartz sand by sol-gel Irradiation source: Xe-lamps (55 W) Irradiation time: 96 h	Bench	Target compounds, DOC, DBO and toxicity	Chronic toxicity of compounds decreased for the green algae and blue-green algae. In addition, the biodegradability of wastewater spiked with pharmaceuticals compounds was slightly improved
Carbajo et al. (2016)	IBP and CBZ at 100 μg/L	Natural ground water	Solar photocatalysis: TiO_2 P25 (200 mg/L) and home-made TiO_2catalyst TiEt-450 (500 mg/L) Organic pollutants: Phenol, dichloroacetic acid and pyrimethanil	Pilot plant	Target compounds, TOC and ions	Pharmaceutical microcontaminants were efficiently treated with very short irradiation times ($t_{30W} < 35$ min) with both titania catalysts
Homogeneous processes						
Heberer (2007)	CBZ and DCF at 1 μg/L	Real waterworks	Ozone doses in the range of 0.5–3.0 mg/L DOC = 1.3 mg/L pH =7.8 T = 23 °C	Bench	Target compounds	In lab scale experiments, 0.5 mg/L ozone was shown to reduce the concentrations of DCF and CBZ by more than 90%
Huber et al. (2003)	IBP and DCF at 0.5 to 5 μg/L	Real municipal wastewater	Ozonation O_3 doses ranging from 0.5 to 5 mg/L Gas flow rate: 200 ± 10 L h^{-1}	Pilot plant	Target compounds and DOC	Pharmaceuticals presents in wastewater can be efficiently oxidized with O_3 and that suspended solids have only a minor influence on the oxidation

Gagnon et al. (2008)	IBP at 608–974 ng/L; DCF at 43–49 ng/L; CBZ at 314–573 ng/L	Real wastewater	Ozone at range from 15–30 mg/L Flow = 50 L min^{-1} 8 UV lamps Performic acid (formic acid: H_2O_2 1:1)	Pilot plant	Trace organic compounds	Higher removal rates were observed when 20 mg/L of O_3 was used. Removal rates for UV radiation were often below 10% among the substances studied
Rosal et al. (2008)	CBZ at 65 ng/L and DCF at 369 ng/L	Real wastewater	O_3/OH^- and O_3/H_2O_2 pH = 8.04–8.25 T = 25 °C Gas flow = 0.36 N m^3 h^{-1} $[O_3]$ = 46.1 g/Nm^3 H_2O_2 30% v/v = 0.15 mL	Bench	Organic compounds, TOC and inorganic anions	In the absence of H_2O_2, a TOC decay of about 15% after 1 h. On the other hand, by injecting pulses of H_2O_2 (every 5 min), the degree of mineralization over 90%
Lee and von Gunten (2010)	CBZ and IBP at range from 0.2–1 μM	Real wastewater	Chlorine, chlorine dioxide, ozone, $ferrate^{VI}$ and UV/H_2O_2 Each oxidant at various oxidant doses (0-150 μM)	Bench	Organic compounds	UV/H_2O_2 were most efficient for IBP degradation while of CBZ was ozone transformation
Nanaboina and Korshin (2010)	CBZ and IBP at 1 μg/L	Real wastewater	Initial O_3 concentrations at range from 0.25–5.0 mg/L	Bench	Organic compounds	The results indicated possibility to estimate the degradation via the absorbance of ozonated wastewater
Coelho et al. (2010)	IBP and DFC at 200 mg/L	Ultrapure water	Ozonation Gas flow: 50 L/h O_3 production: 0.435 g/h T = 21–25 °C pH = 6.5 ± 0.3.	Bench	Organic compounds, TOC, chloride, ammonium, nitrates, COD, BOD_5 and *Vibrio fischeri* toxicity test	The results show that the total removal of DFC and 90% of IBP is possible using an O_3 dose of 0.20 and 2.3 g/L, respectively

(continued)

Table 10.3 (continued)

References	Target compound/initial concentration	Water matrix	Process conditions parameters	Scale	Measure of degradability	Summary results
Sichel et al. (2011)	CBZ and DCF at 1 μg/L	Distilled water	UV/HOCl, UV/HClO$_2$ and UV/H$_2$O$_2$ (low pressure lampat 40, 80 and 200 W) $[H_2O_2] = 5$ mg/L $[Cl_2]$ and $[ClO_2] = 6$ mg/L	Pilot plant	Organic compounds	Carbamazepine was removed best with UV/H$_2$O$_2$ > UV/HOCl ≥ UV/ClO$_2$. Diclofenac was readily degraded by UV/H$_2$O$_2$ and the chlorine AOP processes
Zimmermann et al. (2011)	22 micropollutants including CBZ, IBP and DCF at low concentrations	Real secondary wastewater	O$_3$ doses range from 0.21 to 1.24 g O$_3$ g^{-1} DOC Flow rate at 15 or 20 m^3 h^{-1}	Bench and full-scale	Organic compounds, DOC, bromide and bromate, and total cell counts for *Escherichia coli*	Substances reacting fast with ozone, such as DFC or CBZ were eliminated within the gas bubble column, except for the lowest ozone dose of 0.21 g O$_3$ g^{-1} DOC
Klamerth et al. (2011)	15 mixed compounds including CBZ, DCF and IBP at 5 or 100 μg/L	Real wastewater	Solar photo-Fenton with oxalic acid, ^{j}HA and mixing ^{k}MWTP influent and effluent $[Fe] = 5$ mg/L pH ≈ 7 $[H_2O_2] = 50$ mg/L	Pilot plant	Organic compounds and DOC	The oxalate and HA-enhanced process provided satisfactory degradation. Mixing of MWTP degradation was unsuccessful in all cases tested
De la Cruz et al. (2012)	32 micropollutants including CBZ, DCF and IBP at 263, 518 and 112 ng/L, respectively	Real municipal wastewater	UV-light, Fenton and photo-Fenton UV$_{254}$ and simulated sunlight pH neutral $[Fe] = 5$ mg/L $[H_2O_2] = 10, 25$ or 50 mg/L	Bench	Micropollutants concentration, TOC and COD	Global percentages of micropollutants removal achieved were 98 after 30 min of treatments. The results revealed the possibility of the micropollutants degradation in higher concentrations of ^{l}DOM

Gerrity et al. (2012)	CBZ and DCF at 220 and 47 ng/L, respectively	Real wastewater	Ozonation at 0.25, 0.50, 1.0, and 1.5 mg O_3/mg TOC O_3/H_2O_2 at 0, 0.5 and 1.0 O_3:H_2O_2 ratio	Bench, pilot- and full-scale	Organic compounds, TOC and microbial inactivation	The results of this study indicate that ΔUV_{254} and Δ^{m}TF can be used as surrogates for target compound elimination
Li et al. (2012)	20 compounds including CBZ, DCF and IBP at 1 μg/L	Real secondary wastewater	Fenton pH = 3, H_2O_2/Fe (II) molar ratio = range from 0.5 to 3. [Fe (II)] = range from 0.625 to 20 mg/L	Bench	Target compounds, DOC, nitrate, aldehydes and carboxylic acids	All examined compounds could be removed by Fenton oxidation. Moreover, treatment caused 13% of DOC to be oxidized to yield formate, acetate, and oxalate
Rodríguez et al. (2012)	CBZ at 14.2 and 19.1 μg/L; DCF at 13.5 and 52 μg/L; IBP at 1.5 and 13.0 μg/L	Real wastewater	Ozonation Ozone flow: 0.30 NL/min Liquid flow: 0.15 or 30 L/min	Bench	Organic compounds, DOC and TOC	The ozone dosage required to treat wastewaters with pollutant depletion of >90% was in the 5.5–8.5 mg/L range
Lekkerkerker-Teunissen et al. (2012)	CBZ at 8.48 mg/L and DCF at 9.24 mg/L	Deionized water	UV and UV/H_2O_2; ^{n}LP 15 W and ^{o}MP 1000 W mercury lamp H_2O_2 doses range from 0–10 mg/L	Bench	Organic compounds, transformation photoproducts	DCF was largely attributed to direct photodegradation, whereas UV or UV/H2O2 treatment did not appreciably remove CBZ
Wols et al. (2013)	40 pharmaceuticals compounds including CBZ and DCF at 1 μg/L	Deionized, tap and natural waters	UV and UV/H_2O_2; LP 60 W and MP 2 kW lamp pH = 8 [H_2O_2] = 10 mg/L	Bench	Organic trace micropollutants	Photolysis with LP lamps is small, which is increased by using a MP lamp. Most of the pharmaceuticals are well removed when applying both UV (either LP or MP) and H_2O_2

(continued)

Table 10.3 (continued)

References	Target compound/initial concentration	Water matrix	Process conditions parameters	Scale	Measure of degradability	Summary results
De la Cruz et al. (2013)	22 micropollutants including CBZ at 237–476 ng/L and DCF at 494–1247 ng/L	Real domestic wastewater	UV_{254}, UV_{254}/H_2O_2 and photo-Fenton Five LP 150 W lamp pH neutral $[H_2O_2] = 20–50$ mg/L $[Fe^{+3}] = 0–4$ mg/L Flow rate = 2–14 $m^3\ h^{-1}$	Pilot plant	Target micropollutants, TOC, ^{P}TC and TIC	Degradation greater than 80% with very low reaction times only adding UV light and H_2O_2 (not exceeded 50 mg/L). Adding of iron to the reactor did not improve the process
Justo et al. (2013)	DCF at 0.605 μg/L and CBZ at 1.038 μg/L	Real domestic wastewater	UV/H_2O_2 and O_3/ LP 8 W lamp O_3 flow rate = 133.5 L h^{-1} $[O_3] = 0.14$ up to 6.93 mg O_3 mgTOC^{-1} $[H_2O_2] =0.04$ to 0.72 mg H_2O_2 mgTOC^{-1}	Bench	TOC, COD, BOD_5, bromide, bromate, ammonium, *Vibrio fischeri* toxicity test	UV/H_2O_2process removed the pharmaceuticals and improved the effluent quality, while using significantly less oxidant compared to ozonation
Shu et al. (2013)	DCF and IBP at 20 mg/L; CBZ at 7 mg/L	Ultrapure water	UV and UV/H_2O_2/ MP 1 kW Hg-lamp $[H_2O_2] = 25$ and 50 mg/L	Bench	Target compounds	UV direct photolysis is very effective for the degradation of DCF. However, for the rest of the compounds, the UV/H_2O_2 treatment is the major degradation pathway
Klamerth et al. (2013)	62 micropollutants including IBP at 5295 ng/L and DCF at 1326.9 ng/L	Real municipal wastewater	Solar photo-Fenton pH 3 and neutral $[Fe^{+3}] = 5$ mg/L $[H_2O_2] = 50$ mg/L	Pilot plant	Organic micropollutants, TIC, and DOC	It was demonstrated in all cases the removal of over 95% of the contaminants. Photo-Fenton at pH 3 provided the best treatment time

Altmann et al. (2014)	CBZ at 1.2–2.5 μg/L and DCF at 2.6–5.8 μg/L	Real municipal wastewater	O_3 (15 mg/L) and [q]PAC (doses of 2.5–50 mg/L)	Bench	Target compounds and DOC	Concentrations of CBZ and DCF were reduced by more than 90% with 20 mg/L PAC or 5–7 mg/L O_3
Lee et al. (2014)	DCF and CBZ at 1 μM	Ultrapure water	Cu(II)-catalyzed Fenton and photo-Fenton Effect parameters: pH, cu (II) concentration, and radical scavengers	Bench	Target compounds	The optimal degradation of the target contaminants was observed at pH 8
Ahmed et al. (2014)	DCF and CBZ at 50 μM	Real wastewater	Homogeneous photo-Fenton with peroxymonosulfate	Bench	Target compounds and TOC	Kinetic rate constants were always 10 times higher in Fe(II)/UV than in TiO_2/UV system
Yao et al. (2016)	DCF and IBP at 400 μg/L	Real wastewater	Conventional ozonation and the electro-peroxone (E-peroxone)	Bench	Target compounds	The E-peroxone process enhanced the removal kinetics of ozone refractory pharmaceuticals in the four secondary effluents by ~40–170%
Coupling AOPs with other treatment processes						
Nakada et al. (2007)	24 pharmaceutically active compounds including IBP and CBZ at ng/L	Real municipal wastewater	Sand filtration followed by ozonation Flow rate and retention time through the sand were 110 m/day and 1 h [O_3] and retention time were 3 mg/L and 27 min	Full scale	Target compounds	Combination of ozonation and sand filtration with activated sludge treatment gave efficient removal (>80%) of all the target compounds except carbamazepine

(continued)

Table 10.3 (continued)

References	Target compound/initial concentration	Water matrix	Process conditions parameters	Scale	Measure of degradability	Summary results
Hollender et al. (2009)	55 micropollutants at range from µg/L	Real municipal wastewater	Post-ozonation followed by sand filtration O_3 from range of 0.36–1.16 g O_3 g^{-1} DOC	Full scale	Target compounds and its by products	During post-O_3, compounds with activated aromatic moieties, amine functions, or double bonds were eliminated for an O_3 dose of 0.47 g O_3 g^{-1} DOC
Badawy et al. (2009)	DCF at range from 0.48 to 12.37 mg/L	Real wastewater	Fenton-biological (aeration 24 h; sludge weight from 3 to 4 g/L; 20 h detention time) treatment processes Fe^{2+}/H_2O_2 molar ratios equivalente to 1:10, 1:25, 1:50 and 1:100 pH = 3	Bench	Target compounds, TOC	Fenton as a pre-treatment process would increase the biodegradability and/or remove the toxicity of the wastewater
José et al. (2010)	DCF and CBZ at 10 µg/L	Ultrapure water and real wastewater	^{r}MBR treatment (1.43 m^2; 0.04 mm pore size) prior to oxidation by O_3, UV/O_3 and UV/H_2O_2 17 W hg-lamp Gas flow: 2.6 g O_3 h^{-1} 0.5 ml/L of H_2O_2	Bench and pilot plant	Target compounds and DOC	Incomplete elimination of the polar pharmaceutical target compound by MBR treatment. However, AOPs were successfully reduced below their ^{s}LODs for nearly all compounds
Schaar et al. (2010)	IBP at <20–31 ng/L; CBZ at 500–900 ng/L; DCF at 970–2300 ng/L	Real wastewater	Conventional biological treatment with subsequent ozonation step Gas flow: 2.5 m^3 h^{-1} $[O_3] = 86$–153 g nm^{-3}	Pilot plant	Micropollutants concentration, COD, and BOD	0.6 g O_3 g DOC^{-1} increased the removal of most of the micropollutants, especially for compounds that were not degraded in the previous biological process, as for example CBZ and DCF.

Rosal et al. (2010)	CBZ at 129 ng/L; IBP at 2687 ng/L; DCF at 232 ng/L	Real wastewater	Biological treatment (3000 m^3h^{-1}) followed by ozonation Gas flow of 0.36 Nm^3h^{-1} $pH = 8.5 \pm 0.1$	Bench	Organic compounds, TOC, COD, BOD, and inorganic anions	O_3 with doses lower than 90 mM allowed the removal of many individual pollutants including some of those more refractory to biological treatments
Miralles-Cuevas et al. (2013)	CBZ and IBP at 100 μg/L	Natural water	Combined nanofiltration (5.2 m^2; 50 Lh^{-1}) and solar photo-Fenton treatment pH 5 $[Fe^{+2}] = 5$ mg/L	Pilot plant	Target compounds, TOC and ions concentrations	Higher initial concentrations of micropollutants, H_2O_2 was used more efficiently and ^{t}NF pretreatment reduced the photo-Fenton treatment time
Nguyen et al. (2013)	CBZ, IBP and DCF at 5 μg/L	Synthetic wastewater	Combined MBR (0.074 m^2; 0.4 μm) with UV oxidation LP 80 W hg-lamp	Bench	Target compounds, TOC, and TN	The combination of MBR with UV oxidation resulted in a removal ranging from 85% to complete removal of selected compounds
Miralles-Cuevas et al. (2014c)	CBZ and IBP at 15–150 μg/L	Real municipal wastewater	NF (5.2 m^2; 50 L/h) combined with mild solar photo-Fenton $pH = 5–6$ $[Fe^{+2}] =5$ mg/L $[H_2O_2] = <25$ mg/L	Pilot plant	Organic compounds, DOC, TIC and ions concentration	NF produced a permeate containing less than 1.5% of the initial concentration of pharmaceuticals. Solar photo-Fenton process applied to this stream led to a reduction of 88% and 89% in treatment time

(continued)

Table 10.3 (continued)

References	Target compound/initial concentration	Water matrix	Process conditions parameters	Scale	Measure of degradability	Summary results
Miralles-Cuevas et al. (2014a)	CBZ and IBP at 15–150 μg/L	Natural ground water	NF (5.2 m^2; 50 L/h) combined with solar photo-Fenton, photo-Fenton like Fe (III)-^{u}EDDS and O_3 $[O_3] = 8.82$ g O^3 h^{-1} Gas flow: 0.2 Nm^3 h^{-1} $[Fe^{+2}] = 0.1$ mM $[H_2O_2] = 25$ mg/L $Fe_2(SO_4)_3$:EDDS 1:2 M	Pilot plant	Organic compounds, DOC, TIC, ions concentrations and toxicity test by *Vibrio fischeri*	Combined process NF/AOP over direct treatment reduced in the total volume to be treated; consequently, a lower AOP treatment time and more efficient reagent consumption were observed
Miralles-Cuevas et al. (2014b)	CBZ and IBP at 15 μg/L	Real municipal wastewater	NF (5.2 m^2; 50 L/h) combined with mild solar photo-Fenton and complexing agents (EDDS and citrate) H_2O_2 was added 1.5 mM Fe: Complexing agents (1:0.5 to 1:5 M)	Pilot plant	Organic compounds, DOC, TIC and ions concentrations	Pharmaceuticals were efficiently removed (>90%), requiring low accumulated solar energy (2 $kJ_{uv}L^{-1}$), and low iron and H_2O_2 concentrations
Giannakis et al. (2015)	CBZ and DCF at range 6–18 ng/L	Real wastewater	Secondary treatments coupled at UV, UV/H_2O_2, solar irradiation, Fenton, solar photo-Fenton Secondary treatment: Activated sludge Moving bed bioreactor coagulation-flocculation	Bench	Target compounds	Municipal wastewater subjected to biological treatment followed by UV/H_2O_2 resulted in the highest elimination levels

Gimeno et al. (2016)	CBZ and DCF at 200 μg/L	Real wastewater	Aerobic biodegradation followed by different advanced oxidation processes Solar TiO_2 photocatalysis Solar photo-Fenton Ozonation	Bench	Target compounds, TOC, and toxicity by *Daphnia magna*	Solar photocatalytic ozonation with titania significantly favors COD and TOC elimination of domestic wastewater effluent

[a] *IBP* Ibuprofen, [b] *DCF* Diclofeanc, [c] *TOC* total organic carbon, [d] *BOD_5*biochemical oxygen demand, [e] *COD*chemical oxygen demand, [f] *DOC* dissolved organic carbon, [g] *CBZ* carbamazepine, [h] *TN* total nitrogen dissolved, [i] *TIC* total inorganic carbon, [j] *HA*, humic acid, [k] *MWTP* municipal wastewater treatment plant, [l] *DOM* dissolved organic matter, [m] *TF* total fluorescence, [n] *LP* low pressure, [o] *MP* medium pressure, [p] *TC* total carbon, [q] *PAC* powdered activated carbon, [r] *MBR* membrane bioreactor, [s] *LOD* limits of detection, [t] *NF* nanofiltration, [u] *EDDS* (S,S)-Ethylenediamine-N,N′-disuccinic acid trisodium salt

Heterogeneous Photocatalysis

The majority of published research on heterogeneous photocatalysis of selected compounds mediated by TiO_2 employ the semiconductor in the slurry and perform toxicity tests for treated wastewater (Table 10.3). Méndez-Arriaga et al. (2008) studied the influence of different operational conditions on the photocatalytic degradation of anti-inflammatory employing TiO_2, following the variation of toxicity by *Vibrio fischeri* bioluminescence inhibition. The results showed the high rate degradation of ibuprofen and diclofenac was achieved with 1 and 0.1 g/L of optimum amount of catalyst, respectively. The first step in ibuprofen degradation was pointed out as a hydroxylation process in the methylpropyl pheny positions and the arylcarboxylic moiety (Fig. 10.8). This fact promoted increases in *Vibrio fischeri* inhibition, due to the high levels of the hydroxyl metabolites and 4-ethylbenzaldehyde (Méndez-Arriaga et al. 2008; Michael et al. 2014). On the other hand, after 120 min photodegradation, a decrease in the percentage inhibition was observed. In the same approach, Michael et al. (2014) conducted a specific study for the identification and pathways transformation products of diclofenac and ibuprofen under application of sonophotocatalysis. Regarding ibuprofen, hydroxylation occurs firstly and exclusively at the aromatic ring, since the methyl-propyl and carboxylic moieties remained intact after the oxidation processes. The second step is pointed out as demethylation and decarboxylation cleavage of isobutyl moiety in the ibuprofen

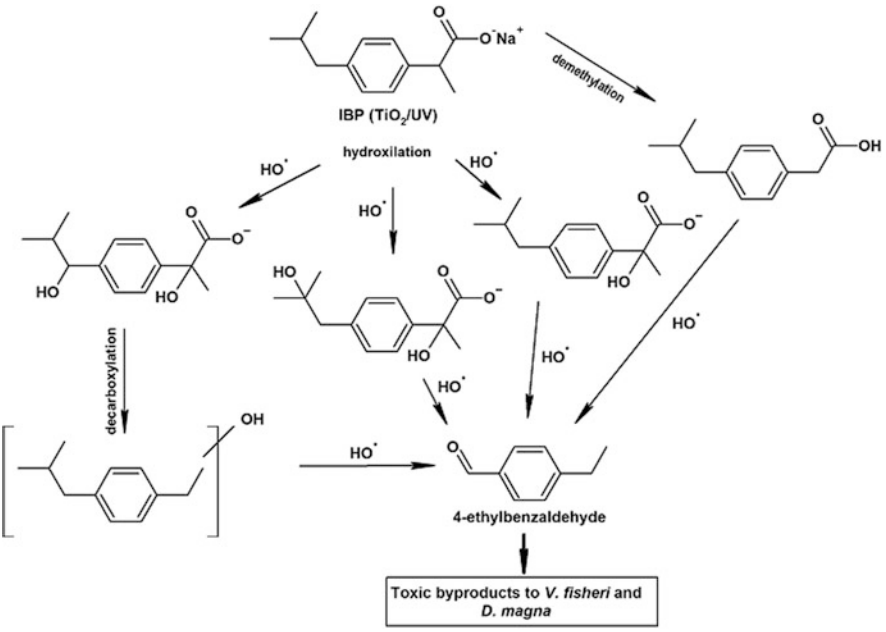


Fig. 10.8 Ibuprofen degradation pathway of TiO_2/UV. Hydroxylation products formation and toxicity evaluation of by-products. (Modified from Méndez-Arriaga et al. 2008; Michael et al. 2014)

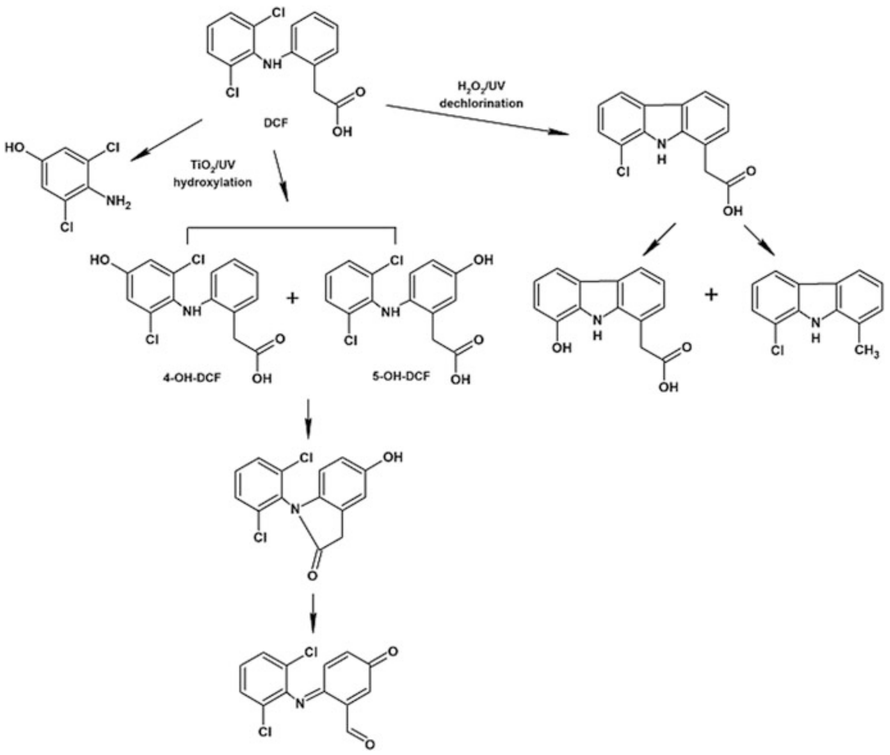


Fig. 10.9 Diclofenac degradation pathway of TiO_2/UV and H_2O_2/UV. Dechlorination and hydroxylation process. (Modified from Lekkerkerker-Teunissen et al. 2012; Michael et al. 2014)

structure (Fig. 10.8). Regarding the diclofenac degradation pathway, the oxidation and hydroxylation were the mains reactions occurred between chloroaniline and phenylacetic acid that produced mono hydroxylated species (e.g., 4′-OH-Diclofenac, 5′-OH-diclofenac) (Fig. 10.9) (Michael et al. 2014). At 15-min ibuprofen and diclofenac photodegradation, toxicity to *D. magna* was almost 100% immobilization, indicating toxic intermediate products, such as hydroxylated species (Michael et al. 2014). Rizzo et al. (2009) evaluated the potential toxicity of urban wastewater treatmenteffluents contaminated with carbamazepine and diclofenac after TiO_2 photocatalysis by performing a several bioassays employing, *D. magna*, *L. sativum*, and *P. subcapitata*. The outcomes revealed that the mixture of compounds photocatalytically treated using different TiO_2 loadings resulted in an increase of toxicity to *D. magna* and *P. subcapitata* than the single pharmaceutical solutions, whereas the profile of both organisms showed a gradual toxicity reduction over time, which means that fewer toxicity intermediates were formed during oxidation. Moreover, *L. sativum* demonstrated a multi-phase toxicity profile.

Another study focusing on the use of low TiO_2 amount was conducted by Prieto-Rodriguez et al. (2012) to evaluate the performance of the photocatalytic degradation of 52 micropollutants un-spiked in wastewater treatment plant including carbamazepine, ibuprofen and diclofenac. The study used a two different engineering reactor systems with different glass tube diameters and light-path lengths of solar pilot-scale compound parabolic collector. The authors reported that more than 85% of the micropollutants were degraded after 480 min in the smaller reactor, while over 90% were degraded at 300 min in reactor with larger dimensions. The design, light-path length of reactor, inner diameter, and thickness of the glass wall are important factors to influence an optimum photocatalyst concentration. To achieve satisfactory degradation of pollutants using low TiO_2 concentrations, a wider tube diameter (i.e., optical thickness of about 13 mm) could be used to allow optimal absorption of photons in order to reduce the overall costs of the treatment. Sun et al. (2013) explored a heterogeneous Fenton-like reaction in aqueous nano-Fe_3O_4 suspensions to evaluate the presence of montmorillonite clay for the degradation of carbamazepine and ibuprofen. Finally, Miranda-García et al. (2014) investigated regeneration approaches for TiO_2 immobilized on glass beads for the degradation of 15 selected pharmaceuticals and personal care products, including carbamazepine, ibuprofen, and diclofenac spiked in distilled water at 100 μg/L. In addition, immobilized TiO_2 was the focus of the study conducted by Sarkar et al. (2015). The photocatalyst was supported in calcium alginate beads and photodegradation experiments performed in the packed bed photo reactor. Using the same approach, He et al. (2016) evaluated the application of photocatalysis for ibuprofen, carbamazepine, and diclofenac removal in real wastewater by combined artificial solar light and immobilized TiO_2. The catalyst was coated on sand (200–500 μm) by the sol-gel technique. In addition, acute and chronic toxicity tests were performed using two algae species *Anabaena flosaquae* and *Pseudokirchneriella subcapitata* and luminescence bacteria (*Vibrio fischeri*) exposed at different interval times. Before photocatalysis, all organisms revealed toxicity by growth inhibition, and the green algae was more sensitive. During photodegradation, chronic toxicity of the pharmaceutical compounds to the algae species decreased significantly. However, for the luminescence bacteria, the intermediate photoproducts demonstrated similar toxicity to the parent compound. Immobilized TiO_2 photocatalysis has the main advantages of cost and step reduction in wastewater treatment. The catalyst separation is not necessary and displays the possibility of recycling and reusing TiO_2nanoparticles. However, several catalyst cycles promote TiO_2 fouling (Miranda-García et al. 2014). Approximately four or five cycles of immobilized TiO_2 are enough to maintain photocatalytic activity (Miranda-García et al. 2014; Sarkar et al. 2015). The use of hydrogen peroxide/ultraviolet and calcination treatment was demonstrated as adequate strategies to TiO_2 regeneration (Miranda-García et al. 2014).

Powdered activated carbon (powdered activated carbon) can increase the photocatalytic activity of TiO_2 due to a synergistic effect between powdered activated carbon/TiO_2 interfaces. Rioja et al. (2014) studied the performance of mixed powdered activated carbon and TiO_2 for carbamazepine, ibuprofen, and diclofenac degradation. A mechanical mixture (i.e., powdered activated carbon/TiO_2 + deionized water) and a chemical mixture (i.e., powdered activated carbon/TiO_2 + acidic alcoholic solution) at 400 °C and 500 °C calcination temperatures were evaluated, respectively. The chemical mixture at 400 °C exhibited the best performance both in the absorption step and in photodegradation phase. Carbajo et al. (2016) synthesized a TiO_2 catalyst by the hydrolysis of titanium (IV) isopropoxide in ethanol and evaluated its performance on the ibuprofen and carbamazepine photodegradation in natural waters using a solar compound parabolic collector pilot plant. The constant rate kinetics were 0.089, 0.043 min^{-1} and 0.081, 0.040 min^{-1} for carbamazepine and ibuprofen at P25 and synthesized TiO_2, respectively.

Homogeneous Oxidation Processes

Ozonation has been one of the most broadly investigated advanced oxidation processes methodology for pharmaceutical degradation. This technique is applied in several polluted matrices, as a clarifying and disinfecting agent. Ozonation is appropriate for the treatment of different kinds of wastewater matrices containing low concentrations of recalcitrant and toxic contaminants. Heberer (2007) studied the effectiveness of different treatment steps to remove diclofenac, carbamazepine, and lipid regulators in waterworks. The authors observed that using at low ozone dose (0.5 mg L^{-1}) removed 97% of diclofenac and carbamazepine. According to Gagnon et al. (2008), the irradiation used for wastewater disinfection does not necessarily promote the cleavage of the molecules (photolysis) of pharmaceuticals compounds presents in wastewater. Thus, they studied the capacity of each disinfection mode in the degradation of selected pharmaceuticals residues. Most of the pharmaceutical compounds were eliminated below 10% under ultraviolet photolysis, while high rate percentage removal (> 50%) was achieved at ozone dose of 10 mg L^{-1}. Applying the same approach, Coelho et al. (2010) evaluated the biodegradability and toxicity of ibuprofen and diclofenac by ozonation. They found a low optimal ozone dose (0.20 g L^{-1}) for total diclofenac removal, while the toxicity did not change in the ozonation treatment. On the other hand, ibuprofen required a more ozonation dose (2.3 g L^{-1}) than diclofenac to reach satisfactory mineralization and toxicity, determined by the *Vibrio fischeri* test, decreased with increasing ozone doses. Zimmermann et al. (2011) studied the degradation of 22 pharmaceuticals and personal care products at seven ozone doses (0.21 to 1.24 g Ozone g^{-1}), including carbamazepine, ibuprofen, and diclofenac. Oxidation transformation products formation, assimilable organic carbon, and disinfection by *Escherichia coli* were also evaluated. Rodríguez et al. (2012) used a continuous flow ozonation reactor equipped with a bubble column to find the optimal operational conditions wastewater treatment plant effluents spiked with 12 pharmaceuticals and personal care products, including ibuprofen, carbamazepine, and diclofenac. They found that energy for satisfactory ozonation was in the 0.03–0.26 kWh/m^3 range, with ozone efficiencies ranging from 90 to 100% and pollutant removal around 67–98%. The ozonation process presented high rate of constants reactivity ($k_{Ozone} > 10^5\ M^{-1}\ s^{-1}$) for diclofenac and carbamazepine. Both compounds have nonaromatic double bonds and deprotonated secondary aromatic amines, respectively, that allow the ozonation reaction (Heberer 2007). Moreover, the ozone preferably attack the benzene ring double bonds, leading to the formation of phenolic compounds that react quickly with ozone or ring cleavage with the formation of carbonyl compounds (Huber et al. 2005). Consequently, hydroxylamines and amine oxides can be formed. From a toxicological point of view, hydroxylamine formation from sulfonamides may cause hypersensitivity reactions (Huber et al. 2005).

Other investigations regarding the detection of low concentrations of pharmaceuticals and personal care products have focused on improving the use of surrogate parameters to development of advanced chromatographic techniques, thus to predict the behavior of pharmaceuticals and personal care products during the processes. Nanaboina and Korshin (2010) applied ozonation and explore transformations of effluent organic matter to provide the behavior of representative pharmaceutical compounds. Gerrity et al. (2012) developed empirical correlations for differential ultraviolet at 254 nm absorbance and total fluorescence for predict the oxidation of 18 organic contaminants, including ibuprofen, diclofenac, and carbamazepine in an ozone-based treatment. The authors concluded that ultraviolet$_{254}$ and total fluorescence could be used as surrogates for elimination of compounds, since these methods require a simple equipment, timework, and cost-effective. Moreover, automated online analyses are available for ultraviolet$_{254}$, and total fluorescence can allow for full-scale implementation. In this context, Altmann et al. (2014) investigated correlations between organic pharmaceuticals and personal care products removals with ultraviolet$_{254}$ reduction and dissolved organic carbon influence through powered activated carbon and transformation oxidant products generated during ozonation in wastewatereffluents. Carbamazepine and diclofenac concentrations were decreased almost 90% at 20 mg L^{-1} of powdered activated carbon and 5–7 mg/L of ozone dose. Also, ultraviolet$_{254}$ an analysis demonstrated to be suitable to follow target compound removal by both processes.

Appropriate combinations of advanced oxidation processes have improved the efficiency of the treatment of pharmaceuticals and personal care products. For example, ozone oxidation can be combined with another oxidant agent and acceptors electrons, as hydrogen peroxide (ozone/hydrogen peroxide), such as in the study carried out by Rosal et al. (2008), who promoted the degradation of 33 pharmaceuticals and personal care products, mainly pharmaceuticals compounds commonly found in wastewatereffluents. The results demonstrated that ozonation achieved only moderate mineralization, whereas the addition of hydrogen peroxide led to complete mineralization. Hydrogen peroxide combined with ultraviolet is a tool to completely remove pharmaceutical compounds, but the removal efficiency of this process is uncertain and depends on the water matrix, ultraviolet process conditions, and specific target organic compounds (Sichel et al. 2011). Regarding this approach, Lekkerkerker-Teunissen et al. (2012) assessed the degradation carbamazepine and diclofenac during ultraviolet photolysis and ultraviolet/hydrogen peroxide treatments applying two different irradiation ultraviolet lamps such as low-pressure lamps and medium pressure. Contrary to the photocatalysis processes (TiO_2/ultraviolet), the diclofenac ultraviolet/hydrogen peroxide degradation pathway occurs first by dechlorination, forming chlorocarbazole acetic acid. After this, the combination of hydroxylation and decarboxylation reactions is observed in the diclofenac structure (Fig. 10.9) (Lekkerkerker-Teunissen et al. 2012). Carbamazepine degradation via ultraviolet/hydrogen peroxide was poor, and the appearance of carbamazepine transformation products mainly 10,11-epoxycarbamazepine was influenced by the ultraviolet treatment rather than hydrogen peroxide dose (Lekkerkerker-Teunissen et al. 2012).

Low-pressure lamps have ultraviolet emission at 254 nm, whereas medium-pressure lamps have a spectrum 200–800 nm of irradiation with excellent potential to directly photodegrade pharmaceuticals and personal care products. Justo et al. (2013) used low-pressure lamps mercury vapor lamps to mitigate reverse osmosis concentrates (i.e., 11 pharmaceutical compounds) by ultraviolet/hydrogen peroxide and ozonation. On the other hand, Shu et al. (2013) applied medium-pressure lamps to photodegrade emerging pharmaceuticals and personal care products using ultraviolet/hydrogen peroxide. Moreover, both types of lamps were employed by Wols et al. (2013) to degrade 40 selected pharmaceuticals spiked in three different water matrices using ultraviolet/hydrogen peroxide. A polychromatic medium-pressure lamps showed better degradation performance than a low-pressure lamps, due to a wider range of wavelengths, increasing the probability of reactions between photons and the pollutants. Hydrogen peroxide/ultraviolet degradation using surface waters led to a 75% reduction of most pharmaceuticals compounds at ultraviolet doses of 500 and 1000 mJ/cm^2 for medium-pressure and low-pressure lamps, respectively (Wols et al. 2013).

Currently, several chemical oxidation processes are now being applied to water treatments to improve the sanitation technologies municipal wastewater treatment plant to protect the aquatic environment from pharmaceuticals and personal care products. In this context, Lee and von Gunten (2010) compared selective oxidants, such as ClO_2, $FeO_4{}^{-2}$ (ferrate (VI)), chlorine, and ozone, to ultraviolet/hydrogen peroxide as non-selective oxidants for the degradation of pharmaceutical compounds, endocrine-disrupting compounds, antibiotic, and anti-hypertensive micropollutants. The authors observed that the specific oxidants reacted with certain electron-rich organic groups such as anilines, phenols, and amines and that the effluent organic matter is main wastewater component that contains electron-rich organic moieties which may consume the oxidants.

The most important source of pharmaceuticals and personal care products into the environment is municipal wastewater treatment plants, where conventional treatment plants are still majorly inefficient in removing pharmaceuticals and personal care products (Michael et al. 2013). Among the advanced oxidation processes technologies able to reduce emergent contaminants in water, the Photo-Fenton processes is particularly attractive, due to its efficient use of sunlight with wavelengths below 580 nm (Malato et al. 2009). Li et al. (2012) examined the Fenton oxidation process regarding pharmaceutical compounds present in wastewater. The transformation of effluent organic matter was used to quantify the Fenton oxidation reaction. Ibuprofen, carbamazepine, and diclofenac were fully removed by this process using a 2.5 hydrogen peroxide/Fe (II) molar ratio. However, the major drawback of the Fenton process is about the need for low pH (around 3) and the formation of iron precipitates at higher pH. In this context, De la Cruz et al. (2012) evaluated the removal of 32 micropollutants by the Photo-Fenton process using ultraviolet$_{254}$ at near neutral pH. The authors observed that wastewater from wastewater treatment plant contain low amounts of iron, sufficient to perform the Photo-Fenton process. In another study, De la Cruz et al. (2013) applied neutral Photo-Fenton process for removal of 22 micropollutants on a pilot scale. The results indicated that the maximum hydrogen peroxide dose was of 50 mg L^{-1} and that the excess iron in the reactor did not improve the process. Klamerth et al. (2011) focused on a modified solar Photo-Fenton, using 5 mg L^{-1} of iron, at initial pH of 7 and 50 mg L^{-1} of hydrogen peroxide for the degradation of 15 micropollutants spiked in wastewatereffluents using a solar compound parabolic collector pilot plant. Additionally, the authors also tested the influence of oxalic acid, humic acid, and the mixing of influents and effluents. The results indicated that oxalate and humic acid (10 mg L^{-1}) enhanced the process, whereas the wastewater treatment plant spiked with a mixture of emergent contaminants was unsuccessful. In another study, Klamerth et al. (2013) compared the conventional and modified Photo-Fenton processes at neutral pH with low iron concentration for the degradation of pharmaceuticals and personal care products in wastewater treatment plant effluents using a solar compound parabolic collector pilot plant. In summary, several mechanism involved in Photo-Fenton pharmaceuticals and personal care products degradation can occur, namely, (i) direct photolysis; (ii) excited dissolved organic matter reacting with pollutant or oxygen to form a singlet molecular oxygen ($^1O_2$); (iii) direct cleavage of hydrogen peroxide (ultraviolet 254 nm) to produce $^{\bullet}OH$; (iv) traditional Fenton reaction in the dark, promoting hydroxyl formation; (v) formed organic radicals can react to oxygen, forming the superoxide and hydroperoxide radicals; and (vi) production of hydrogen peroxide through the reaction of superoxide/hydroperoxide radicals with subsequent $^{\bullet}OH$ formation (De la Cruz et al. 2012, 2013). The schematic mechanism is displayed in Fig. 10.10.

Another possibility regarding the drawback of low pH is the development the Fenton-like reactions using others metals that show effectiveness for pharmaceuticals and personal care products degradation. Copper, via Fenton-like reactions, for example, shows higher activity in alkaline conversion of hydrogen peroxide into reactive oxidants species. In this regard, Lee et al. (2014) evaluated the operating parameters such as pH, amount of copper, and adding radical scavengers that affect carbamazepine and diclofenac degradation employing the combination of Cu(II)/hydrogen peroxide in the dark and under ultraviolet radiation. The results indicated that pH 8 was more efficient for compound degradation, since the Cu(II) reduction rate increased with accelerated hydrogen peroxide decomposition and promoted the formation of oxidant radicals than $^{\bullet}OH$.

As an alternative to conventional oxidant agents, Fenton reactions can be performed by the decomposition of the sulfate radical ($SO_4^{\bullet-}$), which has a strong redox potential (2.5–3.1 V). Using this approach, Ahmed et al. (2014) compared the photo-Fenton mediated peroxymonosulfate as an oxidant for six contaminants including carbamazepine and diclofenac. Except for carbamazepine, k_{app} values

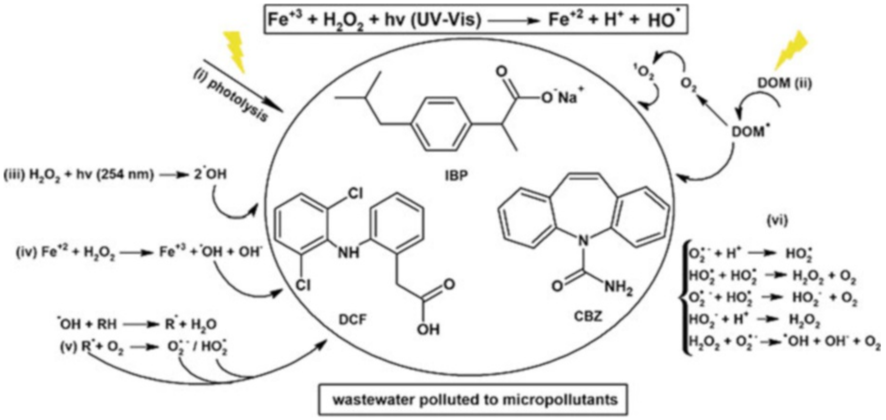


Fig. 10.10 Mechanism reactions of Photo-Fenton pharmaceutical compounds degradation. IBP, ibuprofen; DCF, diclofenac; CBZ, carbamazepine. (Modified from De la Cruz et al. 2012, 2013)

were tenfold higher in the peroxymonosulfate/Fe(II)/ultraviolet process compared to the TiO_2/ultraviolet system, since carbamazepine reacted C-C double bond by electron transfer.

Recently, Yao et al. (2016) developed an advanced oxidation processes system based on the electro-peroxone process, which electrochemically produces in situ hydrogen peroxide from O_2 and compared its effectiveness to conventional ozonation. Several pharmaceutical compounds were tested in four different secondary effluents. Both processes quickly removed the pharmaceuticals compounds, such as diclofenac, while E-peroxone was more efficient for ozone-refractory pharmaceuticals like ibuprofen, becomes the processes more environment friendly with reduced reaction time and electrical energy consumption to eliminate all pharmaceuticals compounds from effluents.

Coupling with Other Treatment Processes

Urbanized countries produce significant amounts of wastewatereffluents containing a high organic composition and persistent pollutants. Wastewater treatment is centralized in municipal wastewater treatment plant but have as the main concern the decrease of C, N, and P loads present in the influents. Several pharmaceutical compounds, such as ibuprofen or paracetamol, can be degraded during the activated sludge process (Joss et al. 2006). On the other hand, many polar compounds, such as antimicrobials and diclofenac, are only partly degraded while the antiepileptic drug carbamazepine is practically not degraded at all by biological treatment (Ternes et al. 2004). Firstly, advanced oxidation processes can be applied as pretreatment before discharge of the effluents into public sewers, since the raw effluent contains high chemical oxygen demand and total suspended solids. In this sense, an extensive study was performed by Nakada et al. (2007), where the removal rates of

24 pharmaceutical compounds were studied during sand filtration, as pretreatment, and ozonation, as post-treatment, in an operating municipal biological plant. Ozonation removed 80% or more of the pharmaceutical compounds, although due to low hydrophobicities the sand filtration was inefficient. Ozonation has been shown a selective to degradation, where the compounds that have amide structures were resident, while electron donors group as C=C or an aromatic presents in the molecule of compounds were susceptible to ozonation.

Badawy et al. (2009) investigated the efficiency of the Fenton as a pretreatment step for the removal pharmaceuticals and personal care products from industrial pharmaceuticalwastewaters before discharge into the biological system. The optimization conditions of the Fenton process was determined by chemical oxygen demand/hydrogen peroxide 1:2.2, Fe^{+2}/hydrogen peroxide 1:50, 1.5 h of reaction time and pH 3, and the chemical oxygen demand reduction ranged from 67 to 87%. The Fenton process as pretreatment thus allowed for subsequent biological degradation to be achieved in a shorter detention time.

Nevertheless, the most common application of advanced oxidation processes is following secondary biological treatment. Hollender et al. (2009) evaluated the ozonation as a treatment step degradation of 220 micropollutants from a municipal wastewater treatment plant and found the formation of toxic transformation products such as nitrosamines and bromate. The authors determined that ibuprofen was easily biodegradable to yields higher than 85%, whereas diclofenac was shown to be moderately persistent and carbamazepine was found to be almost completely persistent during activated sludge treatment. A medium level ozone dose contributed in reaching yields higher than 80% for diclofenac and carbamazepine elimination. Using the same approach, José et al. (2010) applied a biological membrane treatment before oxidation by ozonation. However, the application of the membrane bioreactor treatment was shown to be inefficient. Nevertheless, applications using different combinations of the ozonation process after membrane bioreactor treatment removed all target compounds present, with only the carbamazepine products remaining. The design criteria for wastewater treatment plant present a significant impact on pharmaceuticals and personal care products removal. In this sense, Nguyen et al. (2013) studied the removal of pharmaceuticals and personal care products by a hybrid membrane bioreactor treatment process under ultraviolet photolysis or applying reverse osmosis membrane and nanofiltration. The membrane bioreactor treatment alone removed only ibuprofen, whereas hybrid membrane bioreactor treatments were able to remove both carbamazepine and diclofenac. However, carbamazepine was persistent, since membrane bioreactor and ultraviolet treatment accounted for only 30% removal for each process. Schaar et al. (2010) described the removal of pharmaceuticals and personal care products during high (carbon removal)- and low (nutrient removal)-loaded conditions with subsequent treatment by an ozonation step. Ibuprofen showed better removal under low loaded conditions, whereas carbamazepine and diclofenac were not degraded during activated sludge treatment, requiring a subsequent ozonation step. Ozonation is an advanced oxidation processes technique largely applied after secondary biological treatment. In this context, Rosal et al. (2010) monitored the occurrence and fate of 84 micropollutants belonging to different classes before and after biological treatment with nutrient removal. Subsequently, the impact of ozone exposure on micropollutants found in the secondary effluent coupled to the process was investigated. The results revealed indicated that the efficiency of organic compound removal in the sewage treatment plant was strongly dependent on their hydrophobicity. As expected, ibuprofen was 95% removed, whereas ibuprofen and carbamazepine required the ozonation treatment, where 120 s of ozonation removed both compounds at ozone doses <50 and < 90 mM, respectively.

The Spanish group Plataforma Solar de Almería has exhaustively researched advanced oxidation processes, mainly regarding oxidation processes coupled with other treatments. In this approach, Miralles-Cuevas et al. (2013) investigated if nanofiltration and solar photo-Fenton combination are more effectiveness than photo-Fenton alone to improvement the conventional biological treatment for carbamazepine, flumequine, ibuprofen, ofloxacin, and sulfamethoxazole compounds, as a tertiary treatment. In a subsequent study, Miralles-Cuevas et al. (2014c) used the same model contaminants to assess whether nanofiltration and mild solar photo-Fenton combination process was more effective than nanofiltration or solar Photo-Fenton alone. Moreover, Miralles-Cuevas et al. (2014a) compared traditional advanced oxidation processes, solar photo-Fenton, and ozonation with photo-Fenton-like process employing ethylenediamine-N,N′-disuccinic acid as complexing agent, as tertiary treatments from nanofiltration concentrates to remove the same pharmaceutical compounds from natural waters. In another study, the same author (Miralles-Cuevas et al. 2014b) investigated the treatment of a municipal wastewater treatment plant before and after nanofiltration concentration by the solar mild (neutral pH) photo-Fenton with ethylenediamine-N,N′-disuccinic acid and citrate-like as complexing agents. The main conclusions of these studies were that concentration of pharmaceuticals by nanofiltration produced a clean effluent and resulted in a concentrated stream for subsequent neutral solar photo-Fenton applications. Consequently, combining nanofiltration/advanced oxidation processes reduced treatment time, costs and reagent consumption. Nevertheless, the best option for complexing Fe was the use of ethylenediamine-N,N′-disuccinic acid than citrate (Miralles-Cuevas et al. 2014b).

A study carried out by Giannakis et al. (2015), evaluated three different secondary treatment methods, such as moving bed bioreactor, active sludge, and coagulation-flocculation, coupled to ultraviolet, sunlight irradiation, ultraviolet/hydrogen peroxide, fenton, and solar Photo-Fenton for the degradation of six pharmaceuticals and personal care products. Among the evaluated secondary treatments, the moving bed bioreactor effluent presents advantages for subsequent advanced oxidation processes treatment. The pH and suspended solids content were slightly lower than the active sludge and coagulation-flocculation effluents. Physical-chemistry parameters in the wastewater can influence the degradation efficiency. For example, alkalinity can act as scavenger for $^{\bullet}$OH avoiding the degradation, due the carbonate presence. A girth amount of suspended solids can be a physical barrier between the organic compounds and the photons (Giannakis et al. 2015). Using the same approach, Gimeno et al. (2016) carried out aerobic biodegradation followed by TiO_2 solar photocatalysis, solar photo-Fenton and ozonation in the degradation of carbamazepine and diclofenac that were persistent to biological oxidation treatment. Toxicity assessment indicated no inhibition in *Daphnia magna* immobilization tests. The results revealed that the combination of ozonation with a photocatalytic processes demonstrated higher degradation rates than simple photocatalytic oxidation (i.e., TiO_2/ultraviolet or solar photo Fenton alone).

10.4 Conclusions

Pharmaceuticals and personal care products are recognized as contaminants of emergent concern due to their long-term toxicological effects and possibility to incorporate to a food level chain. The development and improvement of oxidation technologies for removal of these contaminants from municipal wastewater is necessary and a challenging wastewater treatment plant are unsuccessful to remove of pharmaceuticals and personal care products, which then act as a point source of environmental contamination. Advanced oxidation processes are a hot spot system that can remove these compounds without adding complex chemicals. Thus, this review allowed for the following inferences:

- Combined ozonation techniques are the most studied processes for treatment of wastewater contaminated by pharmaceuticals and personal care products.
- TiO_2 immobilization techniques provide a cost-effective solid-liquid separation for heterogeneous photocatalysis. The catalyst separation step is a lost time period that increases treatment costs.
- Advanced oxidation processes research should consider real environmental conditions about residual concentrations from ng/L to µg/L, as mixtures of compounds in different environmental compartments. In addition, the wastewater matrix is a point that should be taken into account. Thus, advanced oxidation processes should be more explored on real tertiary wastewater treatment plants and pilot plant systems.
- Coupling advanced oxidation techniques with biological and physical-chemical systems offers the potential to reduce environmental effects of pharmaceuticals and personal care products. Moreover, effective photoreactor system designs (parabolic solar collector) at industrial scales can be feasible for the economy and the environment, due to higher utilization of solar energy.
- Ecotoxicological assessments during advanced oxidation processes are another hot spot for pharmaceuticals and personal care products treatment. The effects on organisms before, during and after the processes treatment are excellent tools to assess process efficiencies and can determine possible effects of byproduct oxidation on human and environmenthealth. Therefore, chronic and early effects on organisms would be important to assess the several effects between mixtures of compounds in real water matrices even low concentration.

- Recently, chlorination/ultraviolet systems have been satisfactory applied as advanced oxidation processes for pharmaceuticals and personal care products oxidation, whereas the disinfection byproduct formation should be evaluated during the process.

Acknowledgments E. M. Saggioro would like to thank FAPERJ project (E-26/010.002117/2015) and project (E-26/010.000424/2016).

References

Ahmed MM, Brienza M, Goetz V, Chiron S (2014) Solar photo-Fenton using peroxymonosulfate for organic micropollutants removal from domestic wastewater: comparison with heterogeneous TiO2 photocatalysis. Chemosphere 117:256–261. https://doi.org/10.1016/j.chemosphere.2014.07.046

Altmann J, Ruhl AS, Zietzschmann F, Jekel M (2014) Direct comparison of ozonation and adsorption onto powdered activated carbon for micropollutant removal in advanced wastewater treatment. Water Res 55:185–193. https://doi.org/10.1016/j.watres.2014.02.025

Amat AM, Arques A, García-Ripoll A, Santos-Juanes L, Vicente R, Oller I, Maldonado MI, Malato S (2009) A reliable monitoring of the biocompatibility of an effluent along an oxidative pre-treatment by sequential bioassays and chemical analyses. Water Res 43:784–792. https://doi.org/10.1016/J.WATRES.2008.11.017

Andreozzi R, Raffaele M, Nicklas P (2003) Pharmaceuticals in STP effluents and their solar photodegradation in aquatic environment. Chemosphere 50:1319–1330. https://doi.org/10.1016/S0045-6535(02)00769-5

Badawy MI, Wahaab RA, El-Kalliny AS (2009) Fenton-biological treatment processes for the removal of some pharmaceuticals from industrial wastewater. J Hazard Mater 167:567–574. https://doi.org/10.1016/j.jhazmat.2009.01.023

Bahlmann A, Weller MG, Panne U, Schneider RJ (2009) Monitoring carbamazepine in surface and wastewaters by an immunoassay based on a monoclonal antibody. Anal Bioanal Chem 395:1809–1820. https://doi.org/10.1007/s00216-009-2958-7

Bartelt-Hunt S, Snow DD, Damon-Powell T, Miesbach D (2011) Occurrence of steroid hormones and antibiotics in shallow groundwater impacted by livestock waste control facilities. J Contam Hydrol 123:94–103. https://doi.org/10.1016/J.JCONHYD.2010.12.010

Behar D, Behar B (1991) Pulse radiolysis studies of aminobenzenesulfonates: formation of cation radicals. J Phys Chem 95:7552–7556. https://doi.org/10.1021/j100172a078

Ben W, Sun P, Huang CH (2016) Effects of combined ultraviolet and chlorine treatment on chloroform formation from triclosan. Chemosphere 150:715–722. https://doi.org/10.1016/j.chemosphere.2015.12.071

Bolong N, Ismail AF, Salim MR, Matsuura T (2009) A review of the effects of emerging contaminants in wastewater and options for their removal. Desalination 239:229–246. https://doi.org/10.1016/J.DESAL.2008.03.020

Boreen AL, Arnold WA, McNeill K (2003) Photodegradation of pharmaceuticals in the aquatic environment: a review. Aquat Sci – Res Across Bound 65:320–341. https://doi.org/10.1007/s00027-003-0672-7

Brausch JM, Rand GM (2011) A review of personal care products in the aquatic environment: environmental concentrations and toxicity. Chemosphere 82:1518–1532. https://doi.org/10.1016/J.CHEMOSPHERE.2010.11.018

Buser HR, Poiger T, Muller MD (1999) Occurrence and environmental behavior of the chiral pharmaceutical drug ibuprofen in surface waters and in wastewater. Environ Sci Technol 33:2529–2535. https://doi.org/10.1021/es981014w

Calisto V, Bahlmann A, Schneider RJ, Esteves VI (2011) Application of an ELISA to the quantification of carbamazepine in ground, surface and wastewaters and validation with LC–MS/MS. Chemosphere 84:1708–1715. https://doi.org/10.1016/J.CHEMOSPHERE.2011.04.072

Carbajo J, Jiménez M, Miralles S, Malato S, Faraldos M, Bahamonde A (2016) Study of application of titania catalysts on solar photocatalysis: influence of type of pollutants and water matrices. Chem Eng J 291:64–73. https://doi.org/10.1016/j.cej.2016.01.092

Chalew TE, Halden RU (2009) Environmental exposure of aquatic and terrestrial biota to Triclosan and Triclocarban. J Am Water Works Assoc 45:4–13. https://doi.org/10.1111/j.1752-1688.2008.00284.x

Chen X, Richard J, Liu Y, Dopp E, Tuerk J, Bester K (2012) Ozonation products of triclosan in advanced wastewater treatment. Water Res 46:2247–2256. https://doi.org/10.1016/j.watres.2012.01.039

Coelho AD, Sans C, Esplugas S, Dezotti M (2010) Ozonation of NSAID: a biodegradability and toxicity study. Ozone Sci Eng 32:91–98. https://doi.org/10.1080/01919510903508162

Daughton CG, Ternes TA (1999) Pharmaceuticals and personal care products in the environment: agents of subtle change? Environ Health Perspect 107(Suppl 6):907–938. https://doi.org/10.1289/ehp.99107s6907

De la Cruz N, Esquius L, Grandjean D, Magnet A, Tungler A, de Alencastro LF, Pulgarín C (2013) Degradation of emergent contaminants by ultraviolet, ultraviolet/hydrogen peroxide and neutral photo-Fenton at pilot scale in a domestic wastewater treatment plant. Water Res 47:5836–5845. https://doi.org/10.1016/j.watres.2013.07.005

De la Cruz N, Giménez J, Esplugas S, Grandjean D, De Alencastro LF, Pulgarín C (2012) Degradation of 32 emergent contaminants by ultraviolet and neutral photo-fenton in domestic wastewater effluent previously treated by activated sludge. Water Res 46:1947–1957. https://doi.org/10.1016/j.watres.2012.01.014

Deblonde T, Cossu-Leguille C, Hartemann P (2011) Emerging pollutants in wastewater: a review of the literature. Int J Hyg Environ Health 214:442–448. https://doi.org/10.1016/j.ijheh.2011.08.002

Deng Y, Zhao R (2015) Advanced oxidation processes (advanced oxidation Processess) in wastewater treatment. J Ind Eng Chem 1:167–176. https://doi.org/10.1007/s40726-015-0015-z

Dimitrov S, Dimitrova N, Walker J, Veith G, Mekenyan O (2003) Bioconcentration potential predictions based on molecular attributes – an early warning approach for chemicals found in humans, birds, fish and wildlife. QSAR Comb Sci 22:58–68. https://doi.org/10.1002/qsar.200390005

Ding SL, Wang XK, Jiang WQ, Meng X, Zhao RS, Wang C, Wang X (2013) Photodegradation of the antimicrobial triclocarban in aqueous systems under ultraviolet radiation. Environ Sci Pollut Res 20:3195–3201. https://doi.org/10.1007/s11356-012-1239-8

Feng Y, Zhang P, Zhang Z, Shi J, Jiao Z, Shao B (2016) Endocrine disrupting effects of Triclosan on the placenta in pregnant rats. PLoS One 11:e0154758. https://doi.org/10.1371/journal.pone.0154758

Fent K, Weston AA, Caminada D (2006) Ecotoxicology of human pharmaceuticals. Aquat Toxicol 76:122–159. https://doi.org/10.1016/j.aquatox.2005.09.009

Focazio MJ, Kolpin DW, Barnes KK, Furlong ET, Meyer MT, Zaugg SD, Barber LB, Thurman ME (2008) A national reconnaissance for pharmaceuticals and other organic wastewater contaminants in the United States — II) untreated drinking water sources. Sci Total Environ 402:201–216. doi:https://doi.org/10.1016/J.SCITOTENV.2008.02.021

Gagnon C, Lajeunesse A, Cejka P, Gagné F, Hausler R (2008) Degradation of selected acidic and neutral pharmaceutical products in a primary-treated wastewater by disinfection processes. Ozone Sci Eng 30:387–392. https://doi.org/10.1080/01919510802336731

Gao Y, Ji Y, Li G, An T (2014) Mechanism, kinetics and toxicity assessment of OH-initiated transformation of triclosan in aquatic environments. Water Res 49:360–370. https://doi.org/10.1016/J.WATRES.2013.10.027

Gee RH, Charles A, Taylor N, Darbre PD (2008) Oestrogenic and androgenic activity of triclosan in breast cancer cells. J. Appl. Toxicol. 28:78–91. https://doi.org/10.1002/jat.1316

Gerrity D, Gamage S, Jones D, Korshin GV, Lee Y, Pisarenko A, Trenholm RA, von Gunten U, Wert EC, Snyder SA (2012) Development of surrogate correlation models to predict trace organic contaminant oxidation and microbial inactivation during ozonation. Water Res 46:6257–6272. https://doi.org/10.1016/j.watres.2012.08.037

Giannakis S, Gamarra Vives FA, Grandjean D, Magnet A, De Alencastro LF, Pulgarin C (2015) Effect of advanced oxidation processes on the micropollutants and the effluent organic matter contained in municipal wastewater previously treated by three different secondary methods. Water Res 84:295–306. https://doi.org/10.1016/j.watres.2015.07.030

Gil Maia C, Anabela Sousa Oliveira B, Enrico Mendes Saggioro B, Josino Costa Moreira B, Maia ÁAS, Oliveira CG, Oliveira AS, Saggioro ÁJC, Moreira EM (2014) Optimization of the photocatalytic degradation of commercial azo dyes in aqueous TiO 2 suspensions. Reac Kinet Mech Cat 113:305–320. https://doi.org/10.1007/s11144-014-0737-8

Gimeno O, García-Araya JF, Beltrán FJ, Rivas FJ, Espejo A (2016) Removal of emerging contaminants from a primary effluent of municipal wastewater by means of sequential biological degradation-solar photocatalytic oxidation processes. Chem Eng J 290:12–20. https://doi.org/10.1016/j.cej.2016.01.022

Giri RR, Ozaki H, Takayanagi Y, Taniguchi S, Takanami R (2011) Efficacy of ultraviolet radiation and hydrogen peroxide oxidation to eliminate large number of pharmaceutical compounds in mixed solution. Int J Environ Sci Technol 8:19–30. https://doi.org/10.1007/BF03326192

Gledhill WE (1975) Biodegradation of 3,4,4′-Trichlorocarbanilide, Triclocarban ®, sewage and activated sludge. Water Res 9. https://doi.org/10.1016/0043-1354(75)90171-2

Gültekin I, Ince NH (2007) Synthetic endocrine disruptors in the environment and water remediation by advanced oxidation processes. J Environ Manag 85:816–832. https://doi.org/10.1016/J.JENVMAN.2007.07.020

Halden RU, Paull DH (2005) Co-occurrence of triclocarban and triclosan in U.S. water resources. Environ Sci Technol. https://doi.org/10.1021/es049071e

Hayashi Y, Heckmann L-H, Callaghan A, Sibly RM (2008) Reproduction recovery of the crustacean Daphnia magna after chronic exposure to ibuprofen. Ecotoxicology 17:246–251. https://doi.org/10.1007/s10646-008-0191-3

He Y, Sutton NB, Rijnaarts HHH, Langenhoff AAM (2016) Degradation of pharmaceuticals in wastewater using immobilized TiO2 photocatalysis under simulated solar irradiation. Appl Catal B Environ 182:132–141. https://doi.org/10.1016/j.apcatb.2015.09.015

Heath RJ, Rinald RJ, Holland DR, Zhang E, Snow MR, Rock CO et al. (1999) Mechanism of triclosan inhibition of bacterial fatty acid synthesis. J Biol Chem 274(16):11110–11114. https://doi.org/10.1074/jbc.274.16.11110

Heberer T, Reddersen K, Mechlinski A (2002) From municipal sewage to drinking water: fate and removal of pharmaceutical residues in the aquatic environment in urban areas. Water Sci Technol 46:81–88. https://doi.org/10.2166/wst.2002.0060

Heberer T (2007) Removal of pharmaceuticals during drinking water production. Environ Sci Technol 50:3855–3863. https://doi.org/10.1016/S0166-526X(07)50015-2

Heberer T (2002) Occurrence, fate, and removal of pharmaceutical residues in the aquatic environment: a review of recent research data. Toxicol Lett 131:5–17. https://doi.org/10.1016/S0378-4274(02)00041-3

Heidler J, Halden RU (2007) Mass balance assessment of triclosan removal during conventional sewage treatment. Chemosphere 66:362–369. https://doi.org/10.1016/J.CHEMOSPHERE.2006.04.066

Hernández-Leal L, Temmink H, Zeeman G, Buisman CJN (2011) Removal of micropollutants from aerobically treated grey water via ozone and activated carbon. Water Res 45:2887–2896. https://doi.org/10.1016/j.watres.2011.03.009

Hollender J, Zimmermann SG, Koepke S, Krauss M, McArdell CS, Ort C, Singer H, von Gunten U, Siegrist H (2009) Supplementary information elimination of organic micropollutants in a municipal wastewater treatment plant upgraded with a full scale post-ozonation followed by sand filtration. Environ Sci Technol 43:7862–7869. https://doi.org/10.1021/es9014629

Huber MM, Canonica S, Park GY, Von Gunten U (2003) Oxidation of pharmaceuticals during ozonation and advanced oxidation processes. Environ. Sci. Technol. 37:1016–1024. https://doi.org/10.1021/es025896h

Huber MM, Gbel A, Joss A, Hermann N, Lffler D, McArdell SC, Ried A, Siegrist H, Ternes TA, Von Gunten U, Go A (2005) Oxidation of pharmaceuticals during ozonation of municipal wastewater effluents : a pilot study oxidation of pharmaceuticals during ozonation of municipal wastewater effluents : a pilot study. Environ Sci Technol 39:4290–4299. https://doi.org/10.1021/es048396s

Hutt AJ, Caldwell J (1983) The metabolic chiral inversion of 2-arylpropionic acids-a novel route with pharmacological consequences. J Pharm Pharmacol 35:693–704. https://doi.org/10.1111/j.2042-7158.1983.tb02874.x

Ishibashi H, Matsumura N, Hirano M, Matsuoka M, Shiratsuchi H, Ishibashi Y, Takao Y, Arizono K (2004) Effects of triclosan on the early life stages and reproduction of medaka Oryzias latipes and induction of hepatic vitellogenin. Aquat Toxicol 67:167–179. https://doi.org/10.1016/j.aquatox.2003.12.005

Jiménez M, Ignacio Maldonado M, Rodríguez EM, Hernández-Ramírez A, Saggioro E, Carra I, Sánchez Pérez JA (2015) Supported TiO $_2$ solar photocatalysis at semi-pilot scale: degradation of pesticides found in citrus processing industry wastewater, reactivity and influence of photogenerated species. J Chem Technol Biotechnol 90:149–157. https://doi.org/10.1002/jctb.4299

José HJ, Gebhardt W, Moreira RFPM, Pinnekamp J, Schröder HF (2010) Advanced oxidation processes for the elimination of drugs resisting biological membrane treatment. Ozone Sci Eng 32:305–312. https://doi.org/10.1080/01919512.2010.508194

Joss A, Zabczynski S, Göbel A, Hoffmann B, Löffler D, McArdell CS, Ternes TA, Thomsen A, Siegrist H (2006) Biological degradation of pharmaceuticals in municipal wastewater treatment: proposing a classification scheme. Water Res 40:1686–1696. https://doi.org/10.1016/j.watres.2006.02.014

Jung EM, An BS, Choi KC, Jeung EB (2012) Potential estrogenic activity of triclosan in the uterus of immature rats and rat pituitary GH3 cells. Toxicol Lett 208:142–148. https://doi.org/10.1016/j.toxlet.2011.10.017

Justo A, González O, Aceña J, Pérez S, Barceló D, Sans C, Esplugas S (2013) Pharmaceuticals and organic pollution mitigation in reclamation osmosis brines by ultraviolet/hydrogen peroxide and ozone. J Hazard Mater 263:268–274. https://doi.org/10.1016/j.jhazmat.2013.05.030

Jux U, Baginski RM, Arnold H-G, Krönke M, Seng PN (2002) Detection of pharmaceutical contaminations of river, pond, and tap water from Cologne (Germany) and surroundings. Int J Hyg Environ Health 205:393–398. https://doi.org/10.1078/1438-4639-00166

Kim SD, Cho J, Kim IS, Vanderford BJ, Snyder SA (2007) Occurrence and removal of pharmaceuticals and endocrine disruptors in south Korean surface, drinking, and waste waters. Water Res 41:1013–1021. https://doi.org/10.1016/J.WATRES.2006.06.034

Kinney CA, Furlong ET, Kolpin DW, Burkhardt MR, Zaugg SD, Werner SL, Bossio JP, Benotti MJ (2008) Bioaccumulation of pharmaceuticals and other anthropogenic waste indicators in earthworms from agricultural soil amended with biosolid or swine manure. Environ Sci Technol 42:1863–1870. https://doi.org/10.1021/es702304c

Klamerth N, Malato S, Agüera A, Fernández-Alba A (2013) Photo-Fenton and modified photo-Fenton at neutral pH for the treatment of emerging contaminants in wastewater treatment plant effluents: a comparison. Water Res 47:833–840. https://doi.org/10.1016/j.watres.2012.11.008

Klamerth N, Malato S, Maldonado MI, Agüera A, Fernández-Alba A (2011) Modified photo-Fenton for degradation of emerging contaminants in municipal wastewater effluents. Catal Today 161:241–246. https://doi.org/10.1016/j.cattod.2010.10.074

Klamerth N, Malato S, Maldonado MI, Agüera A, Fernández-Alba AR (2010a) Application of photo-Fenton as a tertiary treatment of emerging contaminants in municipal wastewater. Environ Sci Technol 44:1792–1798. https://doi.org/10.1021/es903455p

Klamerth N, Miranda N, Malato S, Agüera A, Fernández-Alba AR, Maldonado MI, Coronado JM (2009) Degradation of emerging contaminants at low concentrations in MWTPs effluents with mild solar photo-Fenton and TiO2. Catal Today 144:124–130. https://doi.org/10.1016/j.cattod.2009.01.024

Klamerth N, Rizzo L, Malato S, Maldonado MI, Agüera A, Fernández-Alba AR (2010b) Degradation of fifteen emerging contaminants at ??g L-1 initial concentrations by mild solar photo-Fenton in MWTP effluents. Water Res 44:545–554. https://doi.org/10.1016/j.watres.2009.09.059

Klavarioti M, Mantzavinos D, Kassinos D (2009) Removal of residual pharmaceuticals from aqueous systems by advanced oxidation processes. Environ Int 35:402–417. https://doi.org/10.1016/J.ENVINT.2008.07.009

Kolpin DW, Furlong ET, Meyer MT, Thurman EM, Zaugg SD, Barber LB, Buxton HT (2002) Pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999-2000: a national reconnaissance. Environ Sci Technol 36:1202–1211. https://doi.org/10.1021/es011055j

Kosma CI, Lambropoulou DA, Albanis TA (2014) Investigation of PPersonal care products s in wastewater treatment plants in Greece: occurrence, removal and environmental risk assessment. Sci Total Environ 466–467:421–438. https://doi.org/10.1016/j.scitotenv.2013.07.044

Kumar V, Chakraborty A, Kural MR, Roy P (2009) Alteration of testicular steroidogenesis and histopathology of reproductive system in male rats treated with triclosan. Reprod Toxicol 27:177–185. https://doi.org/10.1016/j.reprotox.2008.12.002

Kümmerer K (2009) The presence of pharmaceuticals in the environment due to human use – present knowledge and future challenges. J Environ Manag 90:2354–2366. https://doi.org/10.1016/J.JENVMAN.2009.01.023

Lapworth DJ, Baran N, Stuart ME, Ward RS (2012) Emerging organic contaminants in groundwater: a review of sources, fate and occurrence. Environ Pollut 163:287–303. https://doi.org/10.1016/J.ENVPOL.2011.12.034

Latch DE, Packer JL, Arnold WA, McNeill K (2003) Photochemical conversion of triclosan to 2,8-dichlorodibenzo-p-dioxin in aqueous solution. J Photochem Photobiol A Chem 158:63–66. https://doi.org/10.1016/S1010-6030(03)00103-5

Lee HJ, Lee H, Lee C (2014) Degradation of diclofenac and carbamazepine by the copper(II)-catalyzed dark and photo-assisted Fenton-like systems. Chem Eng J 245:258–264. https://doi.org/10.1016/j.cej.2014.02.037

Lee Y, von Gunten U (2010) Oxidative transformation of micropollutants during municipal wastewater treatment: comparison of kinetic aspects of selective (chlorine, chlorine dioxide, ferrateVI, and ozone) and non-selective oxidants (hydroxyl radical). Water Res 44:555–566. https://doi.org/10.1016/j.watres.2009.11.045

Lekkerkerker-Teunissen K, Benotti MJ, Snyder SA, Van Dijk HC (2012) Transformation of atrazine, carbamazepine, diclofenac and sulfamethoxazole by low and medium pressure ultraviolet and ultraviolet/H 2O 2 treatment. Sep Purif Technol 96:33–43. https://doi.org/10.1016/j.seppur.2012.05.005

Li W, Nanaboina V, Zhou Q, Korshin GV (2012) Effects of Fenton treatment on the properties of effluent organic matter and their relationships with the degradation of pharmaceuticals and personal care products. Water Res 46:403–412. https://doi.org/10.1016/j.watres.2011.11.002

Li WC (2014) Occurrence, sources, and fate of pharmaceuticals in aquatic environment and soil. Environ Pollut 187:193–201. https://doi.org/10.1016/j.envpol.2014.01.015

Li X, Zheng W, Kelly WR (2013) Occurrence and removal of pharmaceutical and hormone contaminants in rural wastewater treatment lagoons. Sci Total Environ 445–446:22–28. https://doi.org/10.1016/j.scitotenv.2012.12.035

Lin AY-C, Tsai Y-T (2009) Occurrence of pharmaceuticals in Taiwan's surface waters: impact of waste streams from hospitals and pharmaceutical production facilities. Sci Total Environ 407:3793–3802. https://doi.org/10.1016/J.SCITOTENV.2009.03.009

Liu J-L, Wong M-H (2013) Pharmaceuticals and personal care products (PPersonal care products s): a review on environmental contamination in China. Environ Int 59:208–224. https://doi.org/10.1016/J.ENVINT.2013.06.012

Luo Y, Guo W, Ngo HH, Nghiem LD, Hai FI, Zhang J, Liang S, Wang XC (2014) A review on the occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment. Sci Total Environ 473–474:619–641. https://doi.org/10.1016/j.scitotenv.2013.12.065

Malato S, Fernández-Ibáñez P, Maldonado MI, Blanco J, Gernjak W (2009) Decontamination and disinfection of water by solar photocatalysis: recent overview and trends. Catal Today 147:1–59. https://doi.org/10.1016/j.cattod.2009.06.018

Méndez-Arriaga F, Esplugas S, Giménez J (2008) Photocatalytic degradation of non-steroidal anti-inflammatory drugs with TiO2 and simulated solar irradiation. Water Res 42:585–594. https://doi.org/10.1016/j.watres.2007.08.002

Michael I, Achilleos A, Lambropoulou D, Torrens VO, Pérez S, Petrović M, Barceló D, Fatta-Kassinos D (2014) Proposed transformation pathway and evolution profile of diclofenac and ibuprofen transformation products during (sono)photocatalysis. Appl Catal B Environ 147:1015–1027. https://doi.org/10.1016/j.apcatb.2013.10.035

Michael I, Rizzo L, McArdell CS, Manaia CM, Merlin C, Schwartz T, Dagot C, Fatta-Kassinos D (2013) Urban wastewater treatment plants as hotspots for the release of antibiotics in the environment: a review. Water Res 47:957–995. https://doi.org/10.1016/j.watres.2012.11.027

Miralles-Cuevas S, Arqués A, Maldonado MI, Sánchez-Pérez JA, Malato Rodríguez S (2013) Combined nanofiltration and photo-Fenton treatment of water containing micropollutants. Chem Eng J 224:89–95. https://doi.org/10.1016/j.cej.2012.09.068

Miralles-Cuevas S, Audino F, Oller I, Sánchez-Moreno R, Sánchez Pérez JA, Malato S (2014a) Pharmaceuticals removal from natural water by nanofiltration combined with advanced tertiary treatments (solar photo-Fenton, photo-Fenton-like Fe(III)-EDDS complex and ozonation). Sep Purif Technol 122:515–522. https://doi.org/10.1016/j.seppur.2013.12.006

Miralles-Cuevas S, Oller I, Pérez JAS, Malato S (2014b) Removal of pharmaceuticals from MWTP effluent by nanofiltration and solar photo-Fenton using two different iron complexes at neutral pH. Water Res 64:23–31. https://doi.org/10.1016/j.watres.2014.06.032

Miralles-Cuevas S, Oller I, Ruiz Aguirre A, Sánchez Pérez JA, Malato Rodríguez S (2014c) Removal of pharmaceuticals at microg L-1 by combined nanofiltration and mild solar photo-Fenton. Chem Eng J 239:68–74. https://doi.org/10.1016/j.cej.2013.10.047

Miranda-García N, Suárez S, Maldonado MI, Malato S, Sánchez B (2014) Regeneration approaches for TiO2 immobilized photocatalyst used in the elimination of emerging contaminants in water. Catal Today 230:27–34. https://doi.org/10.1016/j.cattod.2013.12.048

Miranda-García N, Suárez S, Sánchez B, Coronado JM, Malato S, Maldonado MI (2011) Photocatalytic degradation of emerging contaminants in municipal wastewater treatment plant effluents using immobilized TiO2 in a solar pilot plant. Appl Catal B Environ 103:294–301. https://doi.org/10.1016/j.apcatb.2011.01.030

Mohapatra DP, Brar SK, Tyagi RD, Picard P, Surampalli RY (2014) Analysis and advanced oxidation treatment of a persistent pharmaceutical compound in wastewater and wastewater sludge-carbamazepine. Sci Total Environ 470–471:58–75. https://doi.org/10.1016/J.SCITOTENV.2013.09.034

Moncada S, Gryglewski RJ, Bunting S, Vane JR (1976) A lipid peroxide inhibits the enzyme in blood vessel microsomes that generates from prostaglandin endoperoxides the substance (prostaglandin X) which prevents platelet aggregation. Prostaglandins 12:715–737. https://doi.org/10.1016/0090-6980(76)90048-4

Montagner CC, Jardim WF, Von der Ohe PC, Umbuzeiro GA (2014) Occurrence and potential risk of triclosan in freshwaters of São Paulo, Brazil—the need for regulatory actions. Environ Sci Pollut Res 21:1850–1858. https://doi.org/10.1007/s11356-013-2063-5

Munoz M, de Pedro ZM, Casas JA, Rodriguez JJ (2012) Triclosan breakdown by Fenton-like oxidation. Chem Eng J 198–199:275–281. https://doi.org/10.1016/j.cej.2012.05.097

Nakada N, Shinohara H, Murata A, Kiri K, Managaki S, Sato N, Takada H (2007) Removal of selected pharmaceuticals and personal care products (PPersonal care products s) and endocrine-disrupting chemicals (EDCs) during sand filtration and ozonation at a municipal sewage treatment plant. Water Res 41:4373–4382. https://doi.org/10.1016/j.watres.2007.06.038

Nakada N, Tanishima T, Shinohara H, Kiri K, Takada H (2006) Pharmaceutical chemicals and endocrine disrupters in municipal wastewater in Tokyo and their removal during activated sludge treatment. Water Res 40:3297–3303. https://doi.org/10.1016/J.WATRES.2006.06.039

Nanaboina V, Korshin GV (2010) Evolution of absorbance spectra of ozonated wastewater and its relationship with the degradation of trace-level organic species. Environ Sci Technol 44:6130–6137. https://doi.org/10.1021/es1005175

Nguyen LN, Hai FI, Kang J, Price WE, Nghiem LD (2013) Removal of emerging trace organic contaminants by MBR-based hybrid treatment processes. Int Biodeterior Biodegrad 85:474–482. https://doi.org/10.1016/j.ibiod.2013.03.014

Nolen GA, Dierckman TA (1979) Reproduction and teratogenic studies of a 2:1 mixture of 3,4,4-′-trichlorocarbanilide and 3-trifluoromethyl-4,4′-dichlorocarbanilide in rats and rabbits. Toxicol Appl Pharmacol 51:417–425. https://doi.org/10.1016/0041-008X(79)90366-1

O ‘connor N, Dargan PI, Jones AL (2003) Hepatocellular damage from non-steroidal anti-inflammatory drugs. Q J Med 96:787–791. https://doi.org/10.1093/qjmed/hcg138

Oller I, Malato S, Sánchez-Pérez JA (2011) Combination of advanced oxidation processes and biological treatments for wastewater decontamination—a review. Sci Total Environ 409:4141–4166. https://doi.org/10.1016/J.SCITOTENV.2010.08.061

Orvos DR, Versteeg DJ, Inauen J, Capdevielle M, Rothenstein A, Cunningham V (2002) Aquatic toxicity of triclosan. Environ Toxicol Chem 21:1338–1349. https://doi.org/10.1002/etc.5620210703

Paíga P, Santos LHMLM, Amorim CG, Araújo AN, Montenegro MCBSM, Pena A, Delerue-Matos C (2013) Pilot monitoring study of ibuprofen in surface waters of north of Portugal. Environ Sci Pollut Res 20:2410–2420. https://doi.org/10.1007/s11356-012-1128-1

Pemberton RM, Hart JP (1999) Electrochemical behaviour of triclosan at a screen-printed carbon electrode and its voltammetric determination in toothpaste and mouthrinse products. Anal Chim Acta 390:107–115. https://doi.org/10.1016/S0003-2670(99)00194-4

Peng J, Li J, Shi H, Wang Z, Gao S (2016) Oxidation of disinfectants with cl-substituted structure by a Fenton-like system Cu2+/hydrogen peroxide and analysis on their structure-reactivity relationship. Environ Sci Pollut Res 23:1898–1904. https://doi.org/10.1007/s11356-015-5454-y

Prieto-Rodriguez L, Miralles-Cuevas S, Oller I, Agüera A, Puma GL, Malato S (2012) Treatment of emerging contaminants in wastewater treatment plants (WWTP) effluents by solar photocatalysis using low TiO 2 concentrations. J Hazard Mater 211–212:131–137. https://doi.org/10.1016/j.jhazmat.2011.09.008

Pruden A, Pei R, Storteboom H, Carlson KH (2006) Antibiotic resistance genes as emerging contaminants: studies in northern Colorado. Environ Sci Technol 40:7445–7450. https://doi.org/10.1021/es060413l

Rafqah S, Wong-Wah-Chung P, Nelieu S, Einhorn J, Sarakha M (2006) Phototransformation of triclosan in the presence of TiO2 in aqueous suspension: mechanistic approach. Appl Catal B Environ 66:119–125. https://doi.org/10.1016/J.APCATB.2006.03.004

Raut SA, Angus RA (2010) Triclosan has endocrine-disrupting effects in male western mosquitofish, *Gambusia affinis*. Environ Toxicol Chem 29(6):1287–1291. https://doi.org/10.1002/etc.150

Rioja N, Benguria P, Peñas FJ, Zorita S (2014) Competitive removal of pharmaceuticals from environmental waters by adsorption and photocatalytic degradation. Environ Sci Pollut Res 21:11168–11177. https://doi.org/10.1007/s11356-014-2593-5

Rizzo L, Meric S, Guida M, Kassinos D, Belgiorno V (2009) Heterogenous photocatalytic degradation kinetics and detoxification of an urban wastewater treatment plant effluent contaminated with pharmaceuticals. Water Res 43:4070–4078. https://doi.org/10.1016/j.watres.2009.06.046

Rodríguez A, Muñoz I, Perdigón-Melón JA, Carbajo JB, Martínez MJ, Fernández-Alba AR, García-Calvo E, Rosal R (2012) Environmental optimization of continuous flow ozonation for urban wastewater reclamation. Sci Total Environ 437:68–75. https://doi.org/10.1016/j.scitotenv.2012.07.084

Rodríguez PEA, Sanchez MS (2010) Maternal exposure to triclosan impairs thyroid homeostasis and female pubertal development in wistar rat offspring. J Toxicol Environ Heal – Part A Curr 73(24):1678–1688. https://doi.org/10.1080/15287394.2010.516241

Rosal R, Rodríguez A, Perdigón-Melón JA, Mezcua M, Hernando MD, Letón P, García-Calvo E, Agüera A, Fernández-Alba AR (2008) Removal of pharmaceuticals and kinetics of mineralization by ozone/hydrogen peroxide in a biotreated municipal wastewater. Water Res 42:3719–3728. https://doi.org/10.1016/j.watres.2008.06.008

Rosal R, Rodríguez A, Perdigón-Melón JA, Petre A, García-Calvo E, Gómez MJ, Agüera A, Fernández-Alba AR (2010) Occurrence of emerging pollutants in urban wastewater and their removal through biological treatment followed by ozonation. Water Res 44:578–588. https://doi.org/10.1016/j.watres.2009.07.004

Saggioro EM, Oliveira AS, Pavesi T, Moreira JC (2014a) Effect of activated carbon and titanium dioxide on the remediation of an indigoid dye in model waters. Rev Chim 65(2)

Saggioro EM, Oliveira AS, Pavesi T, Tototzintle MJ, Maldonado MI, Correia FV, Moreira JC (2014b) Solar compound parabolic collector pilot plant photocatalytic degradation of bisphenol a in waters and wastewaters using suspended and supported-TiO2. Influence of photogenerated species. Environ Sci Pollut Res 21:12112–12121. https://doi.org/10.1007/s11356-014-2723-0

Sarkar S, Chakraborty S, Bhattacharjee C (2015) Photocatalytic degradation of pharmaceutical wastes by alginate supported TiO2 nanoparticles in packed bed photo reactor (PBPR). Ecotoxicol Environ Saf 121:263–270. https://doi.org/10.1016/j.ecoenv.2015.02.035

Schaar H, Clara M, Gans O, Kreuzinger N (2010) Micropollutant removal during biological wastewater treatment and a subsequent ozonation step. Environ Pollut 158:1399–1404. https://doi.org/10.1016/j.envpol.2009.12.038

Schwaiger J, Ferling H, Mallow U, Wintermayr H, Negele RD (2004) Toxic effects of the non-steroidal anti-inflammatory drug diclofenac: part I: histopathological alterations and bioaccumulation in rainbow trout. Aquat Toxicol 68:141–150. https://doi.org/10.1016/J.AQUATOX.2004.03.014

Shu Z, Bolton JR, Belosevic M, Gamal El Din M (2013) Photodegradation of emerging micropollutants using the medium-pressure ultraviolet/hydrogen peroxide advanced oxidation process. Water Res 47:2881–2889. https://doi.org/10.1016/j.watres.2013.02.045

Sichel C, Garcia C, Andre K (2011) Feasibility studies: ultraviolet/chlorine advanced oxidation treatment for the removal of emerging contaminants. Water Res 45:6371–6380. https://doi.org/10.1016/j.watres.2011.09.025

Singer H, Müller S, Tixier C, Pillonel L (2002) Triclosan: occurrence and fate of a widely used biocide in the aquatic environment: field measurements in wastewater treatment plants, surface waters, and lake sediments. Environ Sci Technol 36:4998–5004. https://doi.org/10.1021/es025750i

Son H-S, Khim J, Zoh K-D (2010) Degradation of triclosan in the combined reaction of Fe2+ and ultraviolet-C: comparison with the Fenton and photolytic reactions. Environ Prog Sustain Energy 29:415–420. https://doi.org/10.1002/ep.10422

Son HS, Ko G, Zoh KD (2009) Kinetics and mechanism of photolysis and TiO2 photocatalysis of triclosan. J Hazard Mater 166:954–960. https://doi.org/10.1016/j.jhazmat.2008.11.107

Son HS, Lee SJ, Cho IH, Zoh KD (2004) Kinetics and mechanism of TNT degradation in TiO2 photocatalysis. Chemosphere 57:309–317. https://doi.org/10.1016/j.chemosphere.2004.05.008

Song Z, Wang N, Zhu L, Huang A, Zhao X, Tang H (2012) Efficient oxidative degradation of triclosan by using an enhanced Fenton-like process. Chem Eng J 198–199:379–387. https://doi.org/10.1016/j.cej.2012.05.067

Stamatis N, Antonopoulou M, Hela D, Konstantinou I (2014) Photocatalytic degradation kinetics and mechanisms of antibacterial triclosan in aqueous TiO 2 suspensions under simulated solar irradiation. J Chem Technol Biotechnol 89:1145–1154. https://doi.org/10.1002/jctb.4387

Stülten D, Zühlke S, Lamshöft M, Spiteller M (2008) Occurrence of diclofenac and selected metabolites in sewage effluents. Sci Total Environ 405:310–316. https://doi.org/10.1016/J.SCITOTENV.2008.05.036

Suarez S, Dodd MC, Omil F, von Gunten U (2007) Kinetics of triclosan oxidation by aqueous ozone and consequent loss of antibacterial activity: relevance to municipal wastewater ozonation. Water Res 41:2481–2490. https://doi.org/10.1016/j.watres.2007.02.049

Sun SP, Zeng X, Lemley AT (2013) Nano-magnetite catalyzed heterogeneous Fenton-like degradation of emerging contaminants carbamazepine and ibuprofen in aqueous suspensions and montmorillonite clay slurries at neutral pH. J Mol Catal A Chem 371:94–103. https://doi.org/10.1016/j.molcata.2013.01.027

Ternes TA (1998) Occurrence of drugs in German sewage treatment plants and rivers. Water Res 32:3245–3260. https://doi.org/10.1016/S0043-1354(98)00099-2

Ternes TA, Joss A, Siegrist H (2004) Peer reviewed: scrutinizing pharmaceuticals and personal care products in wastewater treatment. Environ Sci Technol 38:392A–399A. https://doi.org/10.1021/es040639t

The Council of the European Communities (1976) Council directive: on pollution caused by certain dangerous substances discharged into the aquatic environment of the community. Off J Eur Community:23–29. https://doi.org/10.1039/ap9842100196

Tixier C, Singer HP, Oellers S, Müller SR (2003) Occurrence and fate of carbamazepine, clofibric acid, diclofenac, ibuprofen, ketoprofen, and naproxen in surface waters. Environ Sci Technol 37:1061–1068. https://doi.org/10.1021/es025834r

Tizaoui C, Grima N, Hilal N (2011) Degradation of the antimicrobial triclocarban (Triclocarban) with ozone. Chem Eng Process Process Intensif 50:637–643. https://doi.org/10.1016/j.cep.2011.03.007

Vieno NM, Härkki H, Tuhkanen T, Kronberg L (2007) Occurrence of pharmaceuticals in river water and their elimination in a pilot-scale drinking water treatment plant. Environ Sci Technol 41:5077–5084. https://doi.org/10.1021/es062720x

Wert EC, Gonzales S, Dong MM, Rosario-Ortiz FL (2011) Evaluation of enhanced coagulation pretreatment to improve ozone oxidation efficiency in wastewater. Water Res 45:5191–5199. https://doi.org/10.1016/j.watres.2011.07.021

Wert EC, Rosario-Ortiz FL, Snyder SA (2009) Effect of ozone exposure on the oxidation of trace organic contaminants in wastewater. Water Res 43:1005–1014. https://doi.org/10.1016/j.watres.2008.11.050

Wols BA, Hofman-Caris CHM, Harmsen DJH, Beerendonk EF (2013) Degradation of 40 selected pharmaceuticals by ultraviolet/hydrogen peroxide. Water Res 47:5876–5888. https://doi.org/10.1016/j.watres.2013.07.008

Wu Q, Shi H, Adams CD, Timmons T, Ma Y (2012) Oxidative removal of selected endocrine-disruptors and pharmaceuticals in drinking water treatment systems, and identification of degradation products of triclosan. Sci Total Environ 439:18–25. https://doi.org/10.1016/j.scitotenv.2012.08.090

Yang L-H, Ying G-G, Su H-C, Stauber JL, Adams MS, Binet MT (2008) Growth-inhibiting effects of 12 antibacterial agents and their mixtures on the freshwater microalga Pseudokirchneriella subcapitata. Environ Toxicol Chem 27:1201. https://doi.org/10.1897/07-471.1

Yang X, Sun J, Fu W, Shang C, Li Y, Chen Y, Gan W, Fang J (2016) PPersonal care products degradation by ultraviolet/chlorine treatment and its impact on DBP formation potential in real waters. Water Res 98:309–318. https://doi.org/10.1016/j.watres.2016.04.011

Yao W, Wang X, Yang H, Yu G, Deng S, Huang J, Wang B, Wang Y (2016) Removal of pharmaceuticals from secondary effluents by an electro-peroxone process. Water Res 88:826–835. https://doi.org/10.1016/j.watres.2015.11.024

Ying G-G, Kookana RS, Kolpin DW (2009) Occurrence and removal of pharmaceutically active compounds in sewage treatment plants with different technologies. J Environ Monit 11:1498. https://doi.org/10.1039/b904548a

Yu JC, Kwong TY, Luo Q, Cai Z (2006) Photocatalytic oxidation of triclosan. Chemosphere 65:390–399. https://doi.org/10.1016/j.chemosphere.2006.02.011

Zenker A, Cicero MR, Prestinaci F, Bottoni P, Carere M (2014) Bioaccumulation and biomagnification potential of pharmaceuticals with a focus to the aquatic environment. J Environ Manag 133:378–387. https://doi.org/10.1016/J.JENVMAN.2013.12.017

Zhang Y, Geißen S-U, Gal C (2008) Carbamazepine and diclofenac: removal in wastewater treatment plants and occurrence in water bodies. Chemosphere 73:1151–1161. https://doi.org/10.1016/J.CHEMOSPHERE.2008.07.086

Zhao J-L, Ying G-G, Liu Y-S, Chen F, Yang J-F, Wang L (2010) Occurrence and risks of triclosan and triclocarban in the Pearl River system, South China: from source to the receiving environment. J Hazard Mater 179:215–222. https://doi.org/10.1016/J.JHumicacidZMAT.2010.02.082

Zhao J-L, Zhang Q-Q, Chen F, Wang L, Ying G-G, Liu Y-S, Yang B, Zhou L-J, Liu S, Su H-C, Zhang R-Q (2013) Evaluation of triclosan and triclocarban at river basin scale using monitoring and modeling tools: implications for controlling of urban domestic sewage discharge. Water Res 47:395–405. https://doi.org/10.1016/J.WATRES.2012.10.022

Zimmermann SG, Wittenwiler M, Hollender J, Krauss M, Ort C, Siegrist H, von Gunten U (2011) Kinetic assessment and modeling of an ozonation step for full-scale municipal wastewater treatment: micropollutant oxidation, by-product formation and disinfection. Water Res 45:605–617. https://doi.org/10.1016/j.watres.2010.07.080

Ziylan A, Ince NH (2011) The occurrence and fate of anti-inflammatory and analgesic pharmaceuticals in sewage and fresh water: treatability by conventional and non-conventional processes. J Hazard Mater 187:24–36. https://doi.org/10.1016/j.jhazmat.2011.01.057

Chapter 11
Oily Wastewater Treatment

Mohd Hafiz Dzarfan Othman, Zhong Sheng Tai, Jamilu Usman, Nurul Jannah Ismail, Mukhlis A. Rahman, and Juhana Jaafar

Contents

M. H. D. Othman (✉) · Z. S. Tai · N. J. Ismail · M. A. Rahman · J. Jaafar
Advanced Membrane Technology Research Centre (AMTEC), School of Chemical and Energy Engineering, Faculty of Engineering, Universiti Teknologi Malaysia, Johor Bahru, Johor, Malaysia
e-mail: hafiz@petroleum.utm.my; mukhlis@petroleum.utm.my; juhana@petroleum.utm.my

J. Usman
Advanced Membrane Technology Research Centre (AMTEC), School of Chemical and Energy Engineering, Faculty of Engineering, Universiti Teknologi Malaysia, Johor Bahru, Johor, Malaysia

Department of Chemistry, Faculty of Science, Sokoto State University, Sokoto, Sokoto State, Nigeria

Inamuddin et al. (eds.), *Water Pollution and Remediation: Organic Pollutants*, Environmental Chemistry for a Sustainable World 54,
https://doi.org/10.1007/978-3-030-52395-4_11

Abstract Oily wastewater is generally generated from the industries that are primarily engaged in the refining of crude oil, processing of food, transportation, and extraction. The hazardous nature of the oily wastewater poses serious threats to the environment and human health if it is disposed to the environment without proper treatment. Most of the countries around the world have their distinguished wastewater discharge standards. Therefore, efficient oily wastewater treatment is utterly important to improve the quality of the wastewater according to the wastewater discharge standards before releasing it into the water streams.

In this chapter, we review the conventional and advanced technologies for the treatment of oily wastewater. The major points are the following: (1) There are several conventional oily wastewater treatments, such as flotation, coagulation, and biological treatments. Among these three methods, biological treatment is the least popular method for the oily wastewater treatment due to high difficulty in handling the diverse microbe behaviors under different environmental conditions. (2) Membrane technologies, such as microfiltration, ultrafiltration, nanofiltration, and reverse osmosis, are gaining significant attention due to high emulsion separation efficiency with the minimum use of chemicals, as well as the easy and low-cost operation. However, nanofiltration and reverse osmosis are not well received due to relatively low flux and high energy consumption. (3) Electrochemical treatment is arguably the most effective technique for oily wastewater treatment due to the energy saving process, robust performance, versatility, and simple process control kinetics. This treatment can achieve excellent removal of oil and grease, chemical oxygen demand, and turbidity of more than 90%. (4) The integration of various technologies has become an interest of studies for the improvement of oily wastewater treatment. These hybrid technologies have shown enhanced treatment performances than the treatment with a single technology.

Keywords Oily wastewater · Conventional wastewater treatment · Membrane filtration · Electrochemical treatment · Hybrid technology

11.1 Introduction

Oil and grease have become an ever-growing environmental concern. It creates significant coercions to the environment and human being due to the hazardous nature of these contaminants (Karhu et al. 2013). Oil and grease are important in most industries as they are made up of triglycerides with straight-chain fatty acids attached to the main group (Wakelin and Forster 1997). The glycerides which exist as a liquid at room temperature are known as oils, whereas those that exist as solids are called fats (Sawyer et al. 2003). Generally, these common fatty acids are made up of 12–22 carbon atoms. According to Sawyer et al. (2003), the principal acid composing glycerides are listed in Table 11.1. They are nonpolar and hydrophobic

Table 11.1 List of fatty acids and oils

Name	Formula	Melting point (°C)	Source
Arachidic	$C_{20}H_{40}O_2$	76.5	Peanut oil
Behenic	$C_{22}H_{44}O_2$	81.5	Ben oil
Butyric	C_3H_7COOH	−5.7	Butter
Caproic	$C_5H_{11}COOH$	−3	Butter, coconut oil
Caprylic	$C_7H_{15}COOH$	16.3	Palm oil, butter
Erucic	$C_{22}H_{42}O_2$	34.7	Rape oil, mustard oil
Lauric	$C_{11}H_{23}COOH$	43.2	Coconut oil, spermaceti
Linoleic	$C_{18}H_{32}O_2$	−12	Cottonseed oil
Linolenic	$C_{18}H_{30}O_2$	−11	Linseed oil
Myristic	$C_{13}H_{27}COOH$	53.9	Nutmeg, coconut oil
Oleic	$C_{18}H_{34}O_2$	13.4	Animal & vegetable fats, oils
Palmitic	$C_{15}H_{31}COOH$	63.1	Palm oil, animal fats
Stearic	$C_{17}H_{35}COOH$	69.6	Animal & vegetable fats, oils

From Sawyer et al. (2003)

Table 11.2 Types of oils according to Alther (2002)

Category	Description
Animal oil	Fixed oil or fatty acids which exist as solid at room temperature
Essential oil	Derived from parts of plant and it is volatile and complex
Mineral oil	Flammable, viscous, and insoluble in water but soluble in alcohol
Petroleum products	Consist of solid, liquid, and gaseous components in which their viscosity depends on the mixture composition
Vegetable oil	Extracted from several parts of plant, specifically kernels.

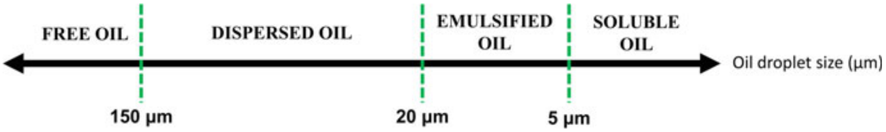


Fig. 11.1 Classification of oil droplets according to sizes. Free oil has the largest droplet size of >150 μm, followed by the dispersed oil with the droplet size ranging from 20–150 μm. Emulsified oil exhibits the droplet size of 5–20 μm, whereas the soluble oil has the smallest droplet size of <5 μm

in nature which can be extracted by certain solvents (Gunstone 2004). On the other hand, oils can be defined as the mixture of high molecular weight naphthene, aromatic hydrocarbon, asphaltene, or paraffins (Alade et al. 2011). There are five categories of oils as tabulated in Table 11.2.

Oily wastewater is a waste emulsion in which the oil droplets disperse uniformly in an aqueous phase. There are four classifications of the oil–water mixture as illustrated in Fig. 11.1. Oil–water mixture with droplet diameters >150 μm is classified as free oil. This type of oil appears on the water surface rapidly due to the larger droplet size. The free oil can be removed using the American Petroleum

Table 11.3 General oil and grease concentration existing in water bodies

Source of wastewater	Oil and grease concentration (mg/L)	References
Poultry slaughterhouse	1500–1800	Kobya et al. (2006)
Palm oil mill	4000–6000	Ahmad et al. (2005)
Food processing industry	3000	Sugimori (2009)
Pet food industry	51,000–114,000	Jeganathan et al. (2006)
Vegetable oil processing	5000–10,000	Chen et al. (2000)
Metallurgic industry	1080–3271	Zhu et al. (1997)

Institute separator. The American Petroleum Institute separator is a gravity separation device specifically designed using Stokes' Law principle. This device works based on the specific gravity difference between the oil and wastewater. The design of the American Petroleum Institute separator follows exactly the standards published by American Petroleum Institute. Dispersed oil has oil droplet sizes ranging between 20 and 150 μm. Under this category, the oils are stable in terms of electrostatic without any influence of emulsifying agents. These oils can be removed using the flotation method. Emulsified oil mixture has the oil droplet sizes smaller than 20 μm. This oil mixture is chemically stable in the presence of the emulsifying agent. Besides, an oil–water mixture with the droplet sizes smaller than 5 μm is categorized as a soluble oil mixture. The soluble oil mixtures are commonly referred as the light end of the spectrum of compounds, such as xylene and toluene (Mohammed and Al-Gurany 2010). Due to the tiny size, the soluble oil can be effectively removed by carbon membrane filtration or adsorption.

The presence of oily wastewater can be sketched back to the municipal and industrial sources. This contaminated water is produced from a broad array of industries, such as oil processing, mechanical, textile, maritime transport, petrochemical and metallurgic industries (Ibrahim et al. 2009). On top of that, municipal sources such as oil-used food preparation, disposal of oil-contaminated garbage and oil-contaminated cleaning also contribute to the generation of the oily wastewater (Chen et al. 2000). The common constituents of the oily wastewater are lubricants, cutting fluids, light hydrocarbon such as kerosene and gasoline, heavy hydrocarbon, crude oil, as well as grease. The concentration of the contaminants and oil droplet size are generally affected by the agitation of the wastewater. Table 11.3 shows the range of oil and grease wastewater concentration released to the water bodies from various sources. The major source of the oil and grease released from the metallurgic industry comes from the metal working operation as oils are commonly used as coolant liquid to cool down the equipment and machineries, as well as for lubricating purposes and dissipate heats during metal strip rolling (Zhu et al. 1997). Oil and grease concentration from vegetable oil processing was reported up to 10,000 mg/L, and most of these effluents came from the cleaning, screening, and crushing of raw materials during extraction (Chen et al. 2000). Pet food manufacturing is also among the industries that release a high concentration of oil and grease with very high chemical oxygen demand (Jeganathan et al. 2006).

Table 11.4 General characteristics of oily wastewater. (Adapted from Greenberg et al. 2005)

Parameters	Description
Temperature	A crucial parameter that affects the chemical reaction rates of the treatment
Solid compound	Solid particles are of various forms and are classified based on the size, chemical properties, and distribution in the wastewater
Biochemical oxygen demand	The amount of oxygen required for the aerobic biological organisms to decompose the organic materials
Chemical oxygen demand	Chemical decay of the dissolved or suspended organic and inorganic pollutants in the water
Turbidity	Water clarity level that affects the optical property of the water. The turbidity is influenced by the availability of the suspended and colloidal substances.
Oil and grease content	Amount of fats, oils, and greases in the water that interferes in aerobic and anaerobic activities, as well as decreases the wastewater treatment effectiveness
Total organic carbon	Compounds containing carbon atoms that involve in dissolving organic pollutants such as hydrocarbons
Metal compounds	Heavy metal compounds, such as cadmium, ferric, and lead which are hazardous to the ecosystem

World water bodies are increasingly polluted by oily water from year to year. The acute toxic effects of oily water pollution can be irreversible for the aquatic living organisms. The consequences of these effects can be transmitted to human beings directly or indirectly as they have direct involvement in the food chain of the ecosystem (Tansel and Pascual 2011). Although the compositions of the oily wastewater vary in terms of types and amounts of hazardous components, the presence of emulsified oil and grease is often recalcitrant and complicated to be treated. The impacts of the oily wastewater to the environment in several aspects are described in Table 11.4. Oil and grease in water bodies specifically on the water surface result in oil layer formation, which consequently leads to serious pollution issues, such as the reduction of light penetration and photosynthesis. Furthermore, the oil layer also inhibits the transfer of oxygen from the atmosphere to the water medium, which then decreases the amount of dissolved oxygen at the bottom of the water. As a result, it afflicts the survival rate and mortality of the aquatic life in water. Stams and Oude (1997) reported that the presence of oil and grease would increase the maintenance cost due to the physical blockage. Since oil is highly flammable, there will be a potential explosion hazard during the treatment process (El-Bestawy 2005). Excessive grease in the wastewater stream can also cause difficulties in the sludge pressing because of the “blinding effect” on the filter cloths (Stams and Oude 1997). Furthermore, oil and grease affect the aerobic biological wastewater treatment processes by reducing the oxygen transfer rates. Similarly, oil and grease reduce the efficacy of anaerobic treatment processes by reducing the transport of the soluble substrates to the bacterial biomass (Rinzema et al. 1994). Likewise, oil and grease can be a source of objectionable taste and odors, turbidity, and film, which makes filtration treatment difficult, especially at municipal water treatment plants.

Most of the countries around the world have their own environmental standards. The standard of effluents discharge can be defined as the concentration limits of the specific contaminant that is permissible to be directly discharged into the water stream. With this standard, enforcement control is much easier to be conducted and early prevention of water pollution can be achieved. The permissible oil and grease discharge concentration varies in different countries. For instance, in Unites States of America, the maximum limits of oil and grease discharge are 42 mg/L day and 29 mg/L month (Fakhru'l-Razi et al. 2009), whereby the Malaysian Department of Environment sets the maximum limit of oil and grease discharge at 1 mg/L for standard A (the effluent discharger at the upstream of water supply intake) and 10 mg/L for standard B (the effluent discharged at the downstream of water supply intake) (Environmental Quality Act and Regulations Handbook 2009). The standard limits may also vary based on the types of industry. For example, Indonesia has set its discharge standards based on the type of industry, in which the limits are 5 mg/L, 25 mg/L, and 30 mg/L for leather tanning and textiles, oil refining and urea fertilizer, and palm oil industries, respectively. On the other hand, Singapore has set the standard limits based on water use in which the limits vary from 5 to 30 mg/L (Tong et al. 1999).

11.2 Conventional Oily Wastewater Treatment Methods

11.2.1 Flotation Treatment

Flotation treatment is a process of removing the suspended oil particles from the wastewater by bringing the oil particles to the surface of the aqueous medium. The froth layer containing the oil particles forms on the surface of the aqueous medium which will then be skimmed and separated from the aqueous medium. The use of flotation in oily wastewater treatment have been attracting much attention owing to the high separation efficiency, availability of the flotation equipment with large processing capacity, and low sludge generation (Rubio et al. 2002; Yu et al. 2017). In addition, the flotation treatment also requires low capital investment and operational costs (Li et al. 2007).

Dissolved Air Flotation

Dissolved air flotation is the most commonly used flotation technique for the industrial oily wastewater treatment (Yu et al. 2017; Zouboulis and Avranas 2000). In this technique, the tiny air bubbles are injected into the wastewater containing oil particles in which the air bubbles attach to the oil droplets. The adhesion of air bubbles increases the buoyancy of the oil particles, and consequently leads to the rapid movement of the oil particles to the surface of the aqueous wastewater. Dissolved air flotation is effective in removing oil droplets with the size greater than 40 μm (Zouboulis and Avranas 2000). There are three basic configurations for the dissolved air flotation process, namely (Shammas and Wang 2016):

(a) Full flow pressurization system, where the entire wastewater feed stream is pressurized before introducing to the flotation tank. This system is commonly used for the feed streams with a high suspended solid concentration of >800 mg/L and those require large volumes of air bubbles.
(b) Partial flow pressurization system, where only about 30–50% of the wastewater feed stream is pressurized and directly introduced to the flotation tank. This system is suitable to be employed in the applications with low suspended solid concentrations that have low air requirement.
(c) Recycle flow pressurization system, where 15–50% of the treated wastewater is pressurized, recycled and mixed with the raw wastewater feed. This system is more frequently used compared to the other two configurations in the oil treatment applications where coagulation and flocculation are necessary ahead of the flotation process (Al-Shamrani et al. 2002; Zouboulis and Avranas 2000).

The efficiency of the dissolved air flotation is closely related to the capturing of particles by the rising bubbles. Hence, it is known that the production of air bubbles with small sizes is particularly important for the dissolved air flotation process. Microbubbles, which are generally defined as the bubbles with the diameter of less than 50 μm, has attracted considerable interest as they have lower rising velocity which provides a longer residence time in the flotation tank, and large interfacial area (Zheng et al. 2015; Agarwal et al. 2011). These characteristics allow greater chances for the bubble-particle collisions and consequently leads to high particle capturing efficiency. The bubble size can be affected by the saturator pressure. For instance, Shannon and Buisson (1980) reported an average bubble size of 66 μm at the pressure of 210 kPa, whereas it was 42 μm at 350 kPa.

Air/solid ratio is another important parameter to be considered in the design and operation of the flotation system. In the oily wastewater treatment system, the air/solid ratio is defined as the mass of air precipitated per unit mass of wastewater solids (oil particles in this case). The air/solid ratio governs the rising rate of the bubble-particle agglomerates in the dissolved air flotation system (Bratby and Marais 1975; Wang et al. 2010). The efficiency of the oil removal of the air flotation system would be afflicted if the air employed is less than the optimum amount. On the other hand, power would be wasted if too much is employed. Hence, the optimization of the air/solid ratio is utterly important in designing the dissolved air flotation system.

The recycle ratio has significant influence over the air/solid ratio (Bratby and Marais 1975; Wang et al. 2010). The mixing of the pressurized recycle flow with the wastewater feed changes the concentration of the supplied air bubbles and affects the bubble-particle collisions (Al-Shamrani et al. 2002). This consequently affects the removal of the bubble-particle agglomerates. In addition, some other design variables such as rising velocity of the particle, hydraulic design of the flotation chamber, type, and concentration of the dissolved materials, suspended matter and oils, surface properties of the suspended matter, degree of bubble dispersion, type of chemicals added, temperature, and pH should also be considered when designing a flotation system for effective oily wastewater treatment (Bennett and Peters 1988; Edzwald et al. 1992).

Dissolved air flotation have shown its outstanding efficiency in oily wastewater treatment with the oil removal performance of up to 95% (Rattanapan et al. 2011; da Rocha e Silva et al. 2015). Several patents on the dissolved air flotation systems for oily wastewater treatment have been filed since the last decade. The improvement trends of the dissolved air flotation systems are towards three main areas, namely (a) the reduction of the treated fluid aeration time, (b) the improvement of the uniformity of the released gas stage distribution, and (c) the integration of the dissolved air flotation with other purification processes (Eskin et al. 2015). Several patents have claimed to have reduced the aeration time through the introduction of pressure vessels with enhanced efficiencies (BKT Co. Ltd and I SAN Co. Ltd 2008; Akim et al. 2010). To improve the uniformity of the released gas stage distribution, some improvement designs such as flotation cells with diamond or cone-shaped guides, ring aerator and propeller blade have been implemented to evenly distribute the saturated fluid (Patrick 2008; Friedman et al. 2006; K-pack Korea Co. Ltd 2008). In addition, the combination of the dissolved air flotation process with thin layer sedimentation, ozonation, and filtration has also been introduced to enhance the efficiency of the oily wastewater treatment (Woodley and Foong 2002; Crowell 2008).

Induced Air Flotation

Induced air flotation is another flotation mode for the oily wastewater separation in which the bubbles are mechanically formed using a high-speed mechanical impeller and an air injection system. The induced air bubbles normally exhibit the diameters in the range of 1000 μm (Moosai and Dawe 2003). This flotation technique has low retention time and can be as low as 4 min which allows small footprint (Moosai and Dawe 2003). Besides, some researchers also suggested that the use of larger bubble size also allows more compact flotation systems (Jameson 1999; Yan and Jameson 2004). In addition, induced air flotation can achieve the airflow rates of 100% in the wastewater stream, whereas the amount of air supplied is typically about 5.6% for dissolved air flotation. However, in practice, the high shear rate in the conventional mechanical flotation cells tends to result in the breakage of fragile flocs and the redispersion of particles before flotation can occur (Jameson 1999; Zabel 1992). Besides, the large bubble size could also lead to poor bubble-particle collision efficiency, and consequently results in the low separation performance (Li and Tsuge 2006). Hence, this flotation mode is not as favorable as dissolved air flotation in the oily wastewater applications.

Electro-Flotation

Electro-flotation involves the electrolysis of water that produces hydrogen and oxygen gas bubbles at both electrodes. The chemical reactions occurring in the electro-flotation process are shown as follows (Eqs. 11.1, 11.2 and 11.3):

Anode:

$$2H_2O\ (l) \rightarrow 4H^+ + O_2(g) + 4e^- \tag{11.1}$$

Cathode:

$$4e^- + 4H_2O\ (l) \rightarrow 2H_2(g) + 4OH^- \tag{11.2}$$

Overall reaction:

$$2H_2O\ (l) \rightarrow 2H_2(g) + O_2(g) \tag{11.3}$$

where H_2O (l), H_2 (g), and O_2 (g) are water, hydrogen gas, and oxygen gas, respectively. The hydrogen ion, hydroxide ion, and electron are denoted as H^+, OH^-, and e^-, respectively in the equations above.

The gas bubbles formed at the electrode attach to the oil particles and subsequently rise to the surface where the oil is removed through skimming. Electro-flotation demonstrates several strengths, such as (a) excellent oil removal efficiency of up to 90%, (b) the gas bubbles have uniform and small diameters of 100 μm which increases the surface area of contact between the oil particles and gas bubbles, (c) small and compact units that require low maintenance and operating costs, and (d) the rate of bubble generation can be controlled easily through the manipulation of current density (Eskin et al. 2015; Mansour and Chalbi 2006; Rubio et al. 2002; Wang et al. 2010). However, this flotation technique suffers from low throughput, emission of hydrogen gas bubbles, and high electrode costs (Rubio et al. 2002).

Other Flotation Techniques

Several other types of flotation techniques have also been reported for the oily wastewater treatment which include jet and column flotations. Jet flotation has shown its potential for the oily wastewater treatment due to the small air bubbles production, high throughput, moderate equipment and maintenance costs as it does not have moving parts, and easy installation (Yu et al. 2017; Rubio et al. 2002). Santander et al. (2011) set up a modified jet (Jameson) cell in an offshore platform. The device demonstrated a high oil removal efficiency of around 81% at a high throughput rate of 24.7 $m^3/h\ m^2$. The results indicate the great prospects of utilizing jet flotation in the oily wastewater treatment applications.

Column flotation is also another flotation mode that has attracted the interest for the oily wastewater treatment applications. Today, several flotation column devices have been developed for quick and high oil separation efficiency. For instance, Gu and Chiang (1999) developed a multistage loop-flow flotation column which greatly improved the contact between the oil particles and gas bubbles, resulting in excellent efficiencies of 90–93% for continuous operation with the feed rates of 1–3.8 L/min. The multistage flotation column developed by Xiao et al. (2002) with air dispersed at the bottom of the tray column showed the oil separation efficiencies reaching 94%. In addition, Li et al. (2007) reported a new type of flotation device which combined the dissolved air flotation with column flotation. This device has also shown its ability for effective oily wastewater treatment with the oil removal efficiency of more than 90%.

11.2.2 Coagulation Treatment

Coagulation is widely used in the oily wastewater treatment due to its capability to remove emulsified and dissolved oils, as well as some difficult biodegradable organic polymer (Yu et al. 2017). This technique utilizes the coagulants to destabilize the colloids through the neutralization of the repulsive forces between the fine colloids. The basic illustration of the coagulation process is as shown in Fig. 11.2. It is known that coagulation is usually coupled with the flocculation process to agglomerate the fine colloids into larger particles. Generally, this process consists of two stages, which are (a) rapid mixing to well disperse the coagulant in the wastewater and (b) gentle agitation after adding flocculant for the agglomeration of the fine colloids into larger flocs.

The coagulation technique has several advantages such as low energy consumption, simple design, easy operation as well as versatility (Wan Ikhsan et al. 2017). However, the coagulation technique also suffers from several weaknesses such as involvement of a large amount of coagulant, corrosion issues associated with the reduced pH, as well as the problems related to the generated sludge (Li et al. 2015).

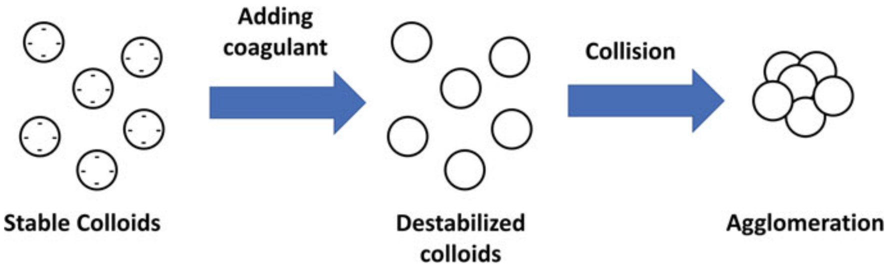


Fig. 11.2 Basic mechanism of coagulation process (Modified after Wan Ikhsan et al. 2017). The colloids are destabilized after adding coagulant, followed by the addition of flocculant to agglomerate the fine colloids into larger flocs

Table 11.5 Types of coagulant for oily wastewater treatment

Types of coagulant	Performance	References
Poly-zinc silicate	Oil removal of >99% with suspended solid value of <5 mg/L	Zeng et al. (2007)
Polyaluminum chloride	Oil removal of 95.3% with chemical oxygen demand, total organic carbon, suspended solid and color removal efficiency of 90.1%, 89.4%, 99.0%, and 99.9%, respectively	Zhai et al. (2017)
Polyferric sulphate	Oil removal of 98.9% with chemical oxygen demand, total organic carbon, suspended solid and color removal efficiency of 86.1%, 86.1%, 99.0%, and 98.2%, respectively	Zhai et al. (2017)
Polyferricsilicate sulphate	Oil and chemical oxygen demand removal of 95–97% and > 60%, respectively	Li et al. (2009)
Chitosan	>95% of suspended solid and residue oil removals	Ahmad et al. (2006)

There are several mechanisms involved in a coagulation process such as ionic layer compression, adsorption and charge neutralization, inter-particle bridging, and sweep coagulation (Menezes et al. 1996). These mechanisms are crucial for the formation of large flocs of residue oil and suspended solids which would easily settle down and be removed. The mechanisms of the coagulation process are greatly influenced by the selection and dosage of coagulant, as well as the characteristics of the oily wastewater. Table 11.5 demonstrates the types of coagulant that have been used for the oily wastewater treatment. It should also be noted that the dosage of coagulant could significantly affect the effectiveness of the coagulation process in treating the oily wastewater. Coagulant overdose could lead to the re-stabilization of the particles, which would affect the residual oil and suspended solid removal efficiencies. In addition, the coagulant overdose would also increase the coagulant residues concentration in the treated wastewater and raise another concern on the toxicity of the coagulant.

11.2.3 Biological Treatment

In biological treatment, microorganisms are used for the treatment of the oily wastewater. The colloidal organic pollutants are degraded into harmless substances such as carbon dioxide and other gases, inorganic substances, water, as well as biomass through the microbial metabolisms (Eweis et al. 1998; Kriipsalu et al. 2007). Biological treatment of the oily wastewater can be conducted through the aerobic and anaerobic mechanisms. In aerobic process, air or oxygen is supplied to support the aerobic microorganisms in stabilizing the organic content of the wastewater through the decomposition of the organic matter. However, this process is very energy-consuming. On the other hand, in the anaerobic process, the microorganisms break down the pollutant into simpler compounds in the absence of oxygen through four basic phenomena, which are hydrolysis, acidogenesis, acetogenesis, and methanogenesis. This process produces a high content of methane as a side product and can be used as fuel.

Activated sludge and biological filter methods have been the most commonly used biological treatment for the oily wastewater treatment applications (Yu et al. 2017). Activated sludge is an aerobic process whereby the oil particles and other organic matters are adsorbed on the surface of the microorganisms in which the organic matters will be decomposed. While in the biological filter method, the microorganisms are attached to the filter surface. The wastewater flows through the filter surface and the adsorption of organic pollutants occurs. The adsorbed organic matters are then decomposed into simpler compounds by the microorganisms. These biological methods are usually employed as a secondary treatment after the wastewater pretreatment process (Kulkarni 2016; Wan Ikhsan et al. 2017). In most cases, a consortium of microorganisms is used in removing hazardous pollutants in oily wastewater. The synergistic interactions among different microorganisms in the consortium may lead to the complete decomposition of the organic matters, hence it is more advantageous compared to pure bacterial culture (Cerqueira et al. 2011). Song et al. (2011) treated oily wastewater by combining a whole-cell lipase together with fungal lipase and a *Yarrowia lipolytica*. The results showed that 97.6% of chemical oxygen demand and 96.9% of the oil were successfully removed after 72 h of treatment. Nevertheless, lower chemical oxygen demand and oil removals of 91.8% and 87.1%, respectively were observed when only *Yarrowia lipolytica* was applied. Meanwhile, 45.1% and 67.5% of oil and chemical oxygen demand were respectively removed from the control system when no cell was added. Another study by Cerqueira et al. (2011) also reported that the bacterial consortium of *Stenotrophomonas acidaminiphila*, *Bacillus megaterium*, *Bacillus cibi*, *Pseudomonas aeruginosa*, and *Bacillus cereus* demonstrated an excellent oily sludge degradation capacity with the aliphatic and aromatic fractions degradation efficiencies of 90.7% and 51.8%, respectively, compared to the pure bacterial cultures.

However, the biological treatment is not practically well embraced in the oily wastewater treatment due to high difficulty in handling the diverse microbe behaviors under different environmental conditions. Yet, recent research in this area has yielded remarkable contaminant removal rates from oily wastewater. Khondee et al. (2012) investigated the treatment of lubricants in wastewater by using an internal loop airlift bioreactor containing chitosan immobilized-*Sphingobium* sp. The chitosan immobilized bacteria demonstrated high efficiency in removing the automotive oils from both synthetic and carwash wastewaters. In fact, the semi-continuous test showed 80–90% of the hydrocarbons was successfully removed from both synthetic and carwash wastewaters. Moreover, 85% of the petroleum hydrocarbons and 73% of the chemical oxygen demand were removed from the carwash wastewater using an airlift bioreactor via the internal loop bioreactor containing 4 g/L immobilized bacteria. Xie et al. (2007) applied a biological aerated filter for the treatment of polluted oily wastewater at the optimum operating conditions with the flow volume ratio of air to water of 5:1, 1 h cycle time and with backwash cycling of 4–7 days. The outcomes showed the average chemical oxygen demand, oil, and suspended solids removal efficiencies of 84.5%, 94%, and 83.4%, respectively. Santo et al. (2013) used activated sludge biological treatment technique to treat the petroleum refinery wastewater with the total carbon, chemical oxygen demand, and suspended solids removals of 85–87%, 94–95%, and 98–99%, respectively. The pseudo first-order reaction kinetic model was used to portray the rate of oil degradation with the rate constant (k) values of 0.055 and 0.059 L/mg VSS day for the treatment with and without the sludge recovering, respectively.

11.3 Membrane Filtration

Recently, membrane filtration technology has received tremendous attention for effective oily wastewater separation. The high emulsion separation efficiency, no phase change operation involving minimum use of chemicals, as well as the easy and low-cost operation have made this technology particularly attractive (Arnot et al. 2000; Dickhout et al. 2017). Generally, the membrane technology used for the oily wastewater treatment is driven by pressure. In the conventional membrane separation process, the oil-contaminated feed solution is pushed towards the membrane by pressure. The membrane pore size will act as a selective barrier which allows the smaller particles and solution to pass through, while the larger-sized oil particles will be blocked and retained at the feed compartment. In general, microfiltration, ultrafiltration, nanofiltration, and reverse osmosis are the major types of membrane technologies for oily wastewater treatment.

11.3.1 Microfiltration

Microfiltration is a separation process which involves the sieving effects by a series of well-defined membrane pore size. Typically, the microfiltration membranes have the pore size of 0.1–10 μm. The microfiltration membranes are commonly fabricated from a wide range of polymers, such as cellulose nitrate, polyamide, polyacrylonitrile, polyvinyl alcohol, polyamide, and polysulfone. It should be noted that the membranes should have great tolerance towards chemicals and temperatures. Hence, the development of ceramic microfiltration membranes from alumina, kaolin, zeolite, and fly ash has also been vibrantly growing in recent years.

Microfiltration process is generally used to separate insoluble suspended particles, yeast cell, broth, bacteria, and colloids from aqueous streams. Since the microfiltration membranes exhibit large pore size, the solution is usually transported through the membrane pores via convection. The rate of the passage of the solution through the pores is directly proportional to the pressure difference across the membrane, assuming the membrane pores are in the cylindrical dimension. In other words, the microfiltration process is driven by the pressure gradient across the membrane pores, which can be in the range of 50–200 kPa (Winston and Sirkar

1992). Microfiltration exhibits higher permeate flux compared to that of ultrafiltration, reverse osmosis, and nanofiltration due to the larger membrane pore size. The separation occurs when the solution with smaller size passes through the membrane pores, whereas the larger unwanted particles are refrained from passing through. It is worth to mention that the entire microfiltration process greatly depends on the types of the membrane used and the interactions of the solution composition with the membrane (Cheryan 1998).

There are two types of operation modes for the microfiltration process, namely (1) dead-end filtration channel and (2) crossflow filtration channel. In the dead-end filtration mode, the feed flows perpendicularly towards the membrane surface as depicted in Fig. 11.3a. The transport of permeate solution across the membrane pores is induced by the transmembrane pressure. However, the permeate flux would drastically decrease after the prolonged separation operations due to fouling. A layer of foulant forms on the membrane surface facing the feed solution which intervenes the passage of the solution across the membrane pores. Hence, constant interruption of the filtration process would be needed to remove the foulant layer or replace the membranes (Scott 1995). In this regard, the crossflow filtration channel appears to be a viable option to circumvent this challenge. In the crossflow microfiltration configuration, the feed solution flows in parallel with the membrane surface as illustrated in Fig. 11.3b. This leads to greater shear force to the membrane surface that reduces the concentration polarization effects. As the result, higher flux can be acquired. The most common type of module used for the dead-end configuration is the frame and plate modules, whereas tubular and hollow fiber modules are particularly favorable for the cross-flow configuration (Oyama and Stagg-Williams 2011; Meyer et al. 2015).

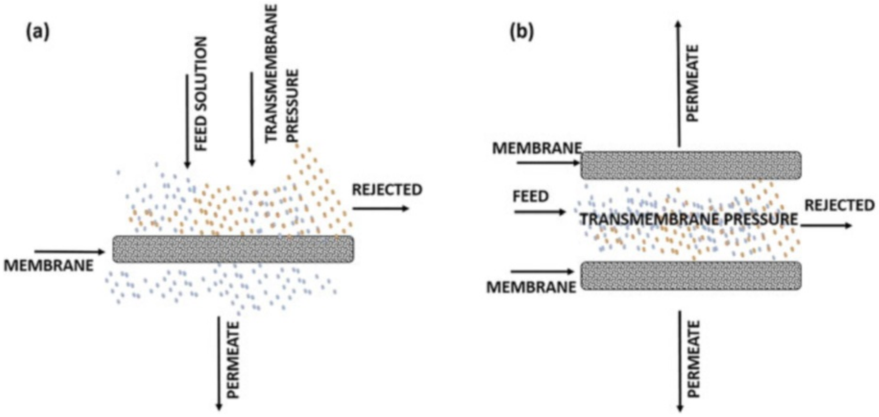


Fig. 11.3 Membrane filtration configurations, as such (**a**) is the dead-end channel and (**b**) is the crossflow channel. (Modified after Gitis and Rothenberg 2016). In the dead-end filtration channel, the feed solution flows perpendicularly to the membrane surface. Meanwhile, the feed solution flows parallelly along the membrane surface in the crossflow filtration channel

The development of microfiltration membranes for oily wastewater treatment has been widely reported. In 1997, Mueller et al. (1997) studied about the crossflow microfiltration of oily water using two α-alumina membranes with the pore sizes of 0.2–0.8 μm and a surface modified polyacrylonitrile membrane with a pore size of 0.1 μm. All the microfiltration membranes showed the oil removal efficiencies of above 98%. The membranes were cleaned using strong acid, base, and detergent after the microfiltration process. However, none of these chemicals were effective in removing the membrane foulants. Moreover, the fouling mechanism modeling showed that internal and external fouling occurred in both α-alumina membranes. Zhong et al. (2003) developed a zirconia microfiltration membrane for the oily wastewater treatment. The membrane successfully reduced the oil concentration of the wastewater from 200 to 8.7 mg/L, which satisfied the wastewater discharge standard of Chinese national. Ebrahimi et al. (2010) studied the performance of alumina microfiltration membrane in the oily wastewater treatment. Prior to the microfiltration process, the wastewater was pretreated via ultrafiltration. The microfiltration membrane demonstrated the oil and total organic carbon removals of 61.4–38.6%, respectively. Furthermore, the microfiltration membrane also showed a permeability of 715 L/m^2 h bar with an oil recovery of 61%.

11.3.2 Ultrafiltration

The membranes employed in the ultrafiltration process exhibit the pore sizes ranging from 1 to 500 nm and can retain solutes with the molecular weight of 300–500,000 Da at the operating pressure of 100–700 kPa. The rejection properties of the ultrafiltration membrane are determined by the molecular weight cutoff. Molecular weight cutoff refers to the lowest molecular weight of solute in which 90% of the solutes is retained by the membrane. The molecular weight cutoff leads to a clear understanding regarding the real efficiency of the rejection phenomenon of the membrane. Ultrafiltration membranes can reject various types of proteins, trypsins, and bovine serum albumin. Some of the other molecules that can be separated via the ultrafiltration processes are polymers, sugar, colloidal particles, biomolecules, colors, odor, and viruses (Winston and Sirkar 1992; Scott 1995). Ultrafiltration has the same modes of operation as those in the microfiltration, which include dead-end and crossflow filtration channels (Fig. 11.3a, b).

Various types of ultrafiltration membranes have been studied for the oily wastewater treatment. For instance, Li et al. (2006) modified the polyvinylidene fluoride ultrafiltration membrane with nano-sized alumina particles for the purification of the oily wastewater. The modified membrane showed a higher performance rate in the elimination of the organic pollutants with the total organic carbon, oil and total suspended solids removals of 98.0%, 98.0% and 98.7%, respectively. The incorporation of nano-sized alumina particles significantly improved the permeate flux and anti-fouling performances, as well as achieved complete flux recovery after the backwash cleaning process using 1 wt% OP-10 surfactant at pH 10. The results indicated that the modified polyvinylidene fluoride membrane could be a cost-effective option for the treatment of oily wastewater. Salahi et al. (2010) employed a hydrophilic 20 kDa polyacrylonitrile ultrafiltration membrane for the separation of oily wastewater. The membrane achieved the high total suspended solids and oil removals of 99%, but with low total dissolved solids removal of only 30%. The membrane demonstrated the highest steady flux at the temperature of 50 °C and pH of 10 with the transmembrane pressure and crossflow velocity of 3 bar and 1 m/s, respectively.

In addition, Ebrahimi et al. (2010) investigated the performance of the ceramic ultrafiltration membrane composed of titania and alumina for the treatment of oily wastewater with an oil concentration of 32.2 mg/L. The result showed a high organic content removal of 78.2% at the applied pressure of 2 bar. Moreover, the membrane could also remove the salt content at a lower pressure of 0.5 bar. In a bid to understand the performance of the ultrafiltration membrane, Teodosiu et al. (1999) used an ultrafiltration membrane system consisting of polyvinylpyrrolidone and polyethersulfone membranes as a pretreatment of oily wastewater for the subsequent reverse osmosis process. The authors also studied the effects of backflushing and chemical cleaning on the rate of fouling and process efficiency. The results revealed the high total suspended solids removal efficiency of 98% with low turbidity of 12.5–14.2 mg/L. However, the membrane system showed a low chemical oxygen demand and total organic carbon. The results suggested that the ultrafiltration membrane could be a feasible option for the pretreatment of the oily wastewater prior to the reverse osmosis process.

11.3.3 Nanofiltration

Nanofiltration is a pressure-driven membrane process that utilizes membranes with nano-sized pores to reject ionic and molecular species. Typically, nanofiltration membranes exhibit pore sizes ranging from 1 to 10 nm, which are much smaller than those of microfiltration and ultrafiltration membrane, but slightly larger than that of the reverse osmosis membrane. Generally, nanofiltration membranes tend to reject multivalent ions and larger particles without selective to the monovalent ions. The passage of the solution (wastewater) through the membrane and the retainment of the solute (oil particles and other pollutant ions) on the membrane is achieved based on the structure of the membrane layer and the type of membrane material.

Several investigations have reported on the application of the nanofiltration membranes for treating the oily wastewater in petroleum plants. Seland et al. (1992) applied the nanofiltration technique to reduce the sulphate concentration in the seawater for the oil reservoir injection. The technique demonstrated an excellent overall salt rejection of 93%. Mondal and Wickramasinghe (2008) utilized two different types of nanofiltration membranes for the treatment of produced water. The investigation revealed that the semi aromatic nanofiltration membrane was able to reduce the total dissolved solids and total organic carbon concentration from 2090 to 1760 mg/L and 136.4 to 98.1 mg/L, respectively. Meanwhile, the fully aromatic nanofiltration membrane demonstrated higher removals of total dissolved solids and total organic carbon with the concentrations from 2090 to 1340 mg/L and 136.4 to 89.7 mg/L, respectively. Ebrahimi et al. (2010) treated the oily wastewater using two different ceramic nanofiltration membranes composed of titania (with 1000 Da), and titania and alumina (with 750 Da). Both the membranes were able to completely remove the oil, and the total organic carbon concentration was reduced by 49.8% at a low pressure of 1 bar.

11.3.4 Reverse Osmosis

The pressure-driven reverse osmosis technology has been widely used for various water separation applications. Osmosis is a natural phenomenon in which the solvent molecules travel from a region of lower solute concentration to a region with higher solute concentration through a semipermeable barrier until the osmotic equilibrium is reached. On the other hand, in reverse osmosis, the solvent molecules are forced to flow in the direction towards a region of lower solute concentration with the aid of applied pressure higher than the osmotic pressure. Reverse osmosis could reject all sort of solutes including the monovalent ions, hence it usually achieves higher solute rejections compared to nanofiltration (da Silva Biron et al. 2018; Li 2007). However, due to small pore sizes, reverse osmosis and nanofiltration are not preferable for oily wastewater treatment applications due to relatively low flux and high energy consumption (Wan Ikhsan et al. 2017).

Reverse osmosis membranes are made from various materials such as polyamide, zeolite, polyethersulfone, and polyvinylidene fluoride. Past studies have witnessed significant efforts to mitigate the limitations of the reverse osmosis membranes in handling the oily wastewater with complex compounds (Mondal and Wickramasinghe 2008; Fakhru'l-Razi et al. 2010; Murray-Gulde et al. 2003; Barrufet et al. 2005; Franks et al. 2009). Lee and Dong (2004) used a synthetic zeolite reverse osmosis membrane to reduce the salinity of the oily wastewater in the upstream process of the oil production. The oily wastewater was reported to have a high total dissolved solids concentration of 181,600 mg/L. The reverse osmosis process managed to reduce the concentration to 32,700 mg/L with a permeate flux of 0.018 kg/m^2h at the pressure of 55 bar. Liu et al. (2008) fabricated the MFI-typed silicate zeolite reverse osmosis membrane for the treatment of the synthetic oily wastewater that contained some organic solvents such as hexane. The membrane demonstrated a high rejection performance of 96.5% with a permeate flux of 0.33 kg/m^2h at a pressure of 27.6 bar. In addition, the membrane also exhibited a salt rejection of 99.4% when 0.1 M salt solution was used.

Fakhru'l-Razi et al. (2010) studied the reverse osmosis performance of polyethersulfone and polyvinylidene fluoride membranes in the oily wastewater treatment. The study was conducted at an operating pressure of 60 bar. The results revealed that the membrane exhibited outstanding removal efficiency of 92–94%

with the permeate flux of 30–80 L/m^{2}h. Mondal and Wickramasinghe (2008) treated the oily wastewater of high concentrations of total organic carbon (136.4 mg/L) and total dissolved solids (2090 mg/L) using the reverse osmosis membrane at the pressure of 1.4–7 bar. The membrane successfully reduced the total organic carbon and total dissolved solids concentrations to 45.2–1090 mg/L, respectively. In addition, a study conducted by Murray-Gulde et al. (2003) showed the outstanding performance of the polymeric reverse osmosis membrane in treating oily wastewater. The membrane attained outstanding total dissolved solids and total organic carbon removal performances of 95.5% and 76.2%, respectively with the flow rates of 0.006–0.028 L/s at a pressure of 18.6 bar.

11.4 Electrochemical Treatment

Electrochemical treatment is arguably the most effective technique for the treatment of oily wastewater. Electrochemical treatment offers several advantages, such as (a) energy saving as the process operates at the ambient temperature and pressure, (b) robust performance with the capability to adjust to the process variations such as influent flow rate and concentration, (c) versatile and can be easily incorporated with other technologies, and (d) ease of control as the process kinetics can be easily controlled through the adjustment of working potential and/or current density (Santos et al. 2006; Radjenovic and Sedlak 2015; Yavuz et al. 2010). However, the electrochemical technique suffers from relatively high costs of electrodes and the generation of toxic side products in the treated water (Radjenovic and Sedlak 2015). There are two types of electrochemical processes, namely (a) electro-Fenton (achieved from several electrodes) and (b) oxidation processes, which can be used to treat oily wastewater of different sources. The electrodes used in the electrochemical technique are made from aluminum, platinum–iridium, boron-doped diamond, and titanium–rubidium (Jamaly et al. 2015).

11.4.1 Electro-Fenton Process

In the electro-Fenton process, the Fenton's reagent consisting of iron (II) ions and hydrogen peroxide can be electrochemically generated on-site. Iron (II) ions can be produced through two different ways, as such, (a) the reduction of iron (III) ions (Eq. 11.4) and (b) the oxidation of a sacrificial iron anode (Eq. 11.5) (Yavuz 2007). And, hydrogen peroxide can be generated via the reduction of dissolved oxygen as demonstrated in Eq. 11.6 (Bellakhal et al. 2006).

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \tag{11.4}$$

$$4Fe \rightarrow 4Fe^{2+} + 8e^- \tag{11.5}$$

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{11.6}$$

where H_2O_2, O_2 and Fe represent hydrogen peroxide, oxygen and iron, respectively. In addition, the iron (II) ion, iron (III) ion, hydrogen ion and electron are denoted as Fe^{2+}, Fe^{3+}, H^+ and e^-, respectively.

The reaction between iron (II) ions and hydrogen peroxide leads to the formation of very reactive hydroxyl radicals according to Fenton's reaction (Eq. 11.7). This strong reactive hydroxyl radical then breaks down the stable chains of organic molecules and degrade them into simpler end products (Radwan et al. 2018).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^\bullet \tag{11.7}$$

where Fe^{2+}, Fe^{3+} and OH^- represent the iron (II), iron (III) and hydroxide ions, respectively. Meanwhile, H_2O_2 and $OH^\bullet$ are the hydrogen peroxide and hydroxide radical, respectively. The performance of the electro-Fenton process could be influenced by several parameters such as the dosage of iron (II) ions and hydrogen peroxide, current density, solution pH, supporting electrolyte concentration, as well as the initial contaminant concentration of the influent (Szpyrkowicz et al. 2001; Yavuz et al. 2010).

11.4.2 Electrochemical Oxidation

Electrochemical oxidation of oily wastewater can be performed through two different methods, namely direct and indirect oxidations as shown in Fig. 11.4. In direct oxidation, the pollutant components in oily wastewater are degraded through adsorption onto the electrode and can occur at relatively low potentials (Radjenovic and Sedlak 2015). The pollutant components are directly oxidized by the metal oxide itself or the hydroxyl radicals present at the electrode surface. This process does not involve any substances other than the electron (Feng et al. 2016). However, this process is prone to electrode fouling due to the formation of polymeric layers on the electrode surface especially in the presence of dissolved solutes, which consequently leads to a decrease in the catalytic activity of the electrode (Chatzisymeon et al. 2009; Rodrigo et al. 2001; Feng et al. 2016). In addition, the rates of direct oxidation are also affected by slow reaction kinetics and diffusion limitations (Radjenovic and Sedlak 2015).

In indirect oxidation, strong oxidizing species is required to mediate the transformation of oil components (Radjenovic and Sedlak 2015). Generally, the active intermediate oxidizing species is first produced at the electrodes followed by the oxidation of the pollutant components at the bulk of the wastewater solution. It is to

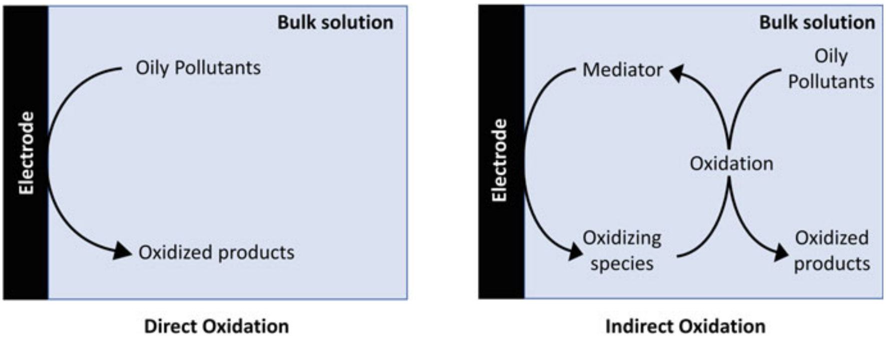


Fig. 11.4 The removal pathways of oily pollutants in direct and indirect electrochemical oxidations. (Modified after Ighilahriz et al. 2013). In direct oxidation, the pollutant components are directly oxidized by the metal oxide itself or the hydroxyl radicals present at the electrode surface. Whereas, strong oxidizing species is required to mediate the transformation of pollutant components for indirect oxidation

be noted that the rates of indirect oxidation process are affected by the generation of oxidizing species as well as the mass transport of oxidizing species to the bulk solution (Botte 2017). In addition, the nature of the oxidizing species is also influenced by the electrode material (for instance, the oxygen overpotential), and the electrode surface properties (Radjenovic and Sedlak 2015). However, the use of this oxidation process has raised the concern on the increase in the toxicity of the wastewater due to the production of oxidizing species (Xianjun 2015).

11.4.3 Recent Development of Electrochemical Treatment

Yavuz et al. (2010) studied the efficiency of three different electrochemical techniques for the treatment of the petroleum refinery wastewater, which included (a) direct electrochemical oxidation with ruthenium mixed metal electrode, (b) direct and indirect electrochemical oxidations with the use of boron-doped diamond anode, and (c) combined electrocoagulation and electro-Fenton using iron electrodes. The outcomes demonstrated that the combination of electrocoagulation and electro-Fenton exhibited the highest efficiency with the 98.7% phenol and 75.7% chemical oxygen demand removals at 6–9 min, respectively. Körbahti and Artut (2010) investigated the influence of different operating conditions on the treatment of bilge water using electrochemical reactor with the platinum-iridium electrode. The results showed the high removals of oil and grease (99.2%), chemical oxygen demand (93.2%), and turbidity (91.1%) when 12.8 mA/cm^2 current density was applied at the temperature of 32 °C.

Sekman et al. (2011) applied the electrocoagulation method in treating oily wastewater produced from the port-waste gathering systems. 98.8% of total suspended solids was removed after 5 min of electrolysis at the current density of

16 mA/cm^2. Meanwhile, the chemical oxygen demand was reduced for 90% after 20 min of electrolysis at the current density of 12 mA/cm^2. In addition, 80% of oil and grease was removed after 10 min of electrolysis at all tested current densities. Giwa et al. (2012) studied the effects of current density, sodium chloride concentration, and electrolysis time on the treatment of the oily wastewater produced from a petrochemical plant. The results showed that 97.43% of the most extreme turbidity was removed at the optimum current density of 21.6 mA/cm^2, salt concentration of 2 g/L and 30 min of electrolysis. Yang (2007) treated a high-turbidity (1800 FAU) oily wastewater via electrocoagulation with the electrodes containing ferrous ions and 100 mg/L sodium chloride. The turbidity of the oily wastewater was significantly reduced to 14 FAU after 4 min of treatment with a current of 2A and the addition of 165.8 mg/L of iron. Xu and Zhu (2004) reported that the treatment of refectory oily wastewater required the optimum current density of 10–14 A/m^2, electrode distance of 10 mm, and pH of 3–10 for a cycle time of 30 min. In addition, the ideal separation distance of the electrodes was found to be 10 mm, which resulted in the efficient removal of 95% oil and chemical oxygen demand.

11.5 Hybrid Technologies for Oily Wastewater Treatment

The combination of various technologies has become an interest of studies for the improvement of the oily wastewater treatment. Earlier in 2004, Mostefa and Tir (2004) coupled electro-flotation with flocculation to improve oily wastewater treatment performance. The authors investigated the competency of three different flocculants, which included iron sulfate, polyacrylamide, and aluminum sulfate. In addition, the concentration of cutting oil also varied between 1 and 4%. Maximum removals of turbidity (99%) and chemical oxygen demand (97%) were achieved at the current density of 11.15 mA/cm^2. 99% of oil was also removed when the iron sulfate and aluminum sulfate flocculants were applied. Yan et al. (2010) employed catalytic vacuum distillation with various promoters, such as iron (III) chloride, kaolin, sulfuric acid, and sodium hydroxide for the treatment of petroleum refinery wastewater with high chemical oxygen demand. The results showed that the catalytic vacuum distillation with sodium hydroxide promoter had higher purification efficiency than the systems with other types of promoters. The system successfully removed 99% of the chemical oxygen demand and lowered the effluent salinity.

Santo et al. (2012) applied the coagulation-flocculation and flotation methods to reduce the organic matter, oil, and grease contents in the wastewater. PAX-18 (17% alumina), aluminum sulfate, and ferric sulfate were chosen for the primary treatment of coagulation-flocculation, whereas the flocculant used was NALCO 71408. The combination of these materials could eliminate up to 95% of total petroleum hydrocarbons from the oily wastewater. Santander et al. (2011) introduced the combination techniques of flocculation and flotation in a modified jet (Jameson) cell. The removal rates of the oily wastewater of the conventional and modified jet cells were compared. The study outcomes demonstrated that the modified jet

(Jameson) cell was more effective to remove oil from the wastewater with an efficiency of 85%. To validate these findings, a test was also conducted on a maritime platform. Again, the modified jet (Jameson) cell achieved a high oil removal rate of 81%.

Besides that, the treatment methods using a combination of the physical and biological processes were also investigated. Peng et al. (2014) introduced a biological-physicochemical pretreatment of the oily wastewater prior to the anaerobic digestion process. The authors found that the digestibility of the oily wastewater was improved after the introduction of oil degradationbacteria, *Bascillus* sp. A study conducted by Rattanapan et al. (2011) has suggested the high efficiency of the combination of dissolved air flotation, acidification, and coagulation in treating biodiesel wastewater. Their findings demonstrated that the dissolved air flotation alone and dissolved air flotation with acidification were not effective enough to give high rejection performance. Meanwhile, the combination of dissolved air flotation, acidification, and coagulation was found to successfully remove 85–95% of biodiesel in wastewater. In addition, Siles et al. (2011) confirmed that the combination of electrocoagulation, acidification, and biomethanization was very efficient for the oily wastewater treatment as it removed up to 99% of the chemical oxygen demand. Meanwhile, a relatively low chemical oxygen demand removal of 94% was achieved when a combination system of acidification, coagulation, flocculation, and biomethanization was applied. The previous works on hybrid technologies to eradicate the contaminants from various sources of oily wastewater are tabulated in Table 11.6.

The combination of different membrane technologies for oily wastewater treatment was studied by Salahi et al. (2012). The research team applied the combined system of ultrafiltration and reverse osmosis and achieved excellent removal efficiencies for oil and grease (100%), total organic carbon (98%), chemical oxygen demand (98%), total dissolved solids (95%) and turbidity (100%). Ong et al. (2014) studied the oil removal performance of the submerged photocatalytic membrane reactors in which the titania-embedded polyvinylidene fluoride membranes were exposed under the ultraviolet light. A high degradation performance was achieved with 80% and > 90% of the total organic carbon and oil removal efficiencies.

In addition, various attempts have been reported on the combination of adsorption and filtration for the oily wastewater treatment. For instance, Abdullah et al. (2010) applied this approach using a kapok fiber as the filtering material to eradicate the oil and grease content in the diesel oil, as well as new and used engine oils. Their results demonstrated that 1 gram of kapok filter could remove up to 36.7 g, 47.4 g and 50.8 g of diesel, new engine oil and used engine oil, respectively. Interestingly, the kapok filter remained stable even after 15 cycles of test. Zhao and his team (2011) developed a sponge-like exfoliated vermiculite and carbon nanotube hybrids and found that the intercalation of carbon nanotube arrays improved the oiladsorption capacities. The results also showed that the oiladsorption capacity was increased from 26.7 to 70.6 g/g when the sponge-like exfoliated vermiculite and carbon nanotube hybrid was transformed into fluffy exfoliated vermiculite and carbon nanotube cotton using a high-speed shearing. Meanwhile, activated carbon has

Table 11.6 List of hybridized methods and systems for oily wastewater treatment

Year	Researchers	Treatment methods	Wastewater source	Removal efficiency of contaminants
2004	Mostefa and Tir	Electro-flotation coupled with flocculation	Synthetic oil-in-water emulsion (chemical oxygen demand: 62,300 mg/L; turbidity: 29,700 NTU)	99% of chemical oxygen demand and 99% of turbidity
2010	Abdullah et al.	Combined sorption with membrane filtration	Diesel oil, new and used engine oil	36.7 g/g of diesel oil, 50.8 g/g of used engine oil and 47.4 g/g of new engine oil
2010	Yan et al.	Catalytic vacuum distillation with promoters (iron (III) chloride, kaolin, sulfuric acid, and sodium hydroxide)	Petroleum refinery wastewater (chemical oxygen demand: 4238 mg/L)	99% of chemical oxygen demand
2011	Yang et al.	Submerged membrane bioreactors with electrocoagulation and electro-flotation	Synthetic oil-in-water emulsion (p-xylene: 3000 mg/L; total organic carbon: 3817 mg/L)	96% of p-xylene and total organic carbon
2011	Zhao et al.	Combined sorption with membrane filtration	Diesel oil	70.6 g/g of diesel oil
2011	Sokker et al.	Adsorption by hydrogel of chitosan-based polyacrylamide prepared by radiation-induced graft polymerization	The aqueous solution with 500–30,000 mg/L of crude oil	1.8 g of crude oil per g of seawater
2011	Santander et al.	Flocculation and flotation in a modified jet cell.	Simulated offshore petroleum effluents with 50–600 mg/L of oil	80–85% of oil removal
2012	Yang et al.	Ceramic microfiltration membranes with powdered activated carbon	Simulated restaurant wastewater with 5 and 100 mg/L oil	98.3% of chemical oxygen demand for 5 mg/L oil content and 99.1% of chemical oxygen demand for 100 mg/L oil content
2012	Santo et al.	Coagulation-flocculation and flotation processes	Refinery wastewater with 580 ± 4 mg/L chemical oxygen demand	> 80% of chemical oxygen demand
2014	Ong et al.	Submerged membrane photocatalytic reactor consisting of polyvinylidene fluoride TiO_2	Synthetic oily wastewater with 250–10,000 mg/L oil	>90% of oil
2014	McLaughlin et al.	Modified jet cell	Shipboard bilge water with oil content of up to 129.56 ± 55.53 mg/L	97% of oil

been widely chosen as the adsorbent material as it exhibits large surface area with plentiful distributed micropores (Coca-Prados et al. 2013). For example, Yang et al. (2012) combined the ceramic microfiltration with the powdered activated carbon which had seen 96% of the total organic carbon and p-xylene was removed from the oily wastewater. However, the presence of powdered activated carbon did not contribute to the removal of oil emulsion.

11.6 Challenges and Future Directions

There are lots of opportunities in the recycling of oily wastewater to improve the raw crude oil exploitation efficiency. Likewise, there are also opportunities for the selling of the concentrated oil obtained from the oily wastewater treatment plant to the oil recycle industries. Moreover, the recuperation of the valuable metals from the oily wastewater, particularly from the petrochemical industries, will present a feasible economic opportunity if it is realized. However, the transformation of these opportunities into reality has remained an entangled endeavor.

In the real industry, the oily industrial effluent generally contains various suspended and dissolved components that are difficult to be removed or recovered using the one-size-fits-all treatment methods. In addition, the continuous review of the regulatory wastewater discharge standards with more stringent limits further increases the challenges faced by the treatment plants. For instance, the Department of Petroleum of China imposes strict standards on the oily wastewater recycle with the maximum allowable discharge limit of only 2 mg/L (Zeng et al. 2007). As the result, the endeavor towards achieving the ideal treatment for the recycle or reuse of the treated oily wastewater continues to be a challenging task (Tir and Moulai-Mostefa 2008; Zouboulis and Avranas 2000). Hence, the treatment plant should be tailored based on the types and conditions of the effluents, as well as the local wastewater discharge standards.

Moreover, studies on the removal or recovery of heavy metals in the oily wastewater are critically lacking. The presence of these heavy metals can be a major hurdle for the recycle and reuse of the oily wastewater. In fact, some industrial oily wastewaters, particularly from the oil and gas refineries, contain various heavy metals, such as chromium, mercury, nickel, cadmium, copper, zinc, silver, and lead (Yavuz et al. 2010). The hazardous features of heavy metals could result in malicious impact if being released into the environment without proper treatment. Therefore, future research should also direct towards the removal or recovery of heavy metals in the oily wastewater. Electrochemical oxidation appears to be a prevailing and effective approach for the removal of heavy metals from oily wastewater. For instance, electrochemical treatment using the boron-doped diamond stone and platinum anodes could considerately remove various kinds of heavy metals (dos Santos et al. 2014). Electrocoagulation treatment is another effective method in removing heavy metals from oily wastewater. However, this method suffers from high operational cost due to heavy electricity consumption. Therefore, there is also a need to develop newer electrode materials with less energy consumption, as well as implement the system integration with sustainable energy sources for enhanced oily wastewater treatment performance.

Membrane technology has been playing an increasingly important role in the oily wastewater treatment, especially for the post-treatment stages. However, the current membrane technology can only cope with small volume treatment, which is less than 190 m^3/day (Zeng et al. 2007). In addition, membrane technology also suffers from the membrane fouling issues. Frequent process interruptions are required for membrane cleaning or replacement of the new membranes, which leads to more economic loss. Hence, the research on the development of membranes from readily recyclable materials with high separation capacity and oil fouling resistance is crucial (Hosseinzadeh and Mohammadi 2014). In recent years, innovative efforts in the development of functionalized materials with unique wettability properties for oily wastewater treatment have been reported, such as activated carbon/iron oxide composite (Ngarmkam et al. 2011), nanocellulose aerogel (Cervin et al. 2012), reduced graphene oxide foam (Niu et al. 2012), and poly(acrylamide) hydrogel (Xue et al. 2011). These materials exhibit different unique wettability properties suitable for oil–water separation, such as (1) superoleophilic and superhydrophobic, (2) underwater superhydrophilic and superoleophobic, (3) superoleophobic and superhydrophilic, and (4) switchable wettability (Wang et al. 2015; Chen and Xu 2013). The incorporation of these materials in the development of membranes could be interesting to improve the oil–water separation performance of the membranes.

Lastly, the economic analysis of the advanced treatment technologies is essential to identify the feasibility of scaling up the technologies for large scale industrial use. However, the economic analysis on these technologies are still limited. Today, most of the studies on the advanced oily wastewater treatment technologies are still in small or laboratory scale. Therefore, future studies should focus on the pilot scale research and comprehensive economic analysis so that the technologies can be scaled up for industrial applications.

11.7 Conclusion

The direct discharge of oily wastewater would pollute the water sources which consequently affects the environment and the health of the surrounding community. The effects of water pollution have been widely discussed and efforts have been devoted to the development of the treatment technologies for oily wastewater to combat these challenges. In this chapter, we have reviewed various types of oil wastewater treatment technologies, which include the conventional oily wastewater treatment technologies and advanced technologies such as membrane, electrochemical, and hybrid technologies. The advanced technologies have shown some promising results and could be the future trends for the commercial implementation of oily wastewater treatment. However, the operative support from the organization and authorities are also essential to ensure the effectiveness of these technologies in complying to the wastewater discharge standards.

In a nutshell, the development of the sustainable treatment technologies is pivotal towards the preservation of the quality of the environment. Most of the conventional methods are costly and involves the use of chemicals that require long degradation time. Hence, this chapter discusses comprehensively on the effective advanced technologies to treat the oily wastewater. Furthermore, the presence of the extremely toxic contaminants in the oily wastewater such as radionuclides, persistent organic pollutants, hydrocarbon and some endocrine disruptor components should also be given more attention. The release of these substances to the environment would pose serious threats to the survival of the living organisms and environmental sustainability. However, the use of single technology is not efficient enough to satisfy all the discharge requirements for different contaminants. Hence, the approach of integrating different technologies is perceived to be more effective and could provide the best solution to these never-ending problems.

Acknowledgements The authors would like to thank the Ministry of Education Malaysia for the financial support under the Higher Institution Center of Excellence Scheme (Project number: R.J090301.7809.4J430). In addition, deepest appreciation would also be extended to Universiti Teknologi Malaysia for the research fund under the Transdiciplinary Research (TDR) Grant (Project number: Q.J130000.3509.05G75).

References

Abdullah MA, Rahmah AU, Man Z (2010) Physicochemical and sorption characteristics of Malaysian Ceiba pentandra (L.) Gaertn. As a natural oil sorbent. J Hazard Mater 177:683–691. https://doi.org/10.1016/j.jhazmat.2009.12.085

Agarwal A, Ng WJ, Liu Y (2011) Principle and applications of microbubble and nanobubble technology for water treatment. Chemosphere 84:1175–1180. https://doi.org/10.1016/j.chemosphere.2011.05.054

Ahmad AL, Bhatia S, Ibrahim N, Sumathi S (2005) Adsorption of residual oil from palm oil mill effluent using rubber powder. Braz J Chem Eng 22(3):371–379. https://doi.org/10.1590/S0104-66322005000300006

Ahmad AL, Sumathi S, Hameed BH (2006) Coagulation of residue oil and suspended solid in palm oil mill effluent by chitosan, alum and PAC. Chem Eng J 118:99–105. https://doi.org/10.1016/j.cej.2006.02.001

Akim EL, Smirnov MN, Aldokhin NA, Mazitov LA (2010) Method of sewage treatment by pressure floatation. Russia RU2386590C1

Alade AO, Jameel AT, Muyubi SA, Abdul Karim MI, Alam MZ (2011) Removal of oil and grease as emerging pollutants of concern (EPC) in wastewater stream. IIUM Eng J 12(4):161–169. https://doi.org/10.31436/iiumej.v12i4.218

Al-Shamrani AA, James A, Xiao H (2002) Separation of oil from water by dissolved air flotation. Colloids Surf A Physicochem Eng Asp 209:15–26. https://doi.org/10.1016/S0927-7757(02)00208-X

Alther GR (2002) Removing oil from water with organoclays. J Am Water Work Assn 94 (7):115–121. https://doi.org/10.1002/j.1551-8833.2002.tb09512.x

Arnot T, Field RW, Koltuniewicz AB (2000) Cross-flow and dead-end microfiltration of oily-water emulsions: part II Mechanisms and modelling of flux decline. J Membrane Sci 169(1):1–15. https://doi.org/10.1016/S0376-7388(99)00321-X

Barrufet MA, Burnett DB, Mareth B (2005) Modeling and operation of oil removal and desalting oilfield brines with modular units. In: SPE annual technical conference and exhibition. Society of Petroleum Engineers, Dallas. https://doi.org/10.2118/95647-MS

Bellakhal N, Oturan MA, Oturan N, Dachraoui M (2006) Olive oil mill wastewater treatment by the electro-fenton process. Environ Chem 3:345–349. https://doi.org/10.1071/EN05080

Bennett GF, Peters RW (1988) The removal of oil from wastewater by air flotation: a review. Crit Rev Environ Control 18:189–253. https://doi.org/10.1080/10643388809388348

Bkt Co. Ltd., I San Co. Ltd (2008) Decanting unit with an air cylinder for controlling the operation thereof, and a wastewater processing apparatus employing the same. Korea 1008118460000

Botte GG (2017) Electrochemical technologies for water treatment, management, and efficiency. Electrochem Soc Interface 26:53–61. https://doi.org/10.1149/2.F04172if

Bratby J, Marais GVR (1975) Saturator performance in dissolved-air (pressure) flotation. Water Res 9:929–936. https://doi.org/10.1016/0043-1354(75)90120-7

Cerqueira VS, Hollenbach EB, Maboni F, Vainstein MH, Camargo FAO, Peralba MDCR, Bento FM (2011) Biodegradation potential of oily sludge by pure and mixed bacterial cultures. Bioresour Technol 102:11003–11010. https://doi.org/10.1016/j.biortech.2011.09.074

Cervin NT, Aulin C, Larsson PT, Wågberg L (2012) Ultra porous nanocellulose aerogels as separation medium for mixtures of oil/water liquids. Cellulose 19:401–410. https://doi.org/10.1007/s10570-011-9629-5

Chatzisymeon E, Dimou A, Mantzavinos D, Katsaounis A (2009) Electrochemical oxidation of model compounds and olive mill wastewater over DSA electrodes: 1. The case of Ti/IrO$_2$ anode. J Hazard Mater 167:268–274. https://doi.org/10.1016/j.jhazmat.2008.12.117

Chen P-C, Xu Z-K (2013) Mineral-coated polymer membranes with superhydrophilicity and underwater superoleophobicity for effective oil/water separation. Sci Rep 3:2776. https://doi.org/10.1038/srep02776

Chen X, Chen G, Yue PL (2000) Separation of pollutants from restaurant wastewater by electrocoagulation. Sep Purif Technol 19:65–76. https://doi.org/10.1016/S1383-5866(99)00072-6

Cheryan M (1998) Ultrafiltration and microfiltration handbook. CRC Press, Boca Raton. https://doi.org/10.1201/9781482278743

Coca-Prados J, Gutiérrez G, Benito JM (2013) Treatment of oily wastewater by membrane hybrid processes. In: Coca-Prados J, Gutiérrez-Cervelló G (eds) Economic sustainability and environmental protection in Mediterranean countries through clean manufacturing methods NATO science for peace and security series C: environmental security. Springer, Dordrecht, pp 35–61. https://doi.org/10.1007/978-94-007-5079-1_3

Crowell RG (2008) Dissolved air flotation with filter system. Europe EP1944071

Da Rocha E, Silva FCP, Da Rocha E, Silva NMP, De Moura AE, Galdino RA, Luna JM, Rufino RD, Dos Santos VA, Sarubbo LA (2015) Effect of biosurfactant addition in a pilot scale dissolved air flotation system. Sep Sci Technol 50:618–625. https://doi.org/10.1080/01496395.2014.957319

Da Silva Biron D, Dos Santos V, Zeni M (2018) Ceramic membranes applied in separation processes. Springer, Cham. https://doi.org/10.1007/978-3-319-58604-5

Dickhout JM, Moreno J, Biesheuvel PM, Boels L, Lammertink RGH, de Vos WM (2017) Produced water treatment by membranes: a review from a colloidal perspective. J Colloid Interface Sci 487:523–537. https://doi.org/10.1016/j.jcis.2016.10.013

Dos Santos EV, Sena SFM, Da Silva DR, Ferro S, De Battisti A, Martínez-Huitle CA (2014) Scale-up of electrochemical oxidation system for treatment of produced water generated by Brazilian petrochemical industry. Environ Sci Pollut Res 21:8466–8475. https://doi.org/10.1007/s11356-014-2779-x

Ebrahimi M, Willershausen D, Ashaghi KS, Engel L, Placido L, Mund P, Bolduan P, Czermak P (2010) Investigations on the use of different ceramic membranes for efficient oil-field produced water treatment. Desalination 250:991–996. https://doi.org/10.1016/j.desal.2009.09.088

Edzwald JK, Walsh JP, Kaminski GS, Dunn HJ (1992) Flocculation and air requirements for dissolved air flotation. J Am Water Works Ass 84:92–100. https://doi.org/10.1002/j.1551-8833.1992.tb07325.x

El-Bestawy E, El-Masry MH, El-Adl NE (2005) The potentiality of free gram-negative bacteria for removing oil and grease from contaminated industrial effluents. World J Microbiol Biotechnol 21:815–822. https://doi.org/10.1007/s11274-004-2239-8

Environmental Quality Act and Regulations Handbook (2009) Laws of Malaysia: details on environmental quality act 1974 and regulations amendments up to June 2009: act 127 with Inde. MDC Publishers, Kuala Lumpur, pp 34–35

Eskin A, Zakharov G, Tkach N, Tsygankova K (2015) Intensification dissolved air flotation treatment of oil-containing wastewater. Mod Appl Sci 9:114–124. https://doi.org/10.5539/mas.v9n5p114

Eweis JB, Ergas SJ, Chang DPY, Schroeder ED (1998) Bioremediation principles. McGraw-Hill International, Boston. ISBN: 978–0070577329

Fakhru'l-Razi A, Pendashteh A, Abdullah LC, Biak DRA, Madaeni SS, Abidin ZZ (2009) Review of technologies for oil and gas produced water treatment. J Hazard Mater 170(2–3):530–551. https://doi.org/10.1016/j.jhazmat.2009.05.044

Fakhru'l-Razi A, Pendashteh A, Abidin ZZ, Abdullah LC, Biak DRA, Madaeni SS (2010) Application of membrane-coupled sequencing batch reactor for oilfield produced water recycle and beneficial re-use. Bioresour Technol 101:6942–6949. https://doi.org/10.1016/j.biortech.2010.04.005

Feng Y, Yang L, Liu J, Logan BE (2016) Electrochemical technologies for wastewater treatment and resource reclamation. Environ Sci Water Res Technol 2:800–831. https://doi.org/10.1039/C5EW00289C

Franks R, Bartels C, Anit A, Nagghappan LNSP (2009, November 7–12) RO membrane performance when reclaiming produced water from the oil extraction process. IDA World Congress. Atlantis, The Palm, Dubai, UAE

Friedman J, Morse D, Morse WO, Matherly TG (2006) System and method of gas energy management for particle flotation and separation. Mexico 05010261

Gitis V, Rothenberg G (2016) Ceramic membranes: new opportunities and practical applications. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. https://doi.org/10.1002/9783527696550

Giwa S, Ertunç S, Alpbaz M, Hapoglu H (2012) Electrocoagulation treatment of turbid petrochemical wastewater. Int J Adv Sci Technol 5:23–32

Greenberg AE, Eaton AD, Clesceri LS, Rice EW (2005) Standard methods for the examination of water and wastewater. (21st ed.). United State of America: American Public Health Association. ISBN : 0875532233

Gu X, Chiang S-H (1999) A novel flotation column for oily water cleanup. Sep Purif Technol 16:193–203. https://doi.org/10.1016/S1383-5866(99)00004-0

Gunstone FD (2004) The chemistry of oils and fats: sources, composition, properties and uses. Blackwell, Oxford. ISBN: 1405116269

Hosseinzadeh H, Mohammadi S (2014) Synthesis of a novel hydrogel nanocomposite coated on cotton fabric for water–oil separation. Water Air Soil Pollut 225:2115. https://doi.org/10.1007/s11270-014-2115-6

Ibrahim S, Ang HM, Wang S (2009) Removal of emulsified food and mineral oils from wastewater using surfactant modified barley straw. Bioresour Technol 100:5744–5749. https://doi.org/10.1016/j.biortech.2009.06.070

Ighilahriz K, Taleb Ahmed M, Djelal H, Maachi R (2013) Electrocoagulation and electro-oxidation treatment for the leachate of oil-drilling mud. Desalin Water Treat 52(31–33):5833–5839. https://doi.org/10.1080/19443994.2013.811113

Jamaly S, Giwa A, Hasan SW (2015) Recent improvements in oily wastewater treatment: Progress, challenges, and future opportunities. J Environ Sci 37:15–30. https://doi.org/10.1016/j.jes.2015.04.011

Jameson GJ (1999) Hydrophobicity and floc density in induced-air flotation for water treatment. Colloids Surf A Physicochem Eng Asp 151:269–281. https://doi.org/10.1016/S0927-7757(98)00503-2

Jeganathan J, Bassi A, Nakhla G (2006) Pre-treatment of high oil and grease pet food industrial wastewaters using immobilized lipase hydrolyzation. J Hazard Mater B137:121–128. https://doi.org/10.1016/j.jhazmat.2005.11.106

Karhu M, Kuokkanen T, Rämö J, Mikola M, Tanskanen J (2013) Performance of a commercial industrial-scale UF-based process for treatment of oily wastewaters. J Environ Manag 128:413–420. https://doi.org/10.1016/j.jenvman.2013.05.053

Khondee N, Tathong S, Pinyakong O, Powtongsook S, Chatchupong T, Ruangchainikom C, Luepromchai E (2012) Airlift bioreactor containing chitosan-immobilized Sphingobium sp. P 2 for treatment of lubricants in wastewater. J Hazard Mater 213–214:466–473. https://doi.org/10.1016/j.jhazmat.2012.02.018

Kobya M, Hiz H, Senturk E, Aydiner C, Demirbas E (2006) Treatment of potato chips manufacturing wastewater by electrocoagulation. Desalination 190:201–211. https://doi.org/10.1016/j.desal.2005.10.006

Körbahti BK, Artut K (2010) Electrochemical oil/water demulsification and purification of bilge water using Pt/Ir electrodes. Desalination 258:219–228. https://doi.org/10.1016/j.desal.2010.03.008

K-Pack Korea Co. Ltd (2008) Dissolved air floatation system for treatment wastewater. Korea 1007971970000

Kriipsalu M, Marques M, Nammari DR, Hogland W (2007) Bio-treatment of oily sludge: the contribution of amendment material to the content of target contaminants, and the biodegradation dynamics. J Hazard Mater 148:616–622. https://doi.org/10.1016/j.jhazmat.2007.03.017

Kulkarni SJ (2016) Biological treatment of petroleum wastewater: a review on research and studies. Int J Pet Petrochem Eng 2:17–21. https://doi.org/10.20431/2454-7980.0202004

Lee RL, Dong J (2004) Modified reverse osmosis system for treatment of produced waters. New Mexico Institute of Mining and Technology (US). https://doi.org/10.2172/827721

Li K (2007) Ceramic membrane for separation and reaction. Wiley, Hoboken. https://doi.org/10.1002/9780470319475

Li P, Tsuge H (2006) Water treatment by induced air flotation using microbubbles. J Chem Eng Jpn 39:896–903. https://doi.org/10.1252/jcej.39.896

Li YS, Yan L, Xiang CB, Hong LJ (2006) Treatment of oily wastewater by organic–inorganic composite tubular ultrafiltration (UF) membranes. Desalination 196:76–83. https://doi.org/10.1016/j.desal.2005.11.021

Li X-B, Liu J-T, Wang Y-T, Wang C-Y, Zhou X-H (2007) Separation of oil from wastewater by column flotation. J China Univ Min Technol 17:546–577. https://doi.org/10.1016/S1006-1266(07)60143-6

Li LJ, Qi PS, Liu YZ, Qi Z, Zhao JJ (2009) Poly ferric silicate sulphate (pfsis): Characterization, coagulation behavior and applications in oily wastewater treatment. 3rd International Conference on Bioinformatics and Biomedical Engineering, iCBBE 2009. https://doi.org/10.1109/ICBBE.2009.5163205

Li ZY, Xie S, Jiang G, Bao M, Wang Z, Huang X, Xu F (2015) Bioremediation of offshore oily drilling fluids. Energy Sources Part A 37:1680–1687. https://doi.org/10.1080/15567036.2011.633968

Liu N, Li L, Mcpherson B, Lee R (2008) Removal of organics from produced water by reverse osmosis using MFI-type zeolite membranes. J Membr Sci 325:357–361. https://doi.org/10.1016/j.memsci.2008.07.056

Mansour LB, Chalbi S (2006) Removal of oil from oil/water emulsions using electroflotation process. J Appl Electrochem 36:577–581. https://doi.org/10.1007/s10800-005-9109-4

Mclaughlin C, Falatko D, Danesi R, Albert R (2014) Characterizing shipboard bilgewater effluent before and after treatment. Environ Sci Pollut Res Int 21(8):5637–5652. https://doi.org/10.1007/s11356-013-2443-x

Menezes FM, Amal R, Luketina D (1996) Removal of particles using coagulation and flocculation in a dynamic separator. Powder Techno 88:27–31. https://doi.org/10.1016/0032-5910(96)03098-7

Meyer P, Mayer A, Kulozik U (2015) High concentration of skim milk proteins by ultrafiltration: characterisation of a dynamic membrane system with a rotating membrane in comparison with a spiral wound membrane. Int Dairy J 51:75–83. https://doi.org/10.1016/j.idairyj.2015.07.010

Mohammed AA, Al-Gurany AJM (2010) Separation of oil from O/W emulsion by electroflotation technique. J Eng 3(16):5503–5515

Mondal S, Wickramasinghe SR (2008) Produced water treatment by nanofiltration and reverse osmosis membranes. J Membr Sci 322:162–170. https://doi.org/10.1016/j.memsci.2008.05.039

Moosai R, Dawe RA (2003) Gas attachment of oil droplets for gas flotation for oily wastewater cleanup. Sep Purif Technol 33:303–314. https://doi.org/10.1016/S1383-5866(03)00091-1

Mostefa NM, Tir M (2004) Coupling flocculation with electroflotation for waste oil/water emulsion treatment. Optimization of the operating conditions. Desalination 161(4):115–121. https://doi.org/10.1016/S0011-9164(04)90047-1

Mueller J, Cen Y, Davis RH (1997) Crossflow microfiltration of oily water. J Membr Sci 129:221–235. https://doi.org/10.1016/S0376-7388(96)00344-4

Murray-Gulde C, Heatley JE, Karanfil T, Rodgers JH, Myers JE (2003) Performance of a hybrid reverse osmosis-constructed wetland treatment system for brackish oil field produced water. Water Res 37:705–713. https://doi.org/10.1016/S0043-1354(02)00353-6

Ngarmkam W, Sirisathitkul C, Phalakornkule C (2011) Magnetic composite prepared from palm shell-based carbon and application for recovery of residual oil from POME. J Environ Manag 92:472–479. https://doi.org/10.1016/j.jenvman.2010.08.031

Niu Z, Chen J, Hng HH, Ma J, Chen X (2012) A leavening strategy to prepare reduced graphene oxide foams. Adv Mater 24:4144–4150. https://doi.org/10.1002/adma.201200197

Ong CS, Lau WJ, Goh PS, Ng BC, Ismail AF (2014) Investigation of submerged membrane photocatalytic reactor (sMPR) operating parameters during oily wastewater treatment process. Desalination 353:48–56. https://doi.org/10.1016/j.desal.2014.09.008

Oyama ST, Stagg-Williams SM (2011) Inorganic, polymeric and composite membranes: structure, function and other correlations. Elsevier, Amsterdam. ISBN: 978-0-444-53728-7

Patrick V (2008) Method and device for clarification of liquids, particularly water, loaded with material in suspension. Europe EP 1483210 B1

Peng LY, Bao MD, Wang QF, Wang FC, Su HJ (2014) The anaerobic digestion of biologically and physicochemically pretreated oily wastewater. Bioresour Technol 151:236–243. https://doi.org/10.1016/j.biortech.2013.10.056

Radjenovic J, Sedlak DL (2015) Challenges and opportunities for electrochemical processes as next-generation technologies for the treatment of contaminated water. Environ Sci Technol 49:11292–11302. https://doi.org/10.1021/acs.est.5b02414

Radwan M, Gar Alalm M, Eletriby H (2018) Optimization and modeling of electro-Fenton process for treatment of phenolic wastewater using nickel and sacrificial stainless steel anodes. J Water Process Eng 22:155–162. https://doi.org/10.1016/j.jwpe.2018.02.003

Rattanapan C, Sawain A, Suksaroj T, Suksaroj C (2011) Enhanced efficiency of dissolved air flotation for biodiesel wastewater treatment by acidification and coagulation processes. Desalination 280:370–377. https://doi.org/10.1016/j.desal.2011.07.018

Rinzema A, Boone M, van Knippenberg K, Lettinga G (1994) Bactericidal effect of long chain fatty acids in anaerobic digestion. Water Environ Res 66:40–49. https://doi.org/10.2175/WER.66.1.7

Rodrigo MA, Michaud PA, Duo I, Panizza M, Cerisola G, Comninellis C (2001) Oxidation of 4-chlorophenol at boron-doped diamond electrode for wastewater treatment. J Electrochem Soc 148:D60–D64. https://doi.org/10.1149/1.1362545

Rubio J, Souza ML, Smith RW (2002) Overview of flotation as a wastewater treatment technique. Miner Eng 15:139–155. https://doi.org/10.1016/S0892-6875(01)00216-3

Salahi A, Abbasi M, Mohammadi T (2010) Permeate flux decline during UF of oily wastewater: experimental and modeling. Desalination 251:153–160. https://doi.org/10.1016/j.desal.2009.08.006

Salahi A, Badrnezhad R, Abbasi M, Mohammadi T, Rekabdar F (2012) Oily wastewater treatment using a hybrid UF/RO system. Desalin Water Treat 28(1):75–82. https://doi.org/10.5004/dwt.2011.2204

Santander M, Rodrigues RT, Rubio J (2011) Modified jet flotation in oil (petroleum) emulsion/water separations. Colloids Surf A Physicochem Eng Asp 375:237–244. https://doi.org/10.1016/j.colsurfa.2010.12.027

Santo CE, Vilar VJP, Botelho CMS, Bhatnagar A, Kumar E, Boaventura RAR (2012) Optimization of coagulation–flocculation and flotation parameters for the treatment of a petroleum refinery effluent from a Portuguese plant. Chem Eng J 183:117–123. https://doi.org/10.1016/j.cej.2011.12.041

Santo CE, Vilar VJP, Bhatnagar A, Kumar E, Botelho CMS, Boaventura RAR (2013) Biological treatment by activated sludge of petroleum refinery wastewaters. Desalin Water Treat 51:6641–6654. https://doi.org/10.1080/19443994.2013.792141

Santos MRG, Goulart MOF, Tonholo J, Zanta CLPS (2006) The application of electrochemical technology to the remediation of oily wastewater. Chemosphere 64:393–399. https://doi.org/10.1016/j.chemosphere.2005.12.036

Sawyer CN, Mccarty PL, Parkin GF (2003) Chemistry for environmental engineering and science, 5th edn. McGraw-Hill Companies, Inc, New York. ISBN:0072480661

Scott K (1995) Elsevier science, Amsterdam, Netherlands. https://doi.org/10.1016/B978-1-85617-233-2.X5000-4

Sekman E, Top S, Uslu E, Varank G, Bilgili MS (2011) Treatment of oily wastewater from port waste reception facilities by electrocoagulation. Int J Environ Res 5:1079–1086. https://doi.org/10.22059/IJER.2011.466

Seland A, Torleiv B, Surinder M, Bakke R (1992) Membrane filtration of seawater for oil reservoir injection. In: SPE annual technical conference and exhibition. Society of Petroleum Engineers, Washington, D.C. https://doi.org/10.2118/24805-MS

Shammas NK, Wang LK (2016) Water engineering: hydraulics, distribution and treatment. Wiley, Hoboken. ISBN: 978-0-470-39098-6

Shannon WT, Buisson DH (1980) Dissolved air flotation in hot water. Water Res 14:759–765. https://doi.org/10.1016/0043-1354(80)90252-3

Siles JA, Gutiérrez MC, Martín MA, Martín A (2011) Physical-chemical and biomethanization treatments of wastewater from biodiesel manufacturing. Bioresour Technol 102 (10):6348–6351. https://doi.org/10.1016/j.biortech.2011.02.106

Sokker HH, El-Sawy NM, Hassan MA, El-Anadouli BE (2011) Adsorption of crude oil from aqueous solution by hydrogel of chitosan based polyacrylamide prepared by radiation induced graft polymerization. J Hazard Mater 190(1–3):359–365. https://doi.org/10.1016/j.jhazmat.2011.03.055

Song H, Zhou L, Zhang L, Gao B, Wei D, Shen Y, Wang R, Madzak C, Jiang Z (2011) Construction of a whole-cell catalyst displaying a fungal lipase for effective treatment of oily wastewaters. J Mol Catal B Enzym 71:166–170. https://doi.org/10.1016/j.molcatb.2011.04.015

Stams AG, Oude ESJ (1997) Understanding and advancing wastewater treatment. Curr Opin Biotechnol 8:328–334. https://doi.org/10.1016/S0958-1669(97)80012-2

Sugimori D (2009) Edible oil degradation by using yeast coculture of Rhodotorula Pacifica ST3411 and Cryptococcus Laurentii ST3412. Appl Microbiol Biotechnol 82:351–357. https://doi.org/10.1007/s00253-008-1834-2

Szpyrkowicz L, Juzzolino C, Kaul SN (2001) A comparative study on oxidation of disperse dyes by electrochemical process, ozone, hypochlorite and Fenton reagent. Water Res 35:2129–2136. https://doi.org/10.1016/S0043-1354(00)00487-5

Tansel B, Pascual B (2011) Removal of emulsified fuel oils from brackish and pond water by dissolved air flotation with and without polyelectrolyte use: pilot-scale investigation for estuarine and near shore applications. Chemosphere 85(7):1182–1186. https://doi.org/10.1016/j.chemosphere.2011.07.006

Teodosiu CC, Kennedy MD, van Straten HA, Schippers JC (1999) Evaluation of secondary refinery effluent treatment using ultrafiltration membranes. Water Res 33:2172–2180. https://doi.org/10.1016/S0043-1354(98)00433-3

Tir M, Moulai-Mostefa N (2008) Optimization of oil removal from oily wastewater by electrocoagulation using response surface method. J Hazard Mater 158:107–115. https://doi.org/10.1016/j.jhazmat.2008.01.051

Tong SL, Goh SH, Abdulah AR, Tahir NM, Wang CW (1999) Asean marine water quality criteria for oil and grease. Marine Environment Division, Water Quality Management Bureau, Pollution Control Department, pp 1–28

Wakelin NM, Forster CF (1997) An investigation into microbial removal of fats, oils and greases. Bioresour Technol 59:37–43. https://doi.org/10.1016/S0960-8524(96)00134-4

Wan Ikhsan SN, Yusof N, Aziz F, Nurasyikin M (2017) A review of oilfield wastewater treatment using membrane filtration over conventional technology. Malaysian J Anal Sci 21(3):643–658. https://doi.org/10.17576/mjas-2017-2103-14

Wang LK, Shammas NK, Selke WA, Aulenbach DB (2010) Flotation technology. Humana Press. https://doi.org/10.1007/978-1-60327-133-2

Wang B, Liang W, Guo Z, Liu W (2015) Biomimetic super-lyophobic and super-lyophilic materials applied for oil/water separation: a new strategy beyond nature. Chem Soc Rev 44:336–361. https://doi.org/10.1039/C4CS00220B

Winston WS, Sirkar KK (1992) Membrane Handbook. Springer, New York. https://doi.org/10.1007/978-1-4615-3548-5

Woodley P, Foong WC (2002) Method for treatment of wastewater. International WO2002096808

Xianjun D (2015) A review on the electrochemical treatment of the salty organic wastewater. IOP Conf Ser Mater Sci Eng 87:012037. https://doi.org/10.1088/1757-899X/87/1/012037

Xiao KL, Xu SM, Li XG (2002) Study on the treatment of oil-bearing wastwater by multi-stage flotation column. Ind Water Treat 22:37–39

Xie W, Zhong L, Chen J (2007) Treatment of slightly polluted wastewater in an oil refinery using a biological aerated filter process. Wuhan Univ J Nat Sci 12:1094–1098. https://doi.org/10.1007/s11859-007-0080-2

Xu X, Zhu X (2004) Treatment of refectory oily wastewater by electro-coagulation process. Chemosphere 56:889–894. https://doi.org/10.1016/j.chemosphere.2004.05.003

Xue Z, Wang S, Lin L, Chen L, Liu M, Feng L, Jiang L (2011) A novel superhydrophilic and underwater superoleophobic hydrogel-coated mesh for oil/water separation. Adv Mater 23:4270–4273. https://doi.org/10.1002/adma.201102616

Yan Y-D, Jameson GJ (2004) Application of the Jameson cell technology for algae and phosphorus removal from maturation ponds. Int J Miner Process 73:23–28. https://doi.org/10.1016/j.minpro.2003.07.002

Yan L, Ma HZ, Wang B, Mao W, Chen YS (2010) Advanced purification of petroleum refinery wastewater by catalytic vacuum distillation. J Hazard Mater 178(1–3):1120–1124. https://doi.org/10.1016/j.jhazmat.2010.01.104

Yang C-L (2007) Electrochemical coagulation for oily water demulsification. Sep Purif Technol 54:388–395. https://doi.org/10.1016/j.seppur.2006.10.019

Yang Y, Chen R, Xing W (2011) Integration of ceramic membrane microfiltration with powdered activated carbon for advanced treatment of oil-in-water emulsion. Sep Purif Technol 76(3):373–377. https://doi.org/10.1016/j.seppur.2010.11.008

Yang B, Chen G, Chen G (2012) Submerged membrane bioreactor in treatment of simulated restaurant wastewater. Sep Purif Technol 88:184–190. https://doi.org/10.1016/j.seppur.2011.12.026

Yavuz Y (2007) EC and EF processes for the treatment of alcohol distillery wastewater. Sep Purif Technol 53:135–140. https://doi.org/10.1016/j.seppur.2006.08.022

Yavuz Y, Koparal AS, Öğütveren ÜB (2010) Treatment of petroleum refinery wastewater by electrochemical methods. Desalination 258:201–205. https://doi.org/10.1016/j.desal.2010.03.013

Yu L, Han M, He F (2017) A review of treating oily wastewater. Arab J Chem 10:S1913–S1922. https://doi.org/10.1016/j.arabjc.2013.07.020

Zabel TF (1992) Flotation in water treatment. In: Mavros P, Matis KA (eds) Innovations in flotation technology. Springer, Dordrecht, pp 431–454. https://doi.org/10.1007/978-94-011-2658-8_23

Zeng Y, Yang C, Zhang J, Pu W (2007) Feasibility investigation of oily wastewater treatment by combination of zinc and PAM in coagulation/flocculation. J Hazard Mater 147:991–996. https://doi.org/10.1016/j.jhazmat.2007.01.129

Zhai J, Huang Z, Rahaman MH, Li Y, Mei L, Ma H, Hu X, Xiao H, Luo Z, Wang K (2017) Comparison of coagulation pretreatment of produced water from natural gas well by polyaluminium chloride and polyferric sulphate coagulants. Environ Technol 38:1200–1210. https://doi.org/10.1080/09593330.2016.1217937

Zhao M, Huang J, Zhang Q, Luo W, Wei F (2011) Improvement of oil adsorption performance by a sponge-like natural vermiculite-carbon nanotube hybrid. Appl Clay Sci 53(1):1–7. https://doi.org/10.1016/j.clay.2011.04.003

Zheng T, Wang Q, Shi Z, Huang P, Li J, Zhang J, Wang J (2015) Separation of pollutants from oil-containing restaurant wastewater by novel microbubble air flotation and traditional dissolved air flotation. Sep Sci Technol 50:2568–2577. https://doi.org/10.1080/01496395.2015.1062396

Zhong J, Sun X, Wang C (2003) Treatment of oily wastewater produced from refinery processes using flocculation and ceramic membrane filtration. Sep Purif Technol 32:93–98. https://doi.org/10.1016/S1383-5866(03)00067-4

Zhu X, Reed BE, Lin W, Carriere PE, Roark G (1997) Investigation of emulsified oil wastewater treatment with polymers. Sep Purif Technol 32(13):2173–2187. https://doi.org/10.1080/01496399708000762

Zouboulis AI, Avranas A (2000) Treatment of oil-in-water emulsions by coagulation and dissolved-air flotation. Colloids Surf A Physicochem Eng Asp 172:153–161. https://doi.org/10.1016/S0927-7757(00)00561-6

Chapter 12
Remediation of Pollution by Oil Spills

Marzie Fatehi, Maryam Mansoori Kermani, and Ali Mohebbi

Contents

Abstract Oil contamination in seawater, groundwater, and wastewater including vegetable oil, fat and grease, waste oil, gasoline, diesel, heavier fuels, oily white refuse, crude oil, and animal oil has become a serious global challenge in the last decades. The contaminants have negative effects on the marine life, leisure activities, tourism and aesthetic appeal. Some components of oil that are soluble can enter the organs of animals, accumulate, and thus enter the food chain, causing health

---

Marzie Fatehi and Maryam Mansoori Kermani have contributed equally to this chapter.

M. Fatehi · M. Mansoori Kermani · A. Mohebbi (✉)
Department of Chemical Engineering, Faculty of Engineering, Shahid Bahonar University of Kerman, Kerman, Iran
e-mail: amohebbi@uk.ac.ir

Inamuddin et al. (eds.), *Water Pollution and Remediation: Organic Pollutants*, Environmental Chemistry for a Sustainable World 54,
https://doi.org/10.1007/978-3-030-52395-4_12

problems for humans. Thus, remediation technologies to treat oil contamination have attracted great attention. There are two main categories of oil removal technology: remediation and bioremediation. The type and the quality of the contaminants, the type and the environmental situation of the contaminated site, and the cost of treatment determine the best remediation method.

We reviewed the physical and chemical remediation as well as bioremediation methods and in situ and ex-site processes. Physical methods are eco-friendly but these are expensive, time-consuming methods and need a large number of personnel and equipment, resulting in failure to remove spilled oil in harsh and frozen sea conditions. The main disadvantage of the chemical methods is the formation of secondary pollutants, which may have irreparable effects on marine life. However, chemical agents can be used to improve physical removal methods. On the other hand, sorbents are the alternative choice for spilled oil removal process. Natural sorbents are biodegradable, low cost, and eco-friendly compared to synthetic sorbents, but their sorption efficiency is lower than that of synthetic and inorganic sorbents. Bioremediation can be applied in all weather conditions, needs less manpower, is cost-effective, and can mineralize oil to CO_2 and H_2O. However, low capacity of microbes to survive against oil pollutants is its limitation factor. In addition, the performance of bioremediation depends on the indigenous microorganisms and the available nutrients at the contaminated site. As a most important conclusion, it should be notified that the most powerful remediation response to the oil spill is a combination of physical, chemical, and biological treatments, which is also the most cost-effective method.

Keywords Water pollution · Oil spill · Remediation · Bioremediation · Sorbent · Oil-contaminated water · Characteristics of oil spill · Microorganisms · Physical methods · Chemical methods

12.1 Introduction

Nowadays, water pollution with spilled oils has become a global environmental concern. Oil spills are caused by industrial accidents, transport accidents, routine ship operations, and illegal discharge of industrial or domestic wastewater (Putatunda et al. 2019; Jernelöv 2010). Most sources of oil are insoluble in water and float on the top of water surface due to their lower specific gravity. Once an oil spill occurs on the surface of water, the oil is subject to several processes simultaneously, such as floating, spreading, drifting, dispersion, emulsification, sinking, photolysis, formation of tar ball, evaporation, and biodegradation (Fig. 12.1) (Al-Majed et al. 2012). The emulsion and floating film of spilled oil influences on the marine life, the quality of drinking-water sources, air, economy, and tourism.

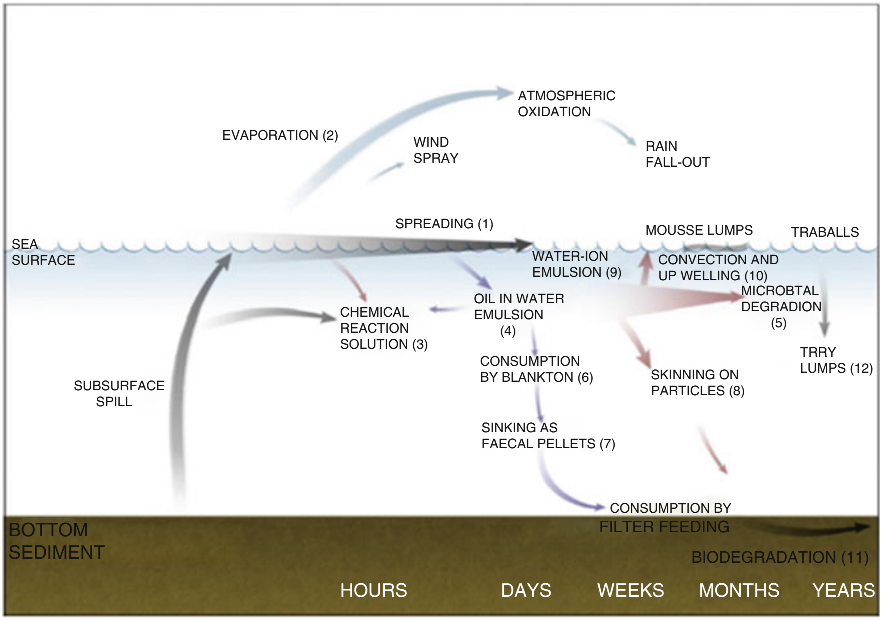


Fig. 12.1 The physical, chemical, and biological variation process of oil after it spills into the sea. Reprinted with permission (*A Sustainable Approach to Controlling Oil Spills*, Al-Majed et al., Elsevier)

Therefore, the treatment of the spilled oil on the water surface becomes an essential and inevitable task.

This work presents an overview of oil removal technologies and their advantages and limitations. There are two broad categories for oil removal technologies: remediation and bioremediation methods. There are three types of remediation technology: physical methods, chemical methods, and oilsorbents, and will be explained in Part I.

One of the most important global challenges of the last decades has been oil-contaminated seawater, groundwater, and wastewater. Municipal runoffs and liquid release are human activities that generate health hazards directly or indirectly (Sajna et al. 2015). Industry activities produce wastewater full of fats, oils, and greases. The components of municipal wastewater are water (99.9%) and a small amount of organic and inorganic materials in solid and dissolved form. The organic materials in sewage include proteins and their decomposition materials, lignin, carbohydrates, fats, soaps, synthetic detergents, different natural and artificial organic chemicals in industries, a number of potentially toxic elements like copper, arsenic, chromium, lead, mercury, cadmium, zinc, and so on (Zhang et al. 2008). Sewage produced by food processing, restaurant trade, and dairy industry (Cammarota et al. 2001; Wakelin and Forster 1997; Vidal et al. 2000) are some samples of the potential contaminants in wastewater because of the high oil concentration. Animal and vegetable oils are handled in some industries like oil extraction from plant grains including olive oil and palm oil mills, butter, dairy, slaughter, and detergent and soap manufacturing where fat or grease are used (Stams and Oude 1997). Greases often cannot dissolve and the emulsified fats efficiently enter the waterremediation system. The oils, fats, and greases that are not treated can enter oceans, seas, and rivers with harmful effects (Stams and Oude 1997). Heavy oil causes physical blockages in pumps, screens, and filters. Light oils may accumulate in the wet wells of pumping stations or floating systems. The major source of energy and one of the most important initial materials for industries are crude oilhydrocarbons that cause significant environmental threats and pollution (Varjani and Upasani 2016; Arulazhagan et al. 2010). Pipelines accidents, vessels, land runoff, offshore exploration, production operations, shipping activities, transport, wide-scale production, coastal oil refining, and illegal bilge water discharges are the main reasons for marine oil pollution (Lucas and MacGregor 2006). Repeated accidental leak and illegal oil disposal impact on the sea ecosystems severely. During the years 1970–2010, around 5.71 million tonnes of oil were entered to seawater due to tanker incidents (Dave and Ghaly 2011). The oil spills have negative effects on marine life, leisure activities, tourism, and aesthetic appeal. Some soluble components of oil can enter the food chain via accumulating in the organs of animals (Mackay and Fraser 2000). The average estimated cost to clean a crude oil spill is $2730 per barrel (Dave and Ghaly 2011). Since the environmental fallout of cleanup methods is inevitable, selecting the best methods is based on a trade-off between the side effects of oil spill and the cleanup method. The type, quantity and characterization of oil spill, age of oil, impact of oil on marine life, environment situation, sea behavior and weather conditions determine the most effective treatment technique (Choi and Cloud 1992; Lessard and Demarco 2000; Buist et al. 1999). Several methods including burning, use of dispersants, mechanical recovery, bioremediation, and use of solidifiers are applicable as response to an oil spill (Dave and Ghaly 2011; Ismail et al. 2019). In bioremediation, microorganisms degrade and metabolize chemical materials in order to restore the environment quality. The ubiquitous microorganisms in the indigenous oil spill site degrade hydrocarbons in marine oil spills. The specie of microorganisms introduced in the site depends on the process design, environmental conditions, and the mode of plant operation (Amin et al. 2013). There is an ideal environment for many microorganisms in an activated sludge system because of the agitation, constant aeration, and recirculation. Today, the activated sludge system widely uses bioremediation processes for both domestic and sewage wastewaters. The main microorganisms in wastewater are fungi, protozoa, bacteria, viruses, and nematodes. Reduction in the levels of oils, fats, and greases in sewage is therefore very desirable and an appropriate potential candidate for bioaugmentation. Biological augmentation includes the addition of archaea or bacterial cultures in order to speed up the rate of degradation of the pollutants. Use of bioaugmentation has other positive effects like increasing the efficiency and reduction of the toxic molecules (Brooksbank et al. 2007).

In this chapter, the source of oilcontaminants, the related prevention regulation and bioremediation techniques, bioremediation mechanisms, its advantages and disadvantages compared with other treatment methods and factors affecting bioremediation were studied in details. Moreover, some case studies that have considered the bioremediation in different locations were reviewed.

12.2 Oil Spills

12.2.1 Characteristics of Oil Spills

Waste oil, gasoline, diesel, heavier fuels, oily white refuse, and crude oil are the components of marine oil spills (Dave and Ghaly 2011). After an oil spill, chemical and physical changes occur in the oil (Annunciado et al. 2005). Different weathering processes such as spreading, drifting, evaporation, dissolution, biodegradation, photolysis, and formation of water–oil emulsions that change the oil viscosity, density and interfacial tensioner processes result from the formation of oil slicks (Daling and StrØm 1999). All these processes form the chocolate mousse and tar ball (Daling and StrØm 1999). Also, formation of many other products is a challenge to oil recovery. Photolysis of oil results in oxygenated products like benzoic acid, aliphatic, aromatic, naphthanoic acids, alcohols, aliphatic ketones, and phenols (Hussein et al. 2009). The quantity of oil and its physical and chemical properties affect transformation and weathering processes. Crude oil includes aliphatic and aromatic hydrocarbons. According to their types, their degradation by microorganism can be easy or complex. Two complex degradation classes of hydrocarbons are aliphatic hydrocarbons with long-chain and polycyclic aromatic hydrocarbons, which are carcinogenic, cytotoxic, and genotoxic (Hasanuzzaman et al. 2007).

12.2.2 Physical Characteristics

The surface tension, color, viscosity, and specific gravity are the physical properties of oil. These properties change based on the kind of spilled oil in waters. The brown and black color of oil can become red, green, and yellow (Dave and Ghaly 2011). The surface tension, viscosity, and specific gravity determine the capacity of oil spill to spread. The surface tension of oil is affected by temperature and in warmer watersthe spreading tendency of oil increases. A lower surface tension of oil means it has a higher and quicker ability to spread even without wind or waves. Most of the oils have a lower density than that of seawater; therefore, they float on the water surface and horizontally disperse but the lighter components of oil can evaporate and increase the oil gravity. This allows the formation of tar balls for heavier oils, which can interact with sediments and rocks in the bottom of water after the oils sink. Oils with higher viscosity tend to spread out less, and form a "chocolate mousse" that is difficult to degrade or treat (Dave and Ghaly 2011). According to the report of Nordvik et al. (1996) 10–50 °C increase in temperature decreases the density and viscosity of oil from 0.88 to 0.855 kg/dm^3 and 5000 to 200 cSt, respectively. This in turn reduces the oil's resistance to flow and increases its ability to horizontally spread out.

12.2.3 Chemical Characteristics

Molecular weight, solubility, explosivity limits, partition coefficient, boiling point, flash point, melting point, and flammability limits are the oil's chemical properties. Different types of oils have different chemical characterizations (Dave and Ghaly 2011). Oil includes hydrocarbons and can include nitrogen, oxygen, sulfur, and some other metals. Hydrocarbons include alkanes (the simplest form of hydrocarbons); alkenes and alkynes (unsaturated molecules); cycloalkanes, which are carbon–hydrogen (ring-like in structure), aromatic hydrocarbons; and a carbon–hydrogen ring. Oils are classified into four groups with various components (Clayton 2005) including unsaturated, saturated, polar compounds, and aromatics. Crude oil has on average 50% naphthenes or cycloalkanes, 15% aromatics, 30% paraffins or alkanes, 5% nitrogen, oxygen, and sulfur. Gasoline includes paraffins, olefins, napthenes, and aromatics (Dave and Ghaly 2011).

Response to Oil Spills and Prevention Guidelines

Table 12.1 shows three events with large marine oil spills and their effect, cost, and cleanup (Dave and Ghaly 2011).

To prevent the oil spills in an offshore environment, the countries have many government regulations. Most of them are related to design of the used device and equipment in the offshore medium as well as safety inspections. The regulations of Canada, USA, and UK are the most detailed regulations.

Canadian Prevention Regulations

According to Canadian regulations, a development schedule including the scope, goal, place, time, and nature of a plan for an oil field or an oil pool has to be approved before starting its construction. This development plan also must contain the evaluations of the area, production rate, recovery methods, potential recovery measures of gas and oil, technical proposals, monitoring processes, costs and environmental agents. The National Energy Board takes the responsibility to review the project to be safe, before its beginning. The board seeks advice from the Chief Safety Officer to decide if the proposed oil field or pool is safe for the environment and workers (Dave and Ghaly 2011).

Table 12.1 The largest oil spill events

Oil spill	Responsible company	Quality of oil and area	Affected industries	Affected wild life	Treatment	Cost of cleanup	Remarks
The Exxon Valdez Disaster (1989) Prince William Sound, Alaska	Exxon mobil corporation	41 million liters over 28,000 km^2	Recreational fishing-loss of $31 million	Sea otters, Harbor seals, Bard eagles, Seabirds, Harlequin, Ducks Salmon fish	Physical recovery methods, (booms and skimmers)	US $3 billion dollars	About 253,000 species loss due to ecosystem damage and depleted fish stock
			Commercial fishing-loss of $\$3 \times 10^2$ million		Dispersants (Corexit 7664 Corexit EC 9580, BP1100X)		Duck Harlequin Harbor seal Pacific herring and pigeon guillemot still have not recovered
			Tourism-35% spending decreased		Bioremediation (fertilizers: Inipol EAP 22 and Customblen)		
The prestige oil spill (2002) coast of Galicia of North-Western Spain	Universe maritime ltd.	63,700 tonnes over 2500 km^2	Commercial fisheries and aquaculture-loss of €64.9 million	Seabirds, shark, marine mollusk, mussels, octopus, sardine, sole goose barnacle	Physical recovery methods (booms and skimmers)	US $12 billion dollars	Caused pollution in the area for ten years subsequent to the initial spill
			Tourism-loss of € 133.8 million		Bioremediation (fertilizer S200)		Caused environmental losses around €574 million

(continued)

Table 12.1 (continued)

Oil spill	Responsible company	Quality of oil and area	Affected industries	Affected wild life	Treatment	Cost of cleanup	Remarks
Gulf of Mexico oil spill (2010) Gulf of Mexico	British petroleum	780 million liters over 11,000 km^2	Recreational fishing-loss of $138 million	Fish, aquatic invertebrates, birds, beach mouse, sea turtles	Physical recovery methods (boom and skimmers)	Over US $632 million by March 2011	Full assessment of the impact is still under investigation
			Commercial fishing-loss of $ 18 million Tourism –loss of $ 2.8 billion		In situ burning Dispersants (Corexit 9500, Corexit EC9527A)		

Modified after Dave and Ghaly (2011)

Response Regulations of Canada

Based on the regulations of Canada, if accidently an oil spill occurs, workers must report that to the Chief Conservation Officer. The workers must do everything possible to prevent more spillage and decrease serious environmental fallout. The Chief Conservation Officer must take emergency environmental measures to clean up and do preventive measures for more impact. The company responsible for the oil spillage must pay all the costs for remedial measures and the destructions and negligence according to the decision of court. Other Canadian organizations are also involved with response to oil spill. One of the organizations that should be informed immediately, especially in oil tanker spill, is the Canadian Coast Guard. The negative effect of the spilled oil on marine life and migratory birds is determined by the Canadian Wildlife Services (Dave and Ghaly 2011).

US Prevention Regulations

According to US regulations, if a facility has more than 1320 gallons or more than 4.2×10^4 gallons of capacity of the aboveground and underground oil storage, respectively, or the certain expectation of the oil leakage in US waters and adjacent shorelines, it must be under the cover of the Regulations by Spill Prevention, Control and Countermeasure. Such a facility must prevent oil spills and the prevention actions concern the oil containers and periodical tests. The oil handling operations, discharge controls, drainage controls, spill prevention practices, staff, instruments, and resources at the facility should be described by Spill Prevention, Control, and Countermeasure plan (Dave and Ghaly 2011).

Response Regulations of USA

In the USA, any oil spill must immediately be notified to the National Response Center, providing all the necessary information for Regional Administrator. In the case that more than 1000 gallons (3785 liters) of oil are spilled into water in one accident or more than 42 gallons (159 L) of oil in any of two spillages to adjacent shorelines or navigable water occurs within any 12-month period, United States Environmental Protection Agency must be notified by the operator or owner of the facility (Dave and Ghaly 2011).

UK Prevention Regulations

All the operators of installations and facilities and also harbor authorities must have a plan for oil contamination based on the regulations of Merchant Shipping. With attention to the regulations of Offshore Activities, applying for a permit that contains the details about the installation, the oil for discharging and the monitoring of the discharge based on the measures planned is mandatory for any oil discharging through an offshore installation. Also the capacity and installation of the oil containers have been regulated according to the Control of Pollution (Oil Storage-England) Regulations 2001 to prevent burst or leak under ordinary use (Dave and Ghaly 2011).

Response Regulations of UK

In the UK, any unplanned or unexpected oil spill to sea must be announced by the Oil Operations Notice No. 1 immediately. In the case that the source of oil spill is not specified, the oil is taken for analysis. Ship owners or operators, persons who handle facility and are responsible for an offshore installation must report any oil spill caused by other ships or offshore installations immediately to the near Coastal State or Her Majesty's coast guard based on the Merchant Shipping (Oil Pollution Preparedness, Response, and Co-operation Convention) Regulations 1998 (Dave and Ghaly 2011).

12.3 Part I: Remediation Technology

12.3.1 Physical Methods

The physical methods, which can be applied for low and high viscous oils, even in the presence of ice are conventional recovery methods to remove the spilled oil. Oil skimmers and booms are the familiar types of this method, explained below.

Skimmers

The skimmers are engineered devices for oily water treatment and can be divided into oleophilic (adhesion), weir, elevating submersion, suction, and centrifuged type according to their function. For example, the oleophilic skimmers use the oleophilic materials to separate oil from water and are classified into drums, discs, and rope mops. For selecting an appropriate oil skimmer, some parameters must be considered such as oil type, oil viscosity, and sea and environmental conditions.

Recently, some researches were performed to improve and increase the recovery rate of these equipments. Broje and Keller (2007b) emphasized the essential role of interfacial tension between various petroleum products and recovery surface of the skimmers. The interfacial tension has important effects on the wetting surface, the oil thickness, and eventually recovery rate. The wetting and oleophilic properties were evaluated by use of the contact angles of oil and hydrocarbon liquids. They used various hard polymers, metals, and elastomers as cover. According to the results, Neoprene and Hypalon (oleophilic elastomers) have high oleophilicity and more

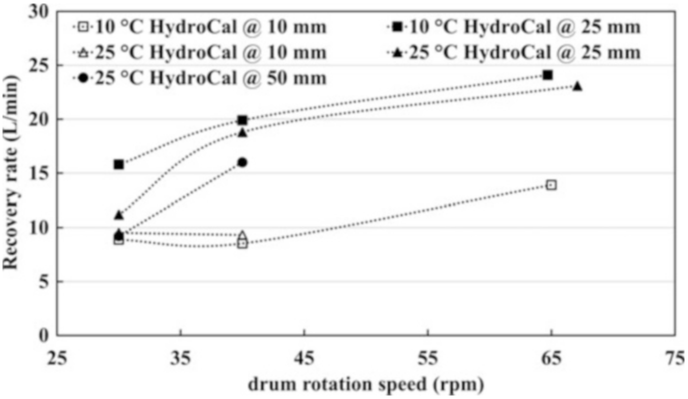


Fig. 12.2 The effect of thickness of oil slick, drum speed, and temperature on the HydroCal recovery rate using aluminum drum. (Modified after Broje and Keller2007a)

ability to keep oil at their surface. On the other hand, an increase in oil viscosity enhances the oil recovery rate.

Moreover, they investigated the effect of operational parameters like recovery surface material, speed of drum, oil properties, thickness of oil slick, and temperature on the efficiency of drum skimmer with oleophilic surface in another study (Broje and Keller 2007a). Three types of drum cover (aluminum, polyethylene, and neoprene) and oils (Diesel, Endicott, and HydroCal 300) were tested.

The results showed that the neoprene cover had better efficiency than aluminum or polyethylene covers in oil removal for thicker slick and low viscosity oil. While, for thin oil slicks polyethylene had the highest effectiveness. The recovery rate also increased for thicker oil slicks and decreased for thinner oil slicks with increasing the oil viscosity. Figure 12.2 illustrates the effect of thickness of oil slick, drum speed, and temperature on the HydroCal recovery rate of drum with aluminum cover.

The obtained results showed that an increase in the thickness of slick (two or three times) increases the recovery rates, but there is no significant change for the light oil. At low temperatures, HydroCal and Endicott oil recovery rates were higher than at the warmer temperatures. This is caused by the temperature impact on the oil viscosity.

However, using conventional skimmers is not feasible in turbulent conditions and when the oil slicks are thin. A 3D (three-dimensional) printed superhydrophobic–oleophilic mesh based oil skimmer was fabricated and its surface modified with octadecyltrichlorosilane (Yan et al. 2016). On-site and rapid fabrication is the notable advantage of the presented production method. This oil skimmer contained a top 3D printed mesh cap to remove the spilled oil and a bottom vessel to collect the removed oil (Fig. 12.3).

The modified mesh had water contact angle of 150°, which shows its superhydrophobicity. The oil removal efficiency of the designed skimmer was more than 90% for hexadecane, gasoline, corn and mineral oils. Pore diameter of

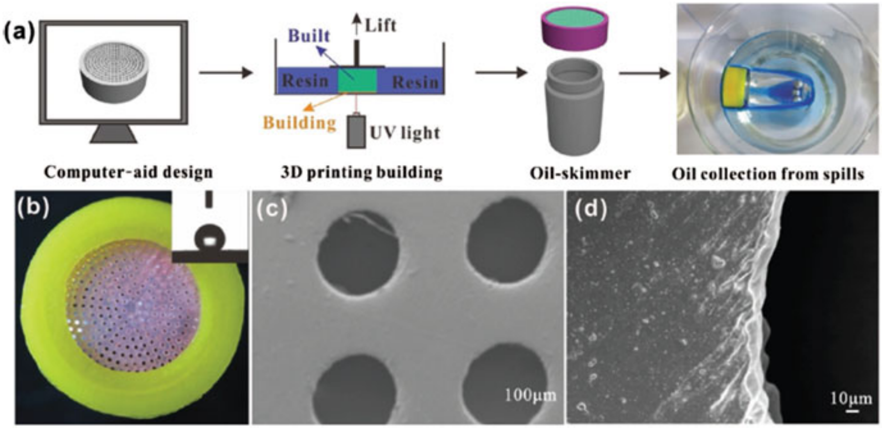


Fig. 12.3 (**a**) The top 3D printed mesh cap and bottom vessel; (**b**) digital photo of the octadecyltrichlorosilane modified printed mesh cap with pore diameter of 500 μm; and (**c** and **d**) different magnifications of scanning electron microscope images of printed mesh. Reprinted with permission from (*3D printing as feasible platform for on-site building oil-skimmer foroilcollection from spills*, Yan et al., Wiley Online Library)

printed mesh had significant effect on the permeation rate, so that the penetration rate of hexadecane increased by enhancing pore size. In addition, the oil removal efficiency of the skimmers was more than 90% during ten oil removal cycles, which shows the durability of the designed skimmer. This skimmer has the high potential to be used under sea wave and even storm because the collected oil is kept stable by the vessel.

This equipment removes oil mechanically and no secondary pollutions remain. Nevertheless, exorbitant energy for oil recovery, expensive operational conditions, and higher removal efficiency in sheltered water condition than in harsh one are its important disadvantages.

Booms

Booms are floating barriers with a variety of sizes, materials, and designs, and are applied as the vanguard of spill control. Above-water freeboard, below-water skirt, flotation foam or buoyant material, longitudinal tension member, and ballast are several types of oil booms. They act as oil containment or oil concentration to prevent oil spread and thicken oil slick, oil deflection to divert spilled oil at the collection point for subsequent removal, and as a protector to divert spilled oil from important biological and economical locations. In turbulent conditions, the application of booms is not feasible (Ivshina et al. 2015). Currents deflect the booms by a transverse dynamic pressure force and the pressure of surface currents and wave motion deform the boom's structure, reducing its effectiveness (Lee and Kang 1997).

The containment booms are of various types according to their operation conditions like coastal, estuary waters, and open sea. The boom design, operation conditions, and improved booms are the subject of much research. Structural analysis of oil booms is an effective method to select suitable oil boom for various environmental conditions, investigate the effect of operational conditions, and optimize the oil boom design. The best position of booms is a less well, which affects the oil containment and boom resistance against currents (Muttin 2015).

Zhu and Strunin (2001) presented a mathematical model using a potential theory for a vertical barrier like a vertical floating boom in oil/water system. The model was formulated by nonlinear integral equations. This model predicts the oil confined by floating boom. Zhu and Strunin investigated the confined oil by use of water–oil upstream contact point with the rigid lid. The results showed that the leakage beneath the barrier was impossible in stagnation contact point, while in tangential contact point, Froude number was used to estimate flow behaviour. In another study, they presented new results of obtained model and discussed the relationship between Froude number, the amount of trapped oil, and the barrier submergence depth (Zhu and Strunin 2002). The viscous effects were used to upgrade the presented model in their previous study.

Muttin (2008) investigated the boom efficiency and its behavior under a strong current. His case study analysis showed that the boom skirt angle changed and decreased the boom efficiency. Moreover, a model was proposed to analyze the structure of oil booms in inshore and estuary waters. The results indicated that the angle (θ) between the cross section of the boom skirt and the vertical axis influenced the containment efficiency. Therefore, controlling the boom position by use of a three-dimensional boom model is essential. On the other hand, the chain and the leach stiffness changed the skirt angle. Figure 12.4 shows the effect of current velocity on the skirt angle. According to the obtained third-degree polynomial for presented data in Fig. 12.4, the inflexion of curve was at 0.45 m/s, while the empiric value was 0.35 m/s for the maximal admitted current velocity.

These results showed the nonlinear manner of the boom structure. To prevent breaking the booms, a computation using tide coefficient of an installation period was suggested. Depending on where the oil pollution occurred, the crisis team should have the best choice with respect to the intrinsic limitation of the booms.

In another study, a realistic physical model was used to investigate the relationship between the design parameters of a floating boom and its efficiency under different waves and current conditions (irregular and regular). In this study, various booms were used, which were different in geometry properties and buoyancy–weight ratio (Castro et al. 2010). Computer Vision system developed ad hoc was applied for analyzing the boom displacements. The effective boom drafts are defined in order to characterize the booms' performance.

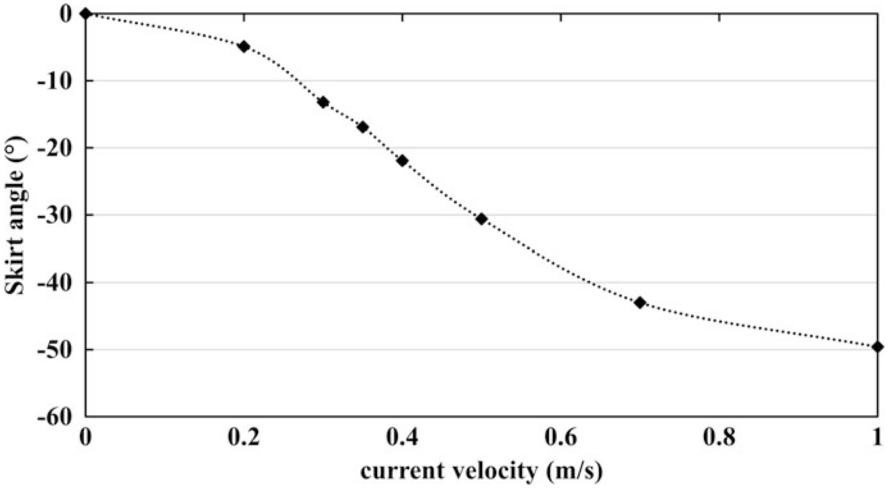


Fig. 12.4 The skirt angle of floating boom versus current velocity. (Modified after Muttin2008)

In regular waves, an increase in the wave height or current velocity had a negative impact on the effective draft. When the current velocity increased, the effect of wave height diminished. On the other hand, an increase in buoyancy–weight ratio decreased the effective draft. The long skirt boom models had higher significant effective drafts than the short skirt booms models, in the absence of current. Moreover, the same behavior was obvious for the minimum effective draft. In irregular waves, the significant effective drafts decreased as the current velocity increased and the effect of wave height is secondary in the absence and presence of current. The effects of buoyancy–weight ratio and skirt length were similar to that of the regular waves' conditions. Forasmuch as the effective boom draft influences on the drainage failure, this research emphasizes the right choice of booms based on the wave and current conditions.

The boom flexibility also affects the floating boom performance to contain spilled oil. Shi et al. (2018) used an improved multiphase Smoothed Particle Hydrodynamics method to simulate contained oil by flexible boom and compared the obtained results with experimental data and the results of rigid boom. This model was applied for simulation of flexible boom movement in the presence of simultaneous waves and currents. The simulated and experimental results showed water vortices were generated in the forepart and behind the boom skirt. An increase in the current velocity decreased the size of the forepart vortex while the rear vortex increased. On the other hand, the skirt of the flexible boom swayed and rolled easily compared to the rigid one. The heave responses of the booms did not depend on the boom flexibility. In one wave cycle, the escaped oil from the rigid boom was lower (about 5%) than that from the flexible one.

The boom characteristics, contained oil properties, and environmental conditions have a considerable effect on the performance of the booms while there is less information about their effect. Moreover, it is suggested that the oil spread model on the surface of water and physio-chemical mechanisms of the spreading should comprehensively be studied to improve and develop a hind cast model for booms. Sometimes, the oil booms are used to improve the skimmer efficiency but there is a main problem with containment booms. The booms collect and concentrate both oil and surrounding ice so that the ice concentration rapidly decreases the skimmer efficiency, contrary to the positive effect of oil concentration.

As a result, the recovery rate of physical methods like booms is a notable weakness. In addition, these methods are unable to remove spilled oil in brush and broken ice conditions and need to improve their application with some chemical agents.

12.4 Chemical Methods

The chemical methods are cheaper than physical methods for spilled oil removal. These methods are quick and used for various oils. However, they have disadvantages like secondary pollution and unrecoverable oil. In the following, different types of chemical methods for oilremediation with some of their advantages and disadvantages are discussed.

12.4.1 In Situ Burning

In situ burning is an easy and fast thermal means to treat oil contaminated sites and requires a minimum of specialized equipment like fire igniters and resistant booms. It provides high rates of oil removal efficiency. In situ burning is applied to treat jet fuel and oil spilled in snow and ice covered waters by ship accidents, pipelines, storage tanks in Scandinavian countries, European countries, USA, and Canada (Mullin and Champ 2003). The method is effective in calm wind conditions and is useful for the spills of light refined products or fresh oils because they can burn quickly and without any danger for marine life, but there is a probability that the residue will sink and cover up an underground water resource (Dave and Ghaly 2011). The residue can be removed using the mechanical techniques. The thickness of oil and the adequate amount of oxygen are the factors that limit the successful performance of burning (Buist et al. 1999). There are two factors including (a) burning agents including light crude oils, gasoline, and (b) wicking factors including wood, straw, silica, and glass beads, in order to sustain the oil combustion and provide sufficient oxygen to the fire (Fingas et al. 1979). In spite of the success of in situ burning for oil spill response, there are some limitations to applying this method, including (a) fear of probable other fires and (b) environmental hazards and danger to human health because of burning by-products (Buist et al. 1999). Burning can have some effects on the aquatic life and vegetation near the site. In situ burning is efficacious as treatment if applied immediately after the oil spill occurs (Dave and Ghaly 2011). Thick oil slicks have an important role in spreading oil and the efficiency of in situ burning. The spilled oil quickly spreads and becomes thin in loose, broken ice conditions. The best range for thick slicks is 2–5 mm (Buist et al. 2011).

Secondary pollution, time consuming, excessive energy, and increasing water temperature are the disadvantages of this method. The thickness of spilled oil is an important factor to choose this method for oil removal.

12.4.2 Chemical Agent

Chemical agents are synthetic materials that are able to change the surface tension or change the structure of oil molecules. These agents are used either alone or to improve other methods like skimmers. Herding, dispersant, and solidifier agents are familiar types of chemical agents that are used in oil removal processes.

Herding

The herding agents are used widely to clear and contract spilled oil in open water due to their high spreading coefficient and specific surface activity. These chemical materials, also called oil herders, form a monolayer on the surface of water and increase the tension of oil/water surface. Then the herders change the balance of interfacial forces and thicken the oil layer (Fig. 12.5).

Silicone-based, hydrocarbon-based, and fluorosurfactant-based are familiar types of herders. Laboratory experiments have proved that the silicone-based herders have the best performance followed by hydrocarbon-based and fluorosurfactant-based herders. In general, the herder can improve some oil removal processes like skimmers and in situ burning techniques.

In light ice conditions, the proper performance of booms is questionable, the challenging behavior of booms is contemplative. The small-scale and mid-scale experiments showed that the herded slicks ignited well in brush and slush ice conditions, even at 17 °C. In these ice conditions, the efficiency of burning was slightly less compared with open water. These results encouraged researchers to carry out meso-scale experiments with 630 L of Heidrun crude. The oil spreading lasted 15 min and thick slicks were reduced to 0.4 mm. After applying the herding agents, the agents contracted and thickened the oil slicks and caused high oil removal by burning (90%).

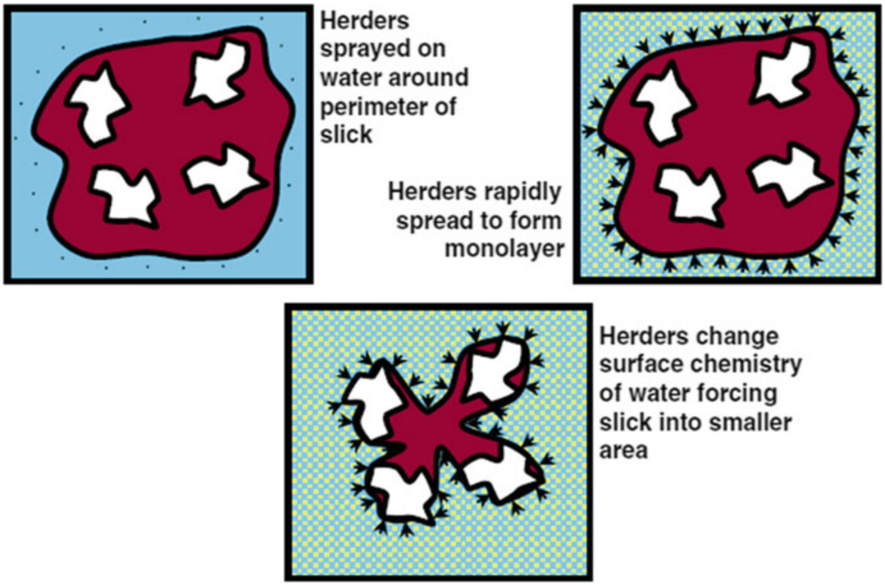


Fig. 12.5 Schematic of herder performance to contract and thicken spilled oil. Reprinted with permission of (*Herding surfactants to contract and thickenoil spillsin pack ice for in situ burning*, Buist et al., Elsevier)

Figure 12.6 shows the ice coverage, ice conditions, volume of crude oil (Alaska North Slope crude) and wind/wave effects on the in situ burn efficiency in small- and mid-scale testing by the hydrocarbon-based herder.

According to these results, the hydrocarbon-based herders had excellent performance in oil removal. The removal efficiency increased by increasing the crude volume but the ice conditions (brush and slush) did not have any notable impact on the oil removal by situ-burning. If the herders were applied before spreading oil, the oil slicks were thicker than using them after spreading oil. The gelatinization of hydrocarbon-based herder at low temperatures (below 0° C) was a fatal problem in cold weather, which was modified by changing the type or amount of solvent in herder formulation (Buist et al. 2011).

Despite all the abilities of these agents, the herders cannot be used in windy conditions because of the effect of breaking waves disrupting the herder layer. In addition, the frazil ice condition in very cold air temperatures has a detrimental effect on the performance of herders by decreasing thick slicks.

Dispersant

A mixture of surfactant and solvent is used to produce dispersant agent. Dispersants are the only option when the spilled oil cannot be collected or contained by other oil

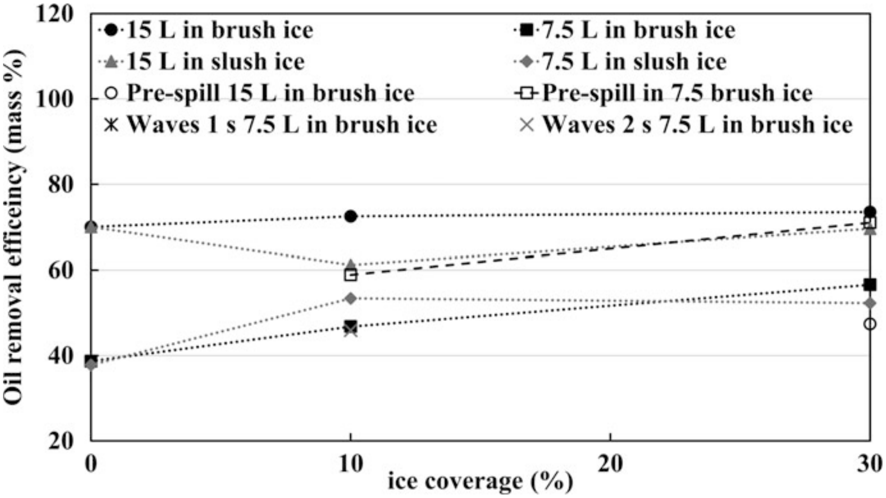


Fig. 12.6 The effect of the ice coverage, ice conditions, volume of crude oil and wind/wave on the in situ burn efficiency by the hydrocarbon-based herder. (Modified after Buist et al. 2011)

removal methods. These chemical agents are applied over the oil slicks in the form of aerosol and help the oil components to naturally break down their structure. Hereupon, the deformed oil compounds are able to connect with water molecule by chemical bond. Therefore, these agents prevent the spread of oil pollution over the surface of water and enhance the chance of microorganism degradation. In contrast to herding agents, dispersants decreased the surface tension between oil and water.

Second generation and third generation are two groups of the current dispersants. Second-generation dispersants, named conventional type, are produced with nonaromatic hydrocarbon solvents. The third generations, named concentrate type, are based on water or hydrocarbons that are facile to use (Putatunda et al. 2019). The application of dispersant agents has several advantages and disadvantages, which are discussed below.

One of the main problems with the use of dispersants to treat spilled oil is that these chemical agents have a disappointing performance on calm water. In these conditions, there is no mixing energy for prompt performance of agents. In optimistic insight, they will act with increasing sea agitation. But the persistence of dispersants on calm waters is a notable issue.

Lewis et al. (2010) investigated the persistence of dispersants during six days on static and flowing water and their performance after six days. They used Intermediate Fuel Oil 30 and Ewing Bank 873 crude oil with different thicknesses. Moreover, Corexit 9500 was used as dispersant with the dispersant–oil ratio 1:20. The results showed that thicker slicks (5 mm) dispersed completely after six days by being exposed to breaking waves (period of 30 min). Dispersants lost their dispersibility for thinner slicks (2.5 mm) and weathered oil after 2 days because of dispersant loss.

In other tests, dispersant loss was determined from crude oil slicks for two conditions: 43 h water soaked process with water current velocity 13 cm/s (sample I) and 91 h water soaked process with water current velocity 5–6 cm/s (sample II). Warren Spring Laboratory effectiveness was used to discuss about dispersant loss. In no-flow conditions by increasing time on the tank water surface, two soaked samples showed an initial increase in dispersibility because of increasing oil density, after which its rapid decline was observed due to surfactant loss. While in flow conditions, the dispersibility decreased with time (more rapid than no current conditions). The result of the different current speeds on dispersant loss also indicated that dispersion was faster and more complete for sample II than sample I.

They also studied the combined effects of thickness of oil slick and oil type on dispersant detriment in calm and flow conditions. The obtained results showed the important role of slick thickness in the dispersion potential. The 55 h soaked thick slick (5 mm) had higher dispersant effectiveness than 18 h soaked thin slick (2.5 mm), for the same oils.

The oil concentration and dispersant agents influence oil removal efficiency. The impacts on the removal of total petroleum hydrocarbons were investigated by Zahed et al. (2010). In initial concentrations of crude oil of 100, 500, 1000, and 2000, the removal efficiency of total petroleum hydrocarbons by dispersant were reported 67.3, 62.5, 56.5, and 44.7%, respectively. Without dispersant, the crude oil removal decreased to 64.2, 55.7, 48.8, and 37.6% for the mentioned oil concentrations. According to the presented results, the removal of crude oil increased by use of dispersant and decreased by increasing concentrations of crude oil.

Dispersant agents are able to effectively and quickly eliminate large volumes of oil compared with other removal methods but they have some limitations. They do not have an effective performance for high viscous oil (>2000 cSt), and thick layers of oil, which are formed in the low temperatures, weathering conditions, and mousse oil. On the other hand, these agents consist of different chemical materials, the presence of which causes environmental problems for marine creatures. In addition, dispersant spraying techniques require a greater understanding of the effective factors on their performance. For example, the wind can change the amount and position of dispersants during spraying with helicopter (Al-Majed et al. 2012).

Solidifier

Oil solidifiers (gelling agents) are dry granular materials that can be divided into two main groups: polymeric and low-molecular-weight solidifiers. The polymeric solidifiers are produced from high-molecular-weight polymers with porous matrix and large oleophilic surface area, which are able to physical contact with hydrocarbons. While the low-molecular-weight solidifiers are derived from amino acids, peptides, sugars, quaternary ammonium salts, metallic soaps, derivatized cholesterols, and hydrocarbons. To improve the solidification process, the combination of different types of solidifiers is recommended. These chemical agents increase the oil's viscosity and form a solid or semi-solid material and prevent oil release in the air and water.

Solidifiers are not toxic and float on water surface and remove easily unlike sorbents but their application is limited to confined spaces like near coastlines, while they are usable in rough sea conditions. The solidifier performance depends on operational conditions (temperature, agitation, and contact time between oil and solidifier) and oil properties (composition, viscosity, and surface area), especially the type and composition of spilled oil and slicks (Motta et al. 2018; Adebajo et al. 2003).

Delaune et al. (1999) investigated the effectiveness of granular solidifier to remediate South Louisiana crude oil in Coastal Wetlands. These researchers efforted to rectify the lake of solidifier's application in a large-scale spill. Over 70% of the crude was recovered by spraying solidifiers over the water surface. The solidified oil was very cohesive, firm, and with no fracture. The results emphasized that the granular solidifier can be used in a large-scale spill like open water with high removal efficiency and solidified oil can be easily removed by either hand or mechanical means.

To improve solidifier effectiveness at various environmental conditions, the effects of type of solidifier and oil and salinity of water were investigated (Sundaravadivelu et al. 2016b). In addition, some operational conditions like mixing energy, solidifier–oil ratio on the removal efficiency of solidifiers were discussed. Five solidifiers and three types of oil (Arabian light crude, Prudhoe Bay crude, and Intermediate Fuel Oil 180) were used in these experiments.

The results showed that the salinity of water had no effect on the oil removal. While an increase in the mixing speed from 0 to 60 rpm enhanced the removal efficiency for medium crude but the higher speed (120 rpm) had no benefit effect on it. The mixing speed did not change the removal efficiency for light and heavy crudes. The product type and solidifier–oil ratio had a significant effect on the solidifiers' performances. The removal efficiencies were about 80% for Arabian light crude and Prudhoe Bay crude crudes while it was 60% for Intermediate Fuel Oil 180 crude at 1:2 solidifier–oil ratios. In these conditions, the highest removal efficiencies were obtained for Waste-Set #3200® solidifier while Rubberizer had the lowest removal. Moreover, the best and worst performances were observed for Waste-Set #3200® and Rubberizer, respectively, at 1:8 solidifier–oil ratio.

In another study, the physical and chemical characteristics of 12 oil solidifiers were measured and correlated to define a good solidifier (Sundaravadivelu et al. 2016a). They observed the best removal performance for solidifiers with a carbonate group with a pore size >5 mm and bulk densities <0.3 g/cm^3. The polymeric solidifiers like Oil Bond, Waste-Set #3200, Rubberizer, and Imbiber Beads had up to 75% removal efficiency at 1:2 solidifier–oil ratio. The bulk density had a main impact on the removal efficiency so that the greatest removal efficiency was observed for the lowest bulk density solidifiers. Moreover, the solidifiers with small grain size were able to form a mat-like solidified oil, which was easily collected. Table 12.2 presents the summary of some researches, which have investigated the effects of properties of solidifiers and solidified oil on the solidifier's performance.

The efficiency of chemical agents is strongly influenced by operational conditions and oil properties. Sometimes, these agents are toxic to marine ecosystem as well as spilled oil. On the other hand, they have high oil removal efficiency and protect marine habitat by changing the chemical and physical properties of spilled oil.

Table 12.2 Summary of some researches for the effects of properties of solidifier and solidified oil on the solidifier's performance

Property	Explanation
Effectiveness [a]	Solidifier consumed for a unit of spilled oil
Rate of solidification [a]	Immobility speed of the solidifier for spilled oil
Phase selectivity [a]	Preference for oil over water
Water uptake [a]	Water uptake of the solidifier that may lead to sink of the solidifier
Oil recovery from final product[a]	Oil recovery from the solidified oil per unit of solidified oil
Buoyancy [b]	Ability of the solidifier to be buoyant on the surface of the water
Toxicity [b]	Solidifier concentration fatal to 50% of a test population
Biodegradability[b]	Capability of the solidifier to be degraded by biological activity
Mechanical strength [c]	Potential of the solidifier to remain intact under the influence of wind and water movement and have adequate mechanical strength to facilitate recovery
Retention of hydrocarbons[c]	Ability of the solidifier to retain volatile components of oils and avoid leaching

Solidifiers
[b] Solidifiers and solidified oil
[c] Solidified oil
Modified after Motta et al. (2018)

12.5 Sorbents

The sorbents are oleophilic and hydrophobic porous products that they sorb hydrocarbons and oil and repel water. The sorbents physically sorb oil by adsorption and capillary and sometimes both of these mechanisms. In oilsorption processes with sorbents, no chemical bonding occurs. The composition and structure of oilsorbents influence their oilsorption capacity. Generally, the oilsorbents are divided into natural, synthetic, and inorganic sorbents.

12.5.1 Natural Sorbents

Recently, growing public environmental concerns have led to more attention being paid to natural sorbents due to their minimal secondary pollution and toxicity. Significant capacity for oil removal compared to synthetic product, high biodegradability, environmental friendly, minimum secondary pollutions, low cost, low density, and some physical and chemical properties make them attractive as potential sorbent materials. Some organic natural sorbents were investigated such as vegetable fibers, cotton fiber, milkweed, kenaf, wool, straw, wood fiber, and so on.

Choi and Cloud (1992) compared the sorption capacity of milkweed floss, cotton fiber, polypropylene web, and milkweed/polypropylene web in the dry and wet (soaking in seawater) state. The experiments were performed with three crude oil

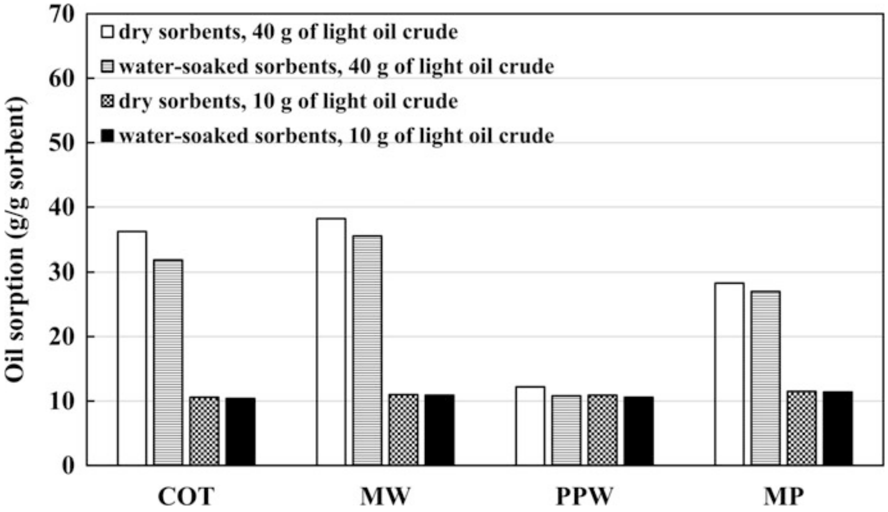


Fig. 12.7 Oilsorption capacity of dry and water-soaked sorbents in water bath with different amounts of light crude oil. COT: cotton fiber, MW: milkweed floss, PPW: polypropylene web, and MP: milkweed/polypropylene web. (Modified after Choi and Cloud1992)

samples and 1 g of sorbents in media with and without water. Due to wax content and void structure of milkweed, the results showed the greatest oil uptake for it (~40 g/g). Cotton fiber had lower capacity than milkweed but it had better sorption behavior than PPW or fiber. Figure 12.7 shows the oilsorption capacity of dry and wet with different amounts of light crude oil.

To investigate the highest sorption, the sorption environment was changed to oil bath. From the results it was concluded that the amount of sorbed oil in oil bath is higher than that in water bath and the sorption capacity is different for various crude oils (Fig. 12.8).

According to the results, milkweed and cotton had more ability to sorb oil than polypropylene web or fiber. Moreover, there was no change in sorption capacity of milkweed and cotton in water and oil baths. In comparison, the oil capacities of scoured cotton and milkweed decreased in oil and water bath. The removal of wax content of these sorbents can be the reason for this reduction. During the first recovery of oil from all sorbents except polypropylene web, approximately 90% of oil was removed after squeezing by two rollers. The reduction of oil recovery from the polypropylene (79–85%) was due to interaction between oil and polymer. Additionally, the results of the second and third compress showed that cotton, milkweed, and polypropylene can be used repeatedly. Finally, according to some disadvantages of two groups of sorbents, they suggested that the combination of natural sorbents with synthetic ones can be useful in the oil spill cleanup process.

Another study was performed by Choi et al. (1993) about partial or complete replacement of synthetic product by cotton nonwovens as oil sorbent. They investigated the effects of compactness of nonwovens, percentage of polypropylene in

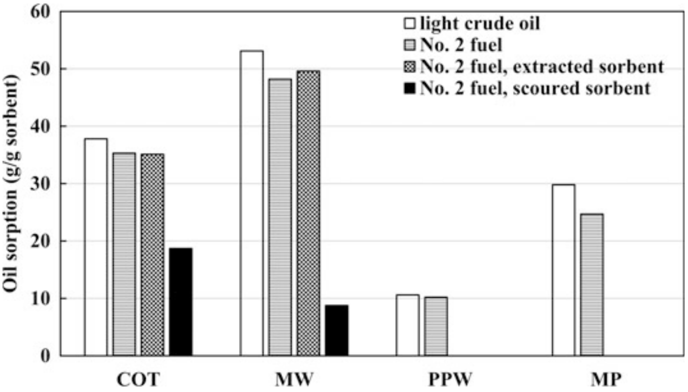


Fig. 12.8 Oilsorption capacity of sorbents in oil bath with different crude oils. COT: cotton fiber, MW: milkweed floss, PPW: polypropylene web, and MP: milkweed/polypropylene. (Modified after Choi and Cloud1992)

blend of cotton/polypropylene and the number of reuse on oil sorption capacity. They also presented detail information about sorption mechanism and kinetics of desorption for these sorbents. They found that cotton fiber sorb oil by adsorption and capillary in lumen, while there was no adsorption phenomenon for polypropylene, and capillary bridges between fibers controlled the oilsorption. The results showed that the amount of watersorption for 100% polypropylene nonwoven was higher than cotton-containing nonwovens (100, 80, 65, and 50% cotton). These sorbents were used several times to determine reusability. Initially, cotton had the greatest oilsorption capacity. But during reuse, it had poor performance with respect to the polypropylene. The results showed that as the amount of cotton increases in the nonwoven, watersorption increases during reuse.

The gravity desorption behaviors of 100% polypropylene and 100% cotton nonwoven were investigated during 5 min. For these sorbents, the rate of desorption was faster during the initial 2 min and changed with increasing the number of passes. The higher number of passes diminished the rate of desorption of cotton fiber and had no significant effect on the polypropylene nonwoven. In conclusion, Choi et al. (1993) emphasized that the cotton-containing nonwovens can be used instead of a synthetic sorbent like polypropylene.

Straw is also one of the natural sorbents that can be used for oil containment and cleanup of water. Monohydroxy alcohols, esters, and long chain fatty acids of wax layer of straw makes it hydrophobic. Adsorption and absorption are two main mechanisms for oilsorption by straw that depend on specifications of surface of stalk and leaf, respectively. The oleophilic property of straw was investigated by Witka-Jezewska et al. (2003) who analyzed contact angles. The contact angles of dry and wet barley straw were measured for water and decane. The results showed that dry straw remained oleophilic and absorbed oil, being in direct contact. Moreover, the contact angle of oil on wet straw was above 150°, which emphasized the oleophilic property of straw in aqueous environment. After 2 weeks, the

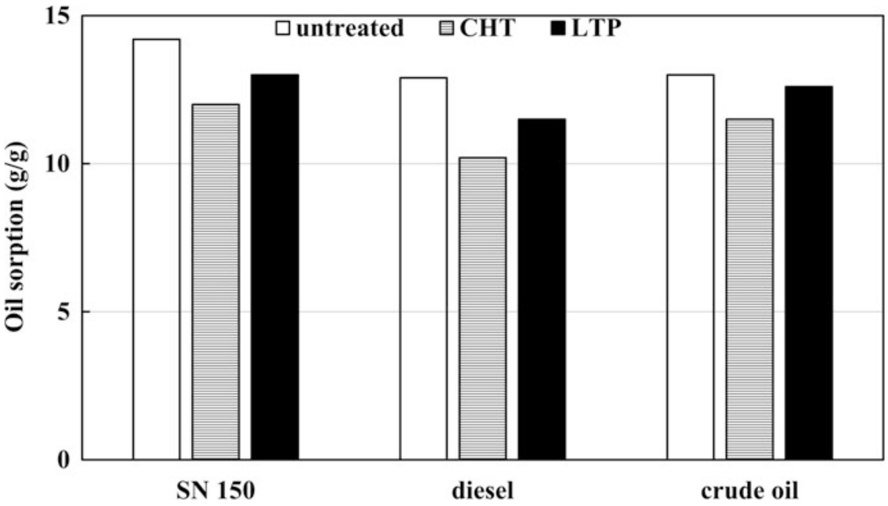


Fig. 12.9 Effect of treatment on sorption capacity of nonwoven wool fiber in artificial seawater bath containing 40 g of oil. CHT: chitosan and LTP: low-temperature air plasma. (Modified after Radetić et al. 2003)

microorganisms completely covered the whole surface of straw and the contact angle of oil on wet straw decreased to 60–70°, which made it hydrophilic. These results show that if straw is used for the oil cleanup, it should be replaced by fresh straw after 15 days because of decomposition of its natural wax.

Another natural sorbent, which has attracted the attention of researchers, is wool fiber. Sorption properties, reusability, and roughness of the recycled wool fibers persuaded Radetić et al. (2003) to study the possibility of replacing synthetic sorbents with wool fiber. They used SN 150, diesel, and crude oil for their experiments. All investigations about wool sorption capacity were performed during a time span of 10 min. The results indicated that amount of oilsorption of the nonwoven rises by increasing the content of oil in samples in the following order: SN 150 > diesel > crude oil. These results show that the sorption behaviors of various oils are different because of their different viscosities.

The sorption behavior of the dry and water-soaked sorbent showed that dry samples had better sorption than wet samples. Figure 12.9 compares the sorption behavior of treated and untreated samples. Treated samples are provided by chitosan and low-temperature air plasma processes. Sorption properties were significant for low-temperature air plasma-treated samples especially in the case of crude oil. In oil bath without any water, the sorption capacity of material was slightly higher.

Recycled wool fibers have different sorption behaviors from raw wool because of the mechanical and chemical changes during reuse. Nature of lanolin and wax of raw wool play a major role in adsorption of oil. Different sorption behaviours are not expected for recycled wool fibres, due to small amount or lack of wax and lanolin or a small mount.

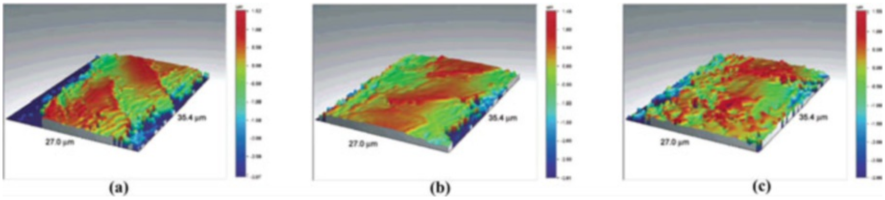


Fig. 12.10 White light scanning interferometry analysis pictures of (**a**)untreated, (**b**) LTP-treated, and (**c**) CHT-treated samples. CHT: chitosan and LTP: low-temperature air plasma. Reprinted with permission of (*Recycled wool-based nonwoven material as anoilsorbent*, Radetić et al.,ACS Publications)

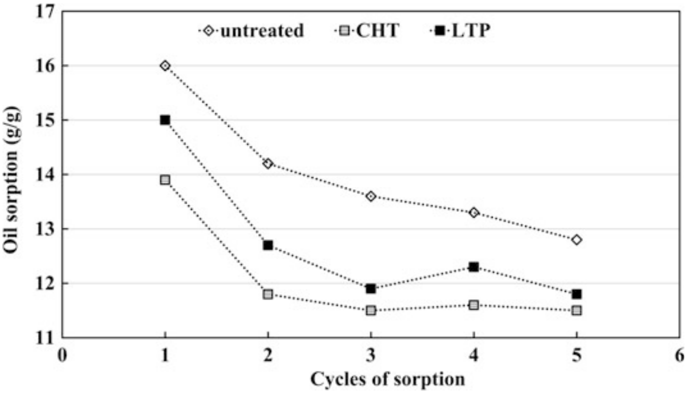


Fig. 12.11 Reusability of untreated, CHT-treated, and LTP-treated nonwoven wool samples for SN 150. CHT: chitosan and LTP: low-temperature air plasma. (Modified after Radetić et al. 2003)

According to the white light scanning interferometry analysis pictures in Fig. 12.10, chitosan-treated sample has the flattest and smoothest surface. The depth of valley analysis pointed that low-temperature air plasma treatment increases the specific surface area and roughness compared to samples without treatment. The good sorption of low-temperature air plasma-treated samples can be explained by these analyses. Thus, an adsorption process by physical trapping governs the oilsorption of low-temperature air plasma-treated samples.

In addition, construction of materials has inevitable impact on the sorption process. The results of adsorption behavior showed that loose fibers have more favorable performance than nonwoven material. Sorption capacities of loose fibers were 103.74 and 111% more than that of nonwoven one for SN 150, diesel, and crude oil, respectively. Finally, the reusable sorbents were studied by comparison of sorption capacity for SN 150 after five cycles. As seen in Fig. 12.11, the sorption capacities decrease with increasing the number of cycles, but are enough for oil separation. Oil removal was performed by squeezing between rollers. This research indicated that recycled wool nonwoven sorbents can be effective in oilsorption processes.

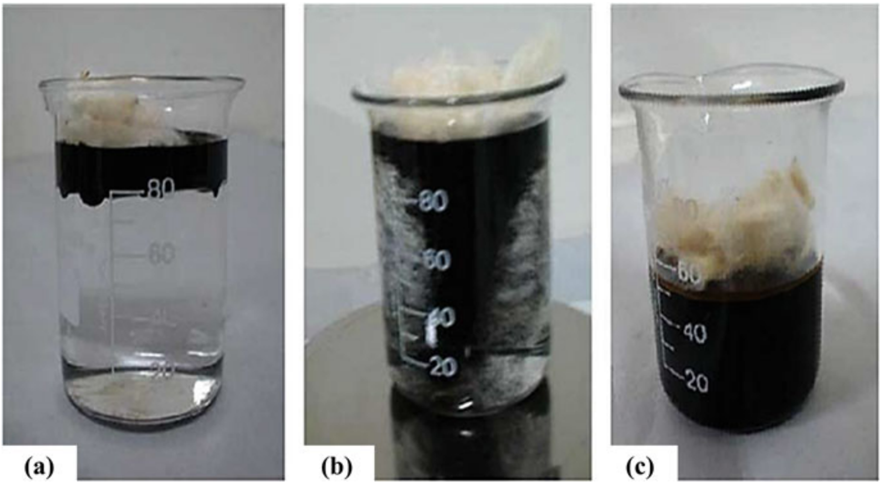


Fig. 12.12 (**a**) Static system, (**b**) dynamic system, and (**c**) dry system after placement of fibers on the oil surface at room temperature. Reprinted with permission of (*Experimental investigation of various vegetable fibers as sorbentmaterials foroil spills*, Annunciado et al. Elsevier)

Hydrophobicity, specific gravity, and buoyancy of sorbents are the effective parameters on the oilsorption capacity. The various vegetable firers are taken into consideration because of favorable sorption, oleophilic properties, affordable, low density, and environment friendly. For this purpose, leaves residues, wood shavings, sisal, coir fiber, *Luffa aegyptiaca* and silk-floss were evaluated by Annunciado et al. (2005). For sorption experiments, they used mixture of crude oil and water (deionized and marine) and experiments were performed with and without agitation. The evaluation of water uptake was performed by weight difference and distillation of sorbents. Figure 12.12 shows the different systems used in tests.

The mean specific gravity of fibers revealed that leaves residues, sisal, coir fiber and wood shavings are weightier than water unlike *Luffa aegyptiaca* and silk-floss, which obviously influences their buoyancy in water. At first, different granulometry ranges of sorbents were used for 60-min experiments. The results indicated that the reduction of size from 3.35 mm to 0.85–1.70 mm increases the oilsorption up to 205%. As a result, the sorption capacity depends on specific surface area. In static and dynamic systems, the sorption ability of sorbent was in the following order: silk-floss > sisal > wood shavings > coir fiber > *Luffa aegyptiaca* > leaves residues. The sorption of all fibers also increases by time increment. The poor sorption performance of the mixed leaves indicated that this sorbent is not the suitable sorbent. Silk-floss had the best performance on the sorption test due to its cotton-like nature. Table 12.3 provides the sorption results of silk-floss fiber in dry, static, and dynamic systems. According to the results of experiments during 24 h, silk-floss sorbs about 80% of oil in initial 5 min.

In static system, water uptake of silk-floss varied between 6.3 to 2.5% (compared with dry system) at 5–1140 min, respectively. The sorption of dynamic system was

Table 12.3 Comparison of sorption capacity of silk-floss in different systems

Sorption time (min)	Dry system	Static system			Dynamic system	
	A Oilsorption (g/g)	B Sorption (g/g)	C Water uptake Weight difference (g)	D Water uptake by distillation (g)	E Sorption (g/g)	F Water uptake by distillation (g)
5	73.9	78.8	5.0	2.7	68.7	2.0
20	75.2	79.2	3.9	–	72.9	–
40	79.5	83.9	4.4	–	74.5	–
60	81.0	85.2	4.3	3.5	77.6	2.7
1440	84.9	87.1	2.2	2.7	85.8	2.3

Modified after Annunciado et al. (2005)

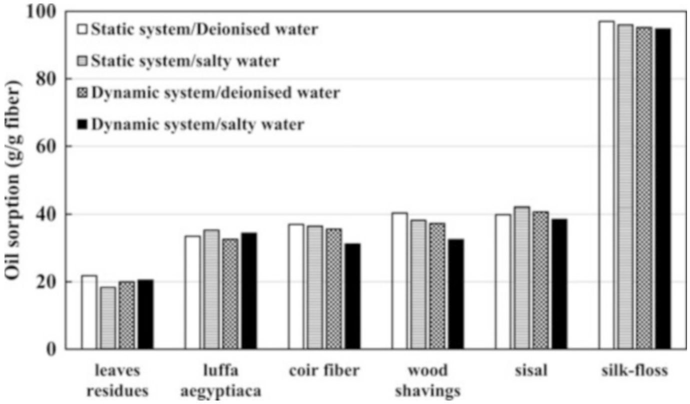


Fig. 12.13 Oilsorption capacity of different fibers at 60 min sorption in static and dynamic system with different water conditions. (Modified after Annunciado et al. 2005)

lower than dry system before 60 min, but after that the sorption was higher. The agitation and frequent water–fiber contact can be the reason of this sorption behavior. Therefore, water and agitation can decrease the oilsorption capacity. In deionized and marine water, silk-floss showed the highest hydrophobicity (around 98%) and sisal and *Luffa aegyptiaca* had the opposite behavior (0% hydrophobicity). The sorption capacities of fibers in various systems are shown in Fig. 12.13.

In total, there is no significant difference between oilsorption of systems with different water conditions, and silk-floss showed the best sorption. Finally, the buoyancy results indicated that silk-floss and sisal had the highest and lowest buoyancy, respectively. The leaves residues and the coir fiber had better performance in marine water than deionized water, whereas sisal, *Luffa aegyptiaca*, and wood shavings had approximately the same buoyancy in different water conditions.

Table 12.4 Experimental results of oil uptake capacities (g/g sorbent) and recovery yields (%) for different sorbents and pollutants. LCO: Light crude oil, GO1: gas oil No. 1, GO2: gas oil No. 2 and HCO: heavy crude oil

Oil pollutant	Sorbent Results	Bagasse Mesh 14–18	Bagasse Mesh 18–45	Polypropylene nonwoven[a]	Rice hull Mesh 10–14
LCO	**Oiluptake**	3.38	5.55	8.26	3.80
	Recovery yield	100.00	93.13	87.70	94.60
GO1	**Oiluptake**	4.01	5.22	7.60	3.70
	Recovery yield	97.75	91.51	94.27	90.29
GO2	**Oiluptake**	4.07	5.39	8.46	3.81
	Recovery yield	94.23	94.53	94.54	92.99
HCO	**Oiluptake**	5.30	5.54	9.12	5.15
	Recovery yield	100.00	96.70	95.67	96.00

[a] Thickness: 5.59 mm, Denier: 12.56, and Mass per area: 593.3 g/m^2

Modified after Bayat et al. (2005)

Rice hull and bagasse were also compared with polypropylene nonwoven web. The sorption capacity and oil recovery of these sorbents were investigated experimentally (Bayat et al. 2005). Light crude oil, gas oil No. 1, gas oil No. 2, and heavy crude oil were used as pollutants. The effect of specific surface area was investigated using two mesh sizes of rice hull and bagasse. In order to easy collect and remove rice hull and bagasse, they were wrapped into a hydrophobic cloth. Whereas, polypropylene nonwoven web was without cloth and floated on the simulated sea water. One gram of sorbent was added to the system containing varying amounts of pollutants (10, 20, and 30 g) and 400 ml of simulated seawater. Table 12.4 represents the oil uptake capacity of different sorbents and their recovery yields.

The results revealed that each gram of polypropylene nonwoven can sorb 7–9 g of different pollutants and has the best oilsorption capacity. Bagasse with mesh 18–45 sorbs oil greater than bagasse with mesh 14–18 and rice hull with mesh 10–14. But these sorbents showed a better performance for heavy crude oil than other oils. The important impact of the viscosity of oils on the sorption behavior was apparent. An increase in the viscosity decreases the oilsorption capacity. On the other hand, low viscous oil removed faster from sorbents. The results of recovery indicated that the oil recovery was greater for 14–18 mesh bagasse than that for 18–45 mesh due to the higher specific surface area. The recovery of heavy crude oil was greater than those of other oils. Polypropylene nonwoven web had the lowest recovery efficiency for light crude oil.

According to these results, all adsorbents have good performance in oil cleanup from seawater and polypropylene nonwoven is the best one. But rice hull and bagasse showed good oilsorption and recovery, indicating that these natural sorbents could be a viable alternative choice instead of synthetic products.

In conclusion, natural sorbents are biodegradable, low cost, and can be burned as fuels. In summary, natural oilsorbents have some deficits like poor recyclability and adequate floatability, while, there is growing regard for use of natural sorbents because of their eco-friendly behavior.

12.5.2 Synthetic Sorbents

Nowadays, fabrication of superoleophilic and superhydrophobic surfaces as oilsorbents has attracted a lot of attention. These porous materials have a significant oilsorption capacity, high floatability, low surface energy, and good reusability. They have some shortcomings like expensive, complex and time-cost fabrication process, and environmental incompatibility. In the following, the performance of some types of synthetic sorbents and their limitations are explained.

Nanofibers

Nanofibers are hydrophobic–oleophilic surfaces, which are able to trap the spilled oil inside of their porous structures and transfer liquid oil to a semi-solid structure. Nowadays, consideration has been given to the development and use of nanofibers based on their good hydrophobicity–oleophilicity, physical and mechanical properties, low surface energy, good buoyancy, high surface area, small pore size, and high uptake capacity. Melt bowling, force spinning, electrospinning, and bicomponent spinning are the common methods to produce polymeric nanofibers. Figure 12.14 shows the melt-blowing process device, the bicomponent spinning machine, and the centrifugal spinning device, which were used in some researches.

Electrospinning is used widely as an efficient and typical procedure for fabricating polymeric nanofibers with micro and nanoscales using various materials. An ordinary electrospinning process is illustrated in Fig. 12.15. Liquid polymer transfers to a needle by a syringe pump. The polymer globule surface changes to the Taylor Cone due to high voltage of needle. A spurt of melt polymer, which errupts from the needle, moves through the air and forms the polymer fibers. The safety of operators of the electrospinning apparatus is the most important concern. Inhalation of nanofibers, high voltage, and evaporation of solvent are disturbing issues.

Surface morphology, porosity, diameter, voids among the fibers and surface tension influence the behavior and oilsorption capacities of the nanofibers. The rough surface of the fibers can enhance the oiladsorption. Porous nanofibers are capable of adsorbing oil due to specific surface area. On the other hand, the high porosity and small diameter of the fibers increase the capacity of oilsorption. As the

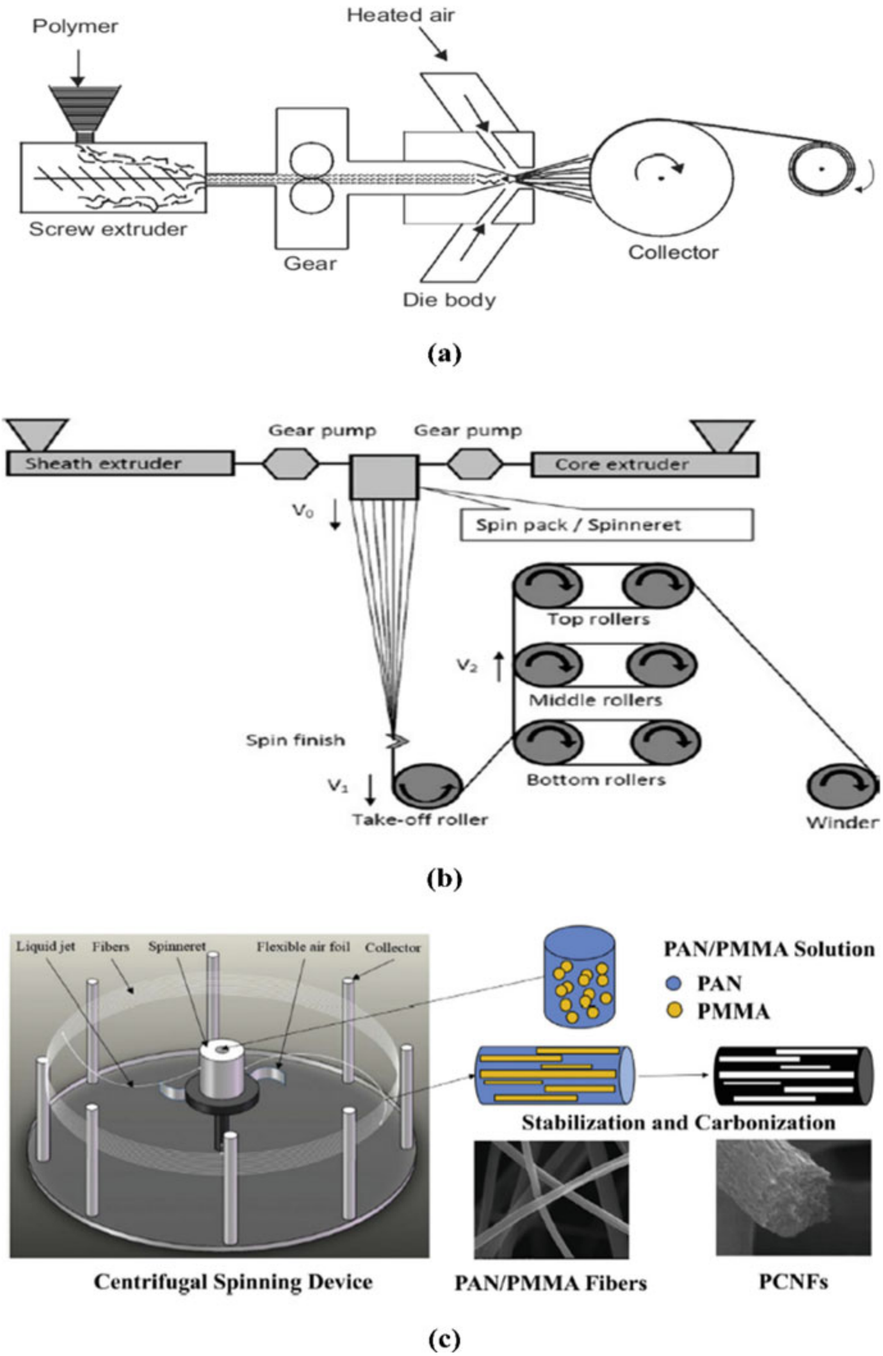


Fig. 12.14 Schematic of (**a**) the melt-blowing process device. Reprinted with permission of (*Textile materials and structures for topical management of wounds*, Gupta and Edwards 2019, Elsevier). (**b**) The bicomponent spinning machine. Reprinted with permission of (*Piezoelectric polymeric bicomponent fibers produced by melt spinning*, Lund et al. 2012, Wiley Online Library).

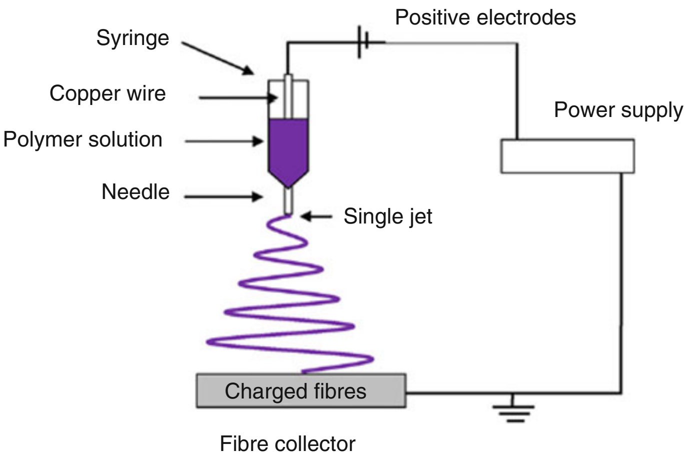


Fig. 12.15 Typical electrospinning process to fabricate polymeric nanofibers. Reprinted with permission of (*A review of polymer nanofibres by electrospinning and their application inoil–waterseparation for cleaning up marineoil spills*, Sarbatly et al., Elsevier)

diameter increases, the sorption rate decreases because of the large void space between fibers. Also, hydrophobicity and oleophilicity characteristics of surface are determined by the surface tension. The favored solid surface for oilsorption has the surface energy similar to that of oil.

Adsorption and capillary action control the oilsorption mechanism of the fibers. Capillary mechanism traps oil on the its surface physically (adsorption) and fills the void spaces between fibers with the van der Waals forces. Table 12.5 presents the sorption capacity of different fibers with various oils. The sorption performance of these sorbents is affected by oil viscosity, surface tension of fabric sorbents, specific surface area, floatability, oil retention time, contact angle of sorbent, viscosity of the spinning solution, kinetic of oilsorption, and pH of environment. Table 12.6 summarizes the effective factors on the oil removal efficiency.

The high viscous oil may have two opposite effects on the oilsorption capacity of fibers. The adsorption of oil increases by adhering the oil to the surface of fiber, whereas the capillary of the oil becomes difficult due to the high viscosity. Additionally, oil thickness has positive effects on the sorption performance. The acceptable oil-water selectivity decreases the water collection and mass of sorbents in the oil spill site. The oil selection of fabric sorbents can be changed by specific surface area. Moreover, the high porous structure increases the oilsorption capacity by retaining the oil in the voids of fibers.

Fig. 12.14 (continued) (**c**) The centrifugal spinning device for preparation of polyacrylonitrile (PAN)/ poly-methyl methacrylate (PMMA) precursor and porous carbon nanofibers (PNFs). Reprinted with permission of (*Centrifugal spinning: a novel approach to fabricate porous carbon fibers as binder-free electrodes for electric double-layer capacitors*, Lu et al. 2015, Elsevier)

Table 12.5 Sorption capacity of different fibers with various oils

Material type	Adsorption capacity (g/g)	
	System with only oil	Water–oil mixture
Polyvinyl chloride–polystyrene fibers	Engine oil: 146 Peanut oil: 119 Ethylene glycol:81 Diesel: 38	Engine oil: 149 Peanut oil: 107 Diesel: 37
Polystyrene fibers	Engine oil: 84.41 Sunflower seed oil: 79.62	Not applicable
Polystyrene fibers	Not applicable	Engine oil: 113.87 Bean oil: 111.80 Sunflower seed oil: 96.89
Composite polystyrene–polyurethane mat	Not applicable	Engine oil: 64.40 Sunflower seed oil: 47.48

Modified after Sarbatly et al. (2016)

The surface roughness of the fibers has an influence on the oiladsorption capacity based on its effects on the pore, the pore size distribution, and the contact angles of oil and water. Fibers with hierarchical roughness have low oil contact angles and high water angles. Nevertheless, surface roughness of fibers has less impact than pore size of fiber. Therefore, oilsorption capacity of small-diameter porous fibers with smooth surface are greater than that of large-diameter porous fibers with rough surface.

Small-diameter and high porosity also reduce fiber's density, which favors the buoyancy property. High buoyancy, low density, small diameter, and high porosity provide a high oilsorption capacity for the fibers. The oil retention behavior of the fibers depends on the porosity. The oil retention of high porosity fibers is less than that of lower porosity fibers. The fibers with different porosity structures have different oilsorption kinetics.

Whole oilsorption process depends on contact time, except oilsorption process of nonporous fibers (which is a constant process). For natural corn fibers, the kinetics of the oilsorption process has a second-order equation. There is not enough information about the oilsorption kinetics of various fibers and needs more study. Tearing, deterioration, and crushing influence the number of effective reuse cycles of fibers. Compression techniques are widely used for oil removal from the fibers. But irreversible changing and undermining of their inner structure decreases the oilsorption capacity. For instance, the oilsorption capacity of polystyrene–polyurethane decreased after two reuses. Therefore, tensile strength of the fibers is important.

Some studies have confirmed that the combined fibers had better sorption performance. Polystyrene–polyurethane fiber exhibits excellent reusability due to its resiliency and strength. In addition, durability at the pressure applied during the reuse process is an important characteristic because of its influence on the

Table 12.6 The factors affecting the oil removal efficiency

Material type	Factor affecting	Value
Polystyrene Polystyrene/ polyurethane	Oil viscosity	Engine oil: 270 $\mathrm{mPa.s}^{-1}$ Sunflower seed oil: 50 $\mathrm{mPa.s}^{-1}$
Polystyrene	Surface tension of oil	Peanut oil: 23.17 $\mu\mathrm{Nm}^{-1}$ Silicon oil: 19.61 $\mu\mathrm{Nm}^{-1}$ Engine oil: 23.53 $\mu\mathrm{Nm}^{-1}$ Diesel oil: 24.39 $\mu\mathrm{Nm}^{-1}$
Polyvinyl chloride/ polystyrene	Oil–water selectivity	1000 times higher than polypropylene fibers
Polystyrene	Specific surface area	Polystyrene 50.64 $\mathrm{m}^2\mathrm{g}^{-1}$
Cellulose acetate (modified) Polystyrene	Surface roughness	Ra ranges from 4 to 1.44 Ra for fiber with smooth surface: 9.26 μm Ra for fiber with rough surface: 21.98 μm
Polyvinyl chloride/ polystyrene	Sorbent buoyancy	Sorbent stay afloat after 60 min in static and dynamic system
Polystyrene/ polyurethane	Oil retention time	0–60 min
Polystyrene Polystyrene (modified) Cellulose acetate (modified)	Contact angle	Water contact angle: 151.3° ± 1.6° Engine oil contact angle: 0° Water contact angle: 155° ± 3° Diesel oil contact angle: 0° Water contact angle: 161° Oil (dichloromethane) contact angle: 3°
Polystyrene Polystyrene/ polyurethane	Spinning solution viscosity	190–73.5 $\mathrm{mPa.s}^{-1}$ 0.265–15 pa.s
Corn straw	Sorption kinetic	Second-order equation
Cellulose acetate (modified)	pH	pH range 2–14

Modified after Sarbatly et al. (2016)

hydrophobicity characteristic. The polystyrene nanofiber membrane has excellent durability and flexibility at pressure lower than 10 kPa.

Lin et al. (2013) represented an improved electrospun fiber that had oil sorption capacity more than that of conventional polypropylene fibers. Strength and resilience of electrosun fibres are reduced during oil sorption process and their recovery. This problem was fixed by the core–shell configuration of fibers via coaxial electrospinning to provide improved sorbent.

They used polystyrene and polyurethane as the shell and core solution, respectively. The oilsorption ability of polystyrene–polyurethane fiber was investigated by use of engine oil and sunflower seed oil. The spinning voltages, solvent compounds, and core solution concentrations influenced fiber morphology and its structure. Moreover, the effects of the specific surface area and structure of as-prepared fiber on the oilsorption capacity, the oil retention, reusability, and resiliency were

Table 12.7 The specific surface area, total pore volume and average pore width of the electrospun composite polystyrene–polyurethane fibers in various applied voltages, solvent composition, and core solution concentration. PU: polyurethane, DMF: N, Ndimethylformamide, and THF: tetrahydrofuran

Samples	Applied voltage (kV)	Core solution concentration (wt% PU)	Solvent composition (DMF:THF)	Specific surface area[a] (m^2/g)	Total pore volume[b] (cm^3/g)	Average pore width[c] (nm)
A	20	100	1:4	6.10	0.043	29.27
B	25	100	1:4	10.99	0.109	37.91
C	25	75	1:4	15.02	0.120	34.37
D	25	50	1:4	19.57	0.139	24.47
E	25	50	1:3	18.43	0.138	28.25
F	20	50	1:0	15.72	0.114	27.79

[a] Specific surface area was calculated by the Brunauer–Emmett–Teller (BET) method

[b] Total pore volume was calculated by the Barrett–Joyner–Halenda (BJH) method from the desorption branch of nitrogen physisorption isotherm

[c] Average pore width indicates BJH desorption average pore width

Modified after Lin et al. (2013)

investigated. Oilsorption capacities (g/g) were measured at 25 °C in oil–water bath (formed by 150 ml water and 20 g oil) with 0.1 g of as-prepared sorbent.

The composite polystyrene–polyurethane fiber possesses the porous structure range 20–80 nm. This three-dimensional structure showed good hydrophobicity–oleophilicity properties with high oilsorption capacity. The applied voltages affect the structure and stretch of as-prepared sorbent. It was noticeable that the polystyrene–polyurethane fibers, which formed at higher voltage, possess a high porous surface and stronger stretching action. Table 12.7 gives the impact of voltage, concentration, and composition of solvent on the specific surface area, volume of pores, and width of the electrospun composite polystyrene–polyurethane fibers.

Figure 12.16 shows amount of oilsorption of these fibers. As one can see from Fig. 12.16, the sample B has the highest oilsorption capacity for engine oil and sunflower seed oil. It is obvious that the inter-fiber voids among the fibers have major impact on the oilsorption capacity than the intra-fiber porosity. The results of engine oil retention of sample A and polypropylene fibers indicated the same trend for two sorbents. The oil release rate was very high in the initial 10 min and after that decreased to achieve steady state. In addition, the polypropylene fibers had more oil retention ability than the composite polystyrene–polyurethane fibrous mats because of their low porosity.

Figure 12.17 illustrates the results of the oilsorption capacity of sample A after five reuses for engine oil.

As can be seen, the oilsorption capacity decreased after first squeezing sorbent. Nevertheless, the oilsorption capacity after five cycles is greater than that of wool sorbents in previous studies. In some cases, polymeric nanofibers were applied to create a superhydrophobic–superoleophilic surface. Lee et al. (2013) achieved the superhydrophobic–superoleophilic stainless steel mesh using one-step deposition of

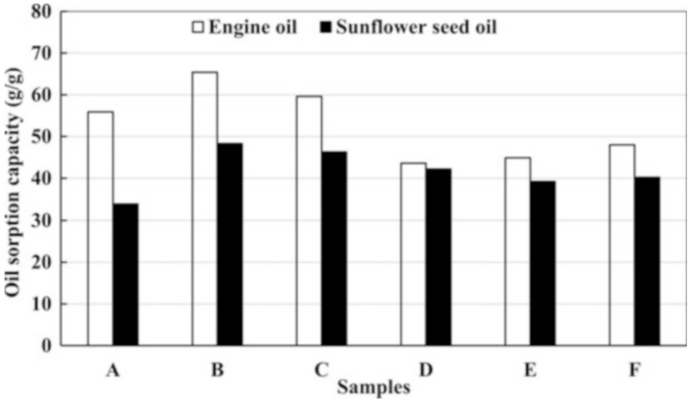


Fig. 12.16 The oilsorption capacity of the polystyrene–polyurethane fibrous mats (properties of A-F samples are presented in Table 12.7) for engine oil and sunflower seed oil. (Modified after Lin et al. 2013)

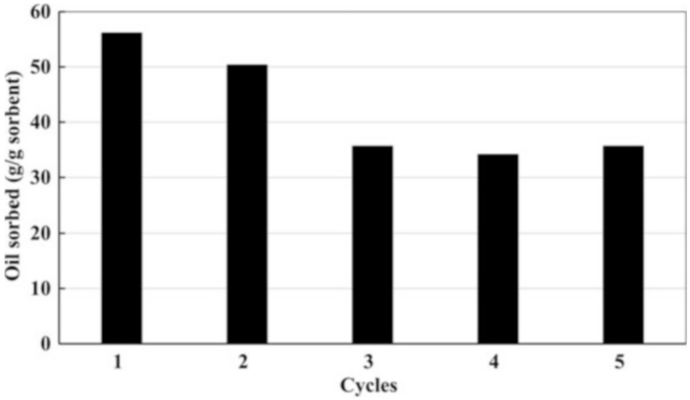


Fig. 12.17 The impact of reuse cycles on the oilsorption of the polystyrene–polyurethane fibrous mat (sample A, its properties are presented in Table 12.7) for engine oil. (Modified after Lin et al. 2013)

PS onto it by electrospinning. Ability of the polystyrene nanofibers for oil–water separation was investigated for low viscosity oil, namely, diesel, gasoline, and mineral oil. Figure 12.18 shows the detailed information on fabrication process of polystyrene nanofibers, the scanning electron microscope pictures of the polystyrene nanofiber with low and high magnifications, oil and water contact angles, and the real scale of the stainless mesh.

The superhydrophobicity and superoleophilicity depend on the porous structure of polystyrene nanofibers. The results of wetting behavior of porous and nonporous structures indicated that the water contact angle decreased in the absence of the pores. The uncovered stainless steel was soaked by oil and water unlike nanofiber membrane. The nanofiber was wetted by diesel oil faster than uncovered stainless

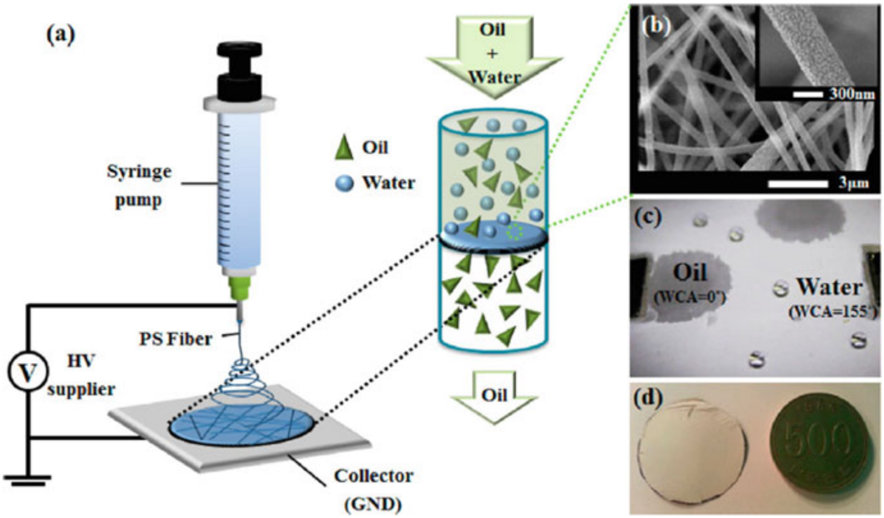


Fig. 12.18 (**a**) Schematic of the electrospun membrane fabrication process, (**b**) scanning electron microscope images of the polystyrene nanofiber membrane with low and high magnifications, (**c**) superoleophilic and superhydrophobic behavior of the polystyrene nanofiber membrane, and (**d**) the real scale of polystyrene nanofiber membrane attached to the stainless mesh. Reprinted with permission of (Electrospun polystyrene nanofiber membrane with superhydrophobicity and superoleophilicity for selective separation of water and low viscous oil, Lee et al., ACS Publications)

steel mesh, which shows superoleophilicity. The results of experiments in Fig. 12.19 confirmed the superhydrophobicity and superoelophilicity properties. As one can see, low water adhesion of the membrane prevents water permeation.

The results of oil-water separation showed that the membrane had approximately 100% separation efficiency in nonsevere conditions. Application of membrane under severe conditions was investigated by the injection pressure of 3 ml water and 5 mL oil, which passed through the membrane. The setup of oil–water separation experiments with diesel oil is illustrated in Fig. 12.20.

According to the results, the oil permeated through the membrane due to its superoleophilicity and accumulated in the box until $t_{inj} = 100$ s, while water did not permeate the membrane. However, there is a serious problem with the pressure of water, which deformed the membrane in $t_{inj} \geq 20$ s. They also studied the effect of different thicknesses of the PS nanofibers membrane on the separation capability and concluded that the thicknesses did not affect the separation.

Sponges

A sponge has a porous structure and can be made of polyester, polyurethane, or vegetal cellulose. Owing to the low density, high sorption capacity, good elasticity,

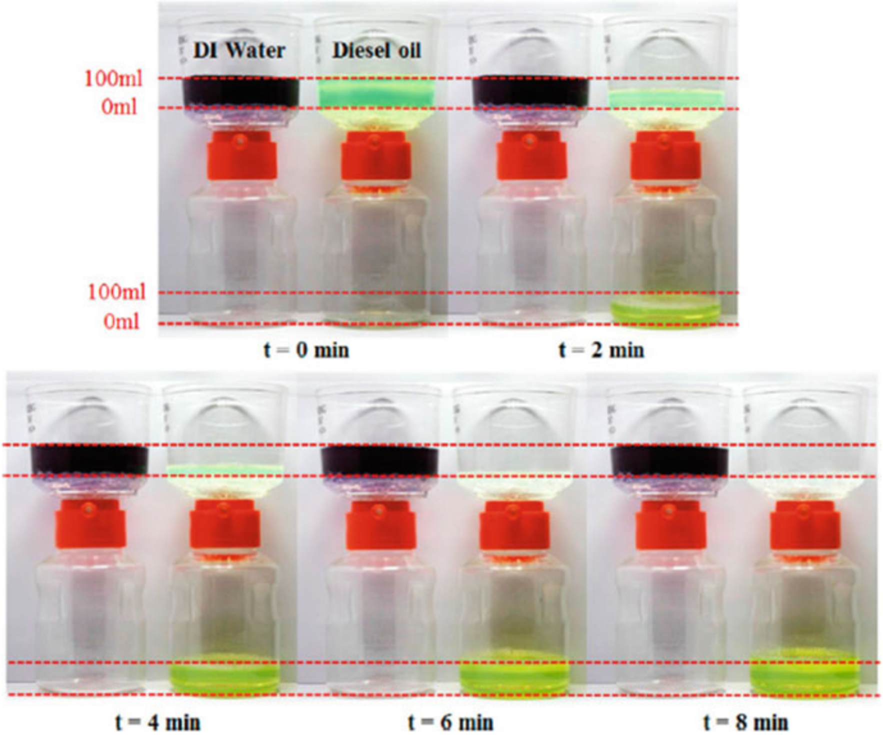


Fig. 12.19 The superoleophilic and superhydrophobic behavior of the membrane at 0, 2, 4, 6, and 8 min of experiment. The left samples show the nonpermeable nature of the membrane for double distilled, deionized (DI) water (black liquid). The right samples show the permeable nature of the membrane for diesel (lemon liquid). Reprinted with permission of (Electrospun polystyrene nanofiber membrane with superhydrophobicity and superoleophilicity for selective separation of water and low viscous oil, Lee et al., ACS Publications)

and easy fabrication, sponges are considered an alternative choice for oil removal. Despite all these specifications, the sponges are hydrophilic and simultaneously sorb oil and water, which makes them inoperative for oilsorption process. Hence, researchers have reported several methods to develop them into high- or superhydrophobic surfaces with high oil removal efficiency. Rapid deformation by mechanical squeezing is another disadvantage of original sponge, which needs to be improved in order to be used in oilsorption process.

Zhu et al. (2011) fabricated a superhydrophobic and -oleophilic surface with polyurethane sponge for sorption of various oils and organic solvents from the water surface. Electroless deposition method was applied to coat the sponge with a film of copper and then it was modified using solution-immersion process. The improved sponges sorbed the oils very quickly while repelling water completely. The sponges showed good stability in reuse process for many cycles and in corrosive conditions.

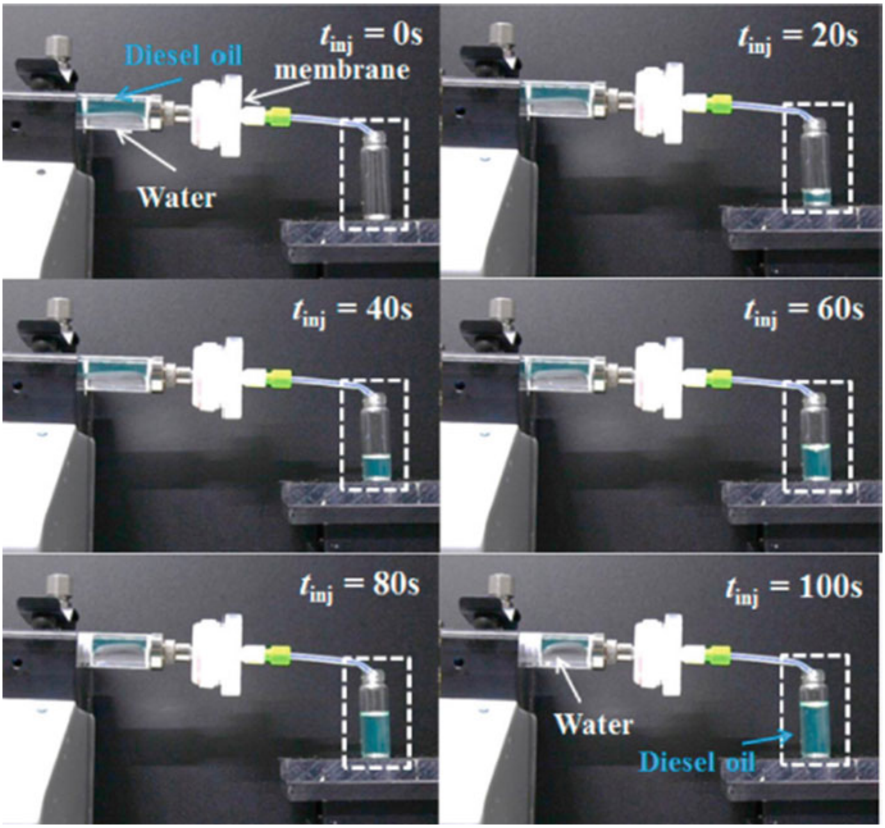


Fig. 12.20 The setup of oil–water separation experiments by a syringe pump using deionized water and diesel oil. The flow rate was constant, 2 ml/min for water and oil. t_{inj}: time of injection. Reprinted with permission of (Electrospun polystyrene nanofiber membrane with superhydrophobicity and superoleophilicity for selective separation of water and low viscous oil, Lee et al., ACS Publications)

Figure 12.21 illustrates the scanning electron microscope images with low and high magnifications of original and copper-coated sponge.

Figure 12.21 (a) and (b) reveal that the copper film changed the smooth structure of the original sponge. The results of contact angle confirmed that the improved sponge is superhydrophobic and superoleophilic and the water contact angle was higher than 170°. The as-prepared sponge floated in water bath while original sponge sank. When the improved sponge was immersed in water, it did not uptake water and immediately floated after releasing the force.

The oilsorption capacities of the as-prepared sponges are shown in Fig. 12.22 for lubricating oil, octane, decane, and dodecane after 1, 5, and 9 recycles. From the obtained results, it is revealed that the as-prepared sponge is capable of sorbing

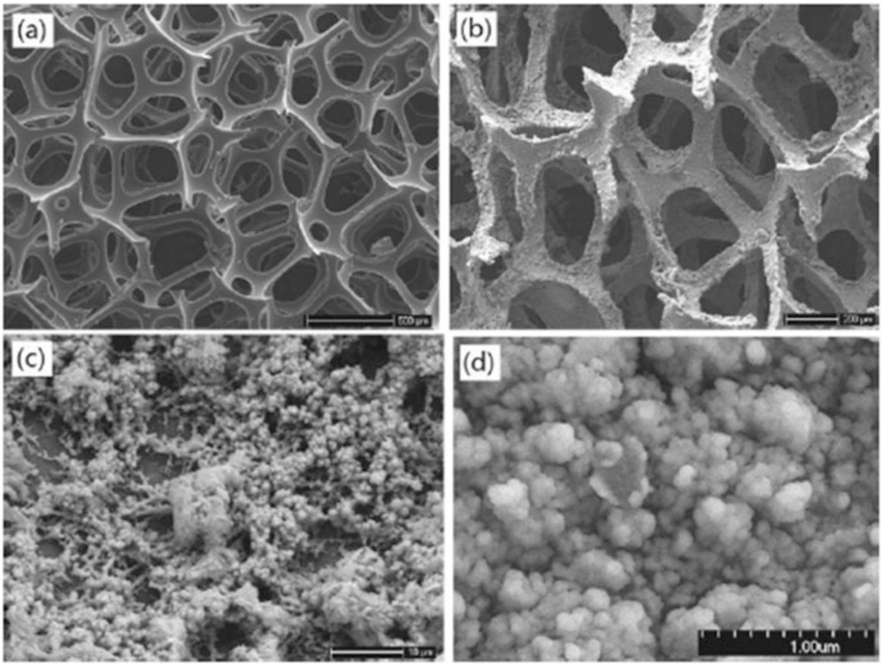


Fig. 12.21 Scanning electron microscope images of the sponge before (**a**) and after (**b**) copper coating with low magnification. (**c**) and (**d**) are high magnification of the scanning electron microscope images of as-prepared sponge. Reprinted with permission of (Facile removal and collection of oils from water surfaces through superhydrophobic and superoleophilic sponges, Zhu et al., ACS Publications)

different oils more than 13 times its weight. The recovered sponges still kept high sorption capacity.

Aerogels

Aerogels are produced with a gel base, where the liquid is replaced in the gel structure by air. The result is a solid three-dimensional structure, large specific surface area, high floatability, large open pores, extremely low density, and high porosity. Based on these ideal characteristics, aerogels have potential as good sorbents to sorb large amounts of spilled oil. Various materials can be used for aerogels production like carbon, silica, polymer material, metal oxide, and natural material. The conventional aerogels are modified by silane and derived by a sol-gel process. The modified aerogels, which are used in oil removal process, are superhydrophobic materials and possess high oilsorption capacity.

Liu et al. (2016) reviewed green and low-cost aerogels based on nanocellulose and presented their fabrication methods, structures, and oilsorption behavior.

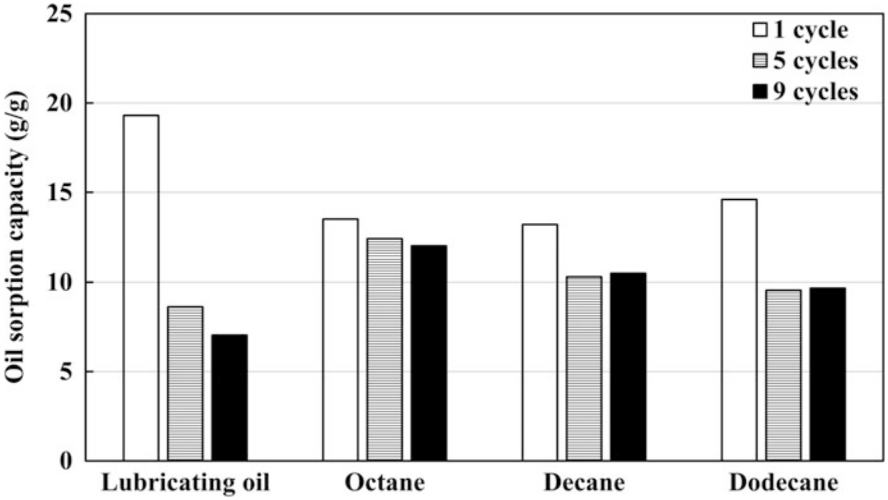


Fig. 12.22 The oil uptake capacity of the as-prepared sponge after recycle process. (Modified after Zhu et al. 2011)

Generally, cellulose aerogels can be grouped into regenerated cellulose aerogels, cellulose derivative-based ones, and nanocellulose-based aerogels. Depending on cellulose sources, the nanocellulose includes three main types: nanocrystalline cellulose, bacterial nanocellulose, and nanofibrillated cellulose. Table 12.8 summarizes the fabrication process, density, porosity, oilsorption performance, and cost of nanocellulose-based aerogels. The sorption ability was investigated by use of different organic pollutants, like methanol, toluene, hexane, chloroform, acetone, diesel, gasoline, plant oil, and paraffin liquid.

The effects of sol-gel characteristics on the oilsorption capacity of silica aerogel were investigated during four reuse cycles by using roll milling (Mahani et al. 2018). Methyltrimethoxysilane-based aerogels were synthesized via two-step acid-base catalyzed sol-gel process. Light and heavy commercial crude oils were considered as pollutants and the sorption experiments were performed in a 3.5% salty water bath containing 50 g of crude oil. Hydrolysis and polycondensation reactions of alkoxysilanes are the base of silica sol-gel process, which are performed in an acidic or basic environment. Therefore, the sol pH influences the structure of the aerogels. Figure 12.23 illustrates the effect of various pHs on the silica aerogels.

According to the results, the aerogels, which were prepared in acidic conditions, possessed larger particle size, higher specific surface area, bigger pores, lower density, and higher porosity than as-prepared aerogels in basic conditions. Therefore, formation of silica network in lower pH increases the oilsorption capacity. In addition, pore structure, hydrophobicity, and deformability of as-prepared aerogels were evaluated by changing the ethanol/methyltrimethoxysilane molar ratio. The ethanol was used as hydrolysis and diluent agent in methyltrimethoxysilane sol-gel process. As presented in Table 12.9, with increasing ethanol contact (5–10), the

Table 12.8 Properties of nanocellulose aerogels and their fabrication methods. A: Inexpensive, B: Less-expensive, C: expensive, D: Very expensive, BETSA: BET Specific Area, CA: contact angle, NFC: nanofibrillated cellulose, NCC: nanocrystalline cellulose and BNC: bacterial nanocellulose

									cost	
Classification	**Cellulose sources**	**Nanocellulose Decomposition**	**Hydrophobic processes**	**Density (g/cm^3)**	**Porousness (%)**	**BETSA (m2/g)**	**CA (deg)**	**Oil-uptake capacity (g/g)**	**Raw material**	**Synthesis process**
NFC-based aerogels	Hardwood Kraft pulp	Mechanical, homogenization	Atom layer deposition (ALD) coated by TiO_2	0.02–0.03 (initial)	>98 (initial)	–	>90	20–40	A	C
	Sulfite-softwood pulp	Carboxymethylation pretreatment, high-pressure homogenization	Octyltrichlorosilane (OTCS) modification by chemical vapor deposition (CVD)	0.004–0.014 (initial)	99.1–99.8 (initial)	11–42 (initial)	150	45	A	C
	Pine needle cellulose	HCl pretreatment, ultrasonic disintegration	Trimethylchlorosilane (TMCS) modification by CVD	0.00312 (initial)	–	20.09 (initial)	135	52	D	C
	Rice straw cellulose	2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) oxidation, mechanical disintegration	Triethoxyl(octyl)silane (OTES) modification by CVD	0.0027 (initial)	99.5–99.6 (initial)	10.9 (initial)	–	139–356	D	C
	Hardwood pulp	Mechanical beating	Acid-hydrolyzed methyltrimethoxysilane (MTMS) modification by CVD	0.0024 (initial)	98.4–99.84 (initial)	–	>150	88–228	A	A
	Oat straw cellulose pulp	Mechanical disintegration	MTMS-hydrolyzed poysilxane modification	0.0067 (initial) 0.0051–0.0173 (final)	99.6 (initial) 99.0–99.7 (final)	24 (initial) 3–25 (final)	110–150	49–102	A	A
	Softwood Kraft pulp	Mechanical disintegration	Chemical grafting by hydrophobic Styrene-acrylic Monomer	0.0232 (final)	98.5 (final)	18.4 (final)	149	20–46.4	A	C
NFC/PVA hybrid aerogels	Fully bleached-eucalyptus Kraft pulp	TEMPO oxidation, mechanical disintegration	Trichloromethylsilane (TCMS) modification by CVD	0.0106 (initial) 0.013 (final)	>98 (final)	195 (initial) 172 (final)	150.3	45–96	A	C

(continued)

Table 12.8 (continued)

									cost	
Classification	**Cellulose sources**	**Nanocellulose Decomposition**	**Hydrophobic processes**	**Density (g/cm^3)**	**Porousness (%)**	**BETSA (m2/g)**	**CA (deg)**	**Oil-uptake capacity (g/g)**	**Raw material**	**Synthesis process**
BCA-based aerogel	BCA	Commercial BCA	TMCS/TEA modification in CH_2Cl_2	0.00674 (initial) 0.00669–0.00677 (final)	99.6 (final)	160.2 (initial) 169.1 – 180.7 (final)	90	90–185	C	C
	BCA/ reduced graphene oxide (rGO)	–	Reduction in H2 at 200 °C	–	99.84 – 99.86	–	–	150	C	C
	BCA/SiO_2	Commercial BCA	Prehydrolyzed methyltrimethoxysilane (MTMS) alcosols modification	0.121 (final)	–	507.8 (final)	133	–	C	C
	BCA/SiO_2	Commercial BCA	Prehydrolyzed MTMS alcosols modification	0.011 (initial)	–	324.5 (final)	145	–	B	B
Nanocellulosederived carbon aerogels	BCA pellicles	–	Carbonization by argon atmosphere	0.004–0.006 (initial)	99.7 (initial)	–	113 – 128	106–212	C	C
	Cellulose microfibrils	Commercial sources	Carbonization by nitrogen	0.010 (final)	99 (final)	145–521 (final)	149	55.8 – 86.6	A	C

Modified after Liu et al. (2016)

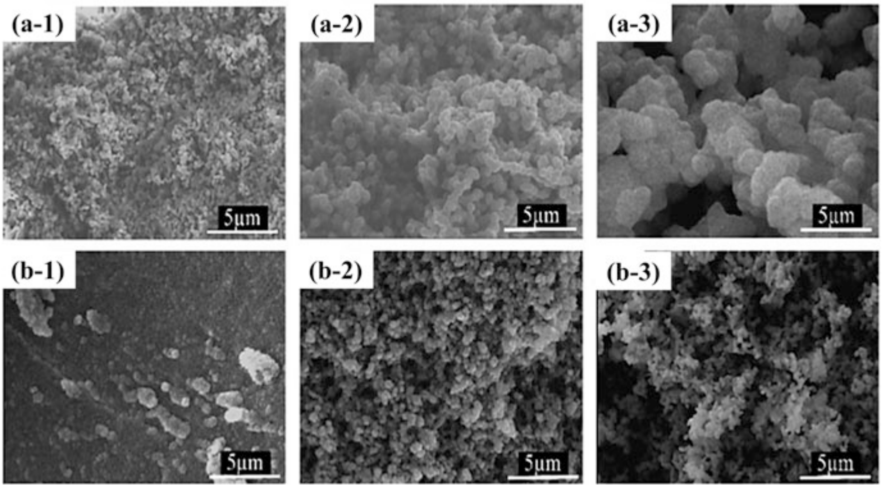


Fig. 12.23 Comparison between the structure of as-prepared aerogels in acidic ((a), pH = 4) and basic ((b), pH = 8) conditions. 1, 2, and 3 refer to low, medium, and high ethanol/methyltrimethoxysilane ratio. Reprinted with permission of (Sol-gel derived flexible silica aerogel as selective adsorbent for water decontamination from crude oil, Mahani et al., Elsevier)

Table 12.9 The effect of pH and ethanol/methyltrimethoxysilane molar ratio on the properties of as-prepared aerogels

pH	Ethanol/ MTMS molar ratio	Density (g/cm^3)	Porosity (%)	Specific surface area (m^2/g)	Pore size (nm)	Pore volume (cm^3/g)	Contact angle (deg)	Shrinkage (%)
4	5	0.2	90.4	508	27	3.40	147	27
	10	0.11	94.7	712	35	3.03	122	11
	15	0.15	92.9	653	54	2.56	107	19
8	5	0.26	87.6	447	15	0.37	141	40
	10	0.18	91.1	491	42	0.61	113	23
	15	0.21	89.8	543	58	0.52	104	36

Modified after Mahani et al. (2018)

porosity, specific surface area increased and then decreased by further increase in the ethanol/methyltrimethoxysilane ratio (10–15) in both acidic and basic conditions. In both conditions, contact angles, which refer to oleophilicity, had greatest value for high concentration of precursor (methyltrimethoxysilane). As a result, the best condition is medium concentration of precursor for as-prepared aerogels with high efficiency.

The results of oilsorption capacity of as-prepared aerogels for light and heavy crude oils revealed that as-prepared samples in high concentration of methyltrimethoxysilane had the lowest sorption due to their compact structures. By increasing the number of reuse cycles, the sorption of these samples increased

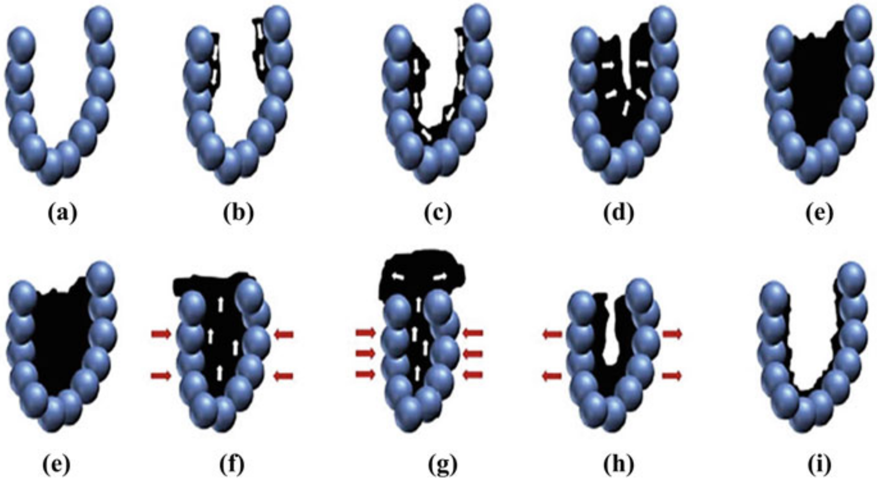


Fig. 12.24 The proposed sorption mechanisms of as-prepared silica aerogels for crude oil. (**a**) empty pore, (**b**) filled pore by capillary action and liquid–liquid interaction, (**c**) covered pore, (**d**) covered pore by liquid–liquid interaction, (**e**) completely filled pore, (**f**) squeezed pore by roll milling, (**g**) crude repelled out from the pore, (**h**) stop pore decompression, and (**i**) remained crude. Reprinted with permission of (Sol-gel derived flexible silica aerogel as selective adsorbent for water decontamination from crude oil, Mahani et al., Elsevier)

because of the effect of roll milling on deformation of their stiff structure. These samples had highest oleophilicity, so their desorption efficiencies are low compared to the other samples.

The highest sorption capacity was reported for as-prepared samples in ethanol/methyltrimethoxysilane molar ratio of 10 in acidic conditions (a-2) followed by (b-2) in basic conditions for light and heavy crudes. Figure 12.24 presents the proposed adsorption (a-e) and desorption (e-i) mechanisms of as-prepared silica aerogels for crude oil. Initially, physical adsorption process including capillary action is dominant. Then, the crude oil fills the pores due to the interaction between the fluid molecules.

The biodegradability and abundant source are the benefits that have attracted the attention of the researchers to produce natural-based aerogels. The aerogels based on graphene, silica, cellulose, and polymer, which are used to separate oil, are fabricated with difficult and high-cost processes. In addition, the superhydrophobic aerogels are blocked by oil during oil/water separation and as a result, the separation efficiency decreases. Moreover, their widespread applications cause environmental concerns.

Hence, Dia et al. (2019) proposed a new and environmentally friendly aerogel based on TiO_2–sodium alginate composite for oil–water separation. Alginate was extracted from brown sea alga, then alginate aerogels were fabricated without chemical modification. But these aerogels are easily damaged by the UV radiation because of their polysaccharides content. Therefore, TiO2 nanoparticles can improve

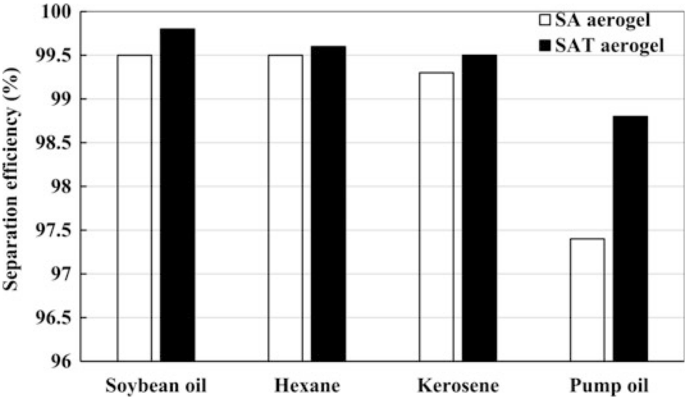


Fig. 12.25 Separation efficiency of oil/water mixture of sodium alginate composite (SA) and TiO2–sodium alginate composite (SAT) aerogels for different organic solvents. (Modified after Dai et al. 2019)

the UV-aging resistance of alginate aerogels due to their photocatalysis property. In the work of Dia et al. (2019), the TiO_2–sodium alginate aerogel was produced by ionic cross-linking and freeze-drying methods. TiO_2nanoparticles were dispersed on hydrophilic alginate matrix to make it oleophobic underwater.

The morphology results of sodium alginate and TiO_2–sodium alginate aerogels showed three-dimensional network structures of these aerogels. The pore size range of 40–150 μm for both aerogels indicated their excellent oil/water separation ability and the TiO_2–sodium alginate aerogel surface was rougher than the sodium alginate aerogel surface.

The results of measuring contact angles for oil and water droplets on the sodium alginate aerogel and TiO_2–sodium alginate surfaces in air indicated that both aerogels were superamphiphilic. This is a result of the presence of hydroxyl groups on the rough and porous structures of both aerogels. After that the underwater oil contact angles were investigated by water-soaked aerogels. The underwater oil contact angles of TiO_2–sodium alginate aerogel were greater than those of sodium alginate aerogel. The lowest underwater oil contact angles of above solvents were 123.1 and 137.2° for sodium alginate and TiO_2–sodium alginate aerogels, respectively.

These results revealed that alginate aerogel possesses excellent water storage capacity and the TiO_2nanoparticles could improve the underwater oleophobicity of this type of aerogel. Moreover, water-soaked alginate aerogel could store more water without chemical modification. Figure 12.25 shows the oil/water separation efficiency of both aerogels for different oil/water mixtures. As one can see from this figure, the separation ability of TiO_2–sodium alginate aerogel was greater than that of sodium alginate aerogel (about 1.4%).

The anti-oil-fouling performance of as-prepared TiO_2–sodium alginate aerogel was evaluated by pump oil (Fig. 12.26). Initially, the white TiO_2–sodium alginate aerogel sank into pump oil (red liquid) and quickly colored. Then the fouled aerogel

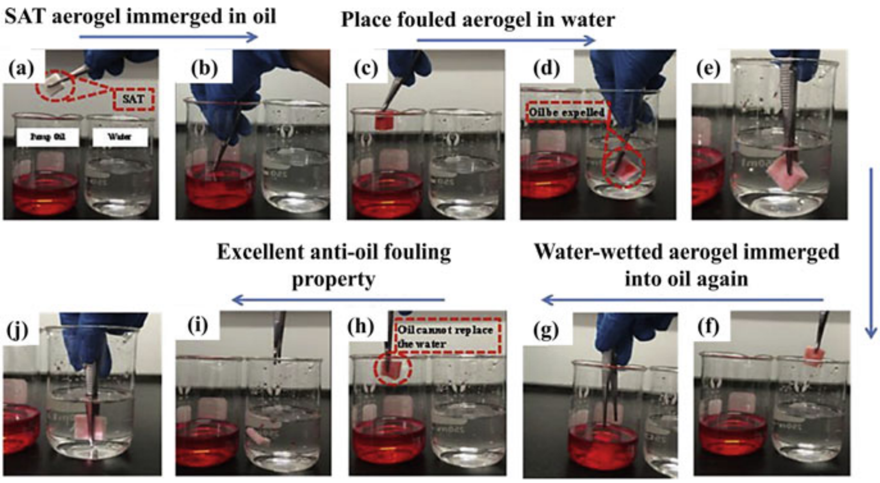


Fig. 12.26 The anti-oil-fouling performance of as-prepared TiO_2–sodium alginate composite (SAT) aerogel into pump oil. Reprinted with permission of (TiO_2-alginate composite aerogels as novel oil/water separation and wastewaterremediation filters, Dai et al., Elsevier)

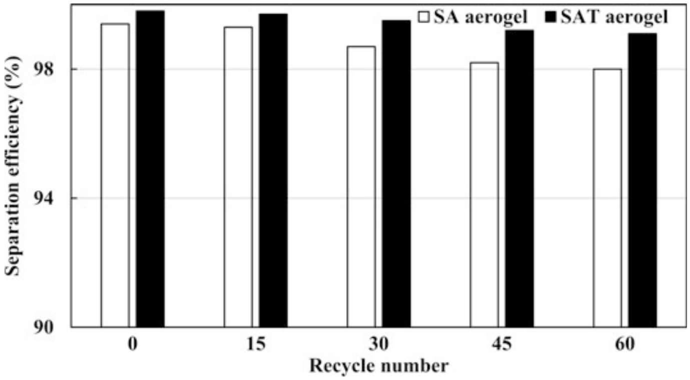


Fig. 12.27 Separation efficiency of sodium alginate composite (SA) and TiO_2–sodium alginate composite (SAT) aerogels during recycling process. (Modified after Dai et al. 2019)

was placed into water and oil brought out by wateradsorption. After that, the water-soaked TiO_2–sodium alginate aerogel sank into the oil again. As displayed in Fig. 12.26 h, the water-soaked TiO_2–sodium alginate aerogel adsorbed oil lower than the TiO_2–sodium alginate aerogel (Fig. 12.26 c).

These results confirmed that the water affinity and excellent anti-penetrating capability of TiO_2–sodium alginate aerogel. These properties were significant after 60 times of reuse. Moreover, repeating oil/water separation experiments showed the excellent reusability of sodium alginate and TiO_2–sodium alginate aerogels (Fig. 12.27). The separation efficiency decreased about 0.5 and 1.4% after

60 times of reuse for TiO_2–sodium alginate and sodium alginate aerogels, respectively.

Finally, the photocatalyticity of both aerogels was investigated by methyl orange degradation under simulated sunlight. The methyl orange degradation rate was constant during 150 min of irradiation. While in the presence of TiO_2, the TiO_2–sodium alginate aerogel was stable against UV corrosion. All of these advantages make the TiO_2–sodium alginate aerogel appropriate for separating oil/water mixture.

Foams

Although the "sponge-like" and "foam-like" structures are frequently used interchangeably, there are many differences between them due to their actual physical properties, ingredients, and molecular structure. A blowing agent (gas or chemical), which can create multiple small bubbles, is needed to produce an air-filled matrix structure from a liquid mixture. One of the most common foams used in oil/water separation is foam rubber. Commercial foam rubbers are generally made of polymers. Three-dimensional porous structure, light weight, low raw material, good mechanical properties, and excellent buoyant ability make them attractive for oilsorption processes. Therefore, the improvement of the foam rubber has a significant effect on their oilsorption behavior. For instance, the ethylene propylene diene monomer foam rubber was improved by trichloromethylsilane to produce a superhydrophobic and superoleophilic sorbent (Liu and Kang 2018). The trichloromethylsilane was used to generate hydrophobic layer on the ethylene propylene diene monomer foam rubber through hydrolysis and polycondensation. The as-prepared foam has lower surface energy and rougher surface than the ethylene propylene diene monomer foam.

The contact angle measurement was used to prove the superhydrophobicity and superoleophilicity of the improved foam. The water contact angle was 104.1° for ethylene propylene diene monomer foam, while it was 159.3° for modified foam. To demonstrate the superoleophilicity of the modified foam, a drop of hexane was dropped on the foam, which permeated into it completely. In addition, the acidic, neutral, and basic droplets were dropped on its surface that retained their spherical shape, which indicates their non-wetting surface and their resistance in corrosive environment. Moreover, the morphology analyses indicated that the surface of modified foam with micro-nanometer pore size was rougher than that of the pristine foam with millimeter pore size. In oilsorption experiments, organic solvents with high and low viscosities were used with viscosity range of 0.326–409 mPa.s. Figure 12.28 shows the oilsorption capacity of both foams for various organic solvents.

The results showed that the oil uptake ability of ethylene propylene diene monomer foam rubber was acceptable in low viscosity solvents. In addition, the oil sorption decreased by increasing the oil viscosity due to the reduction of wettability. While, the modified ethylene propylene diene monomer foam rubber had an excellent oilsorption behavior for various oils and sorbed oils 8–12 times its

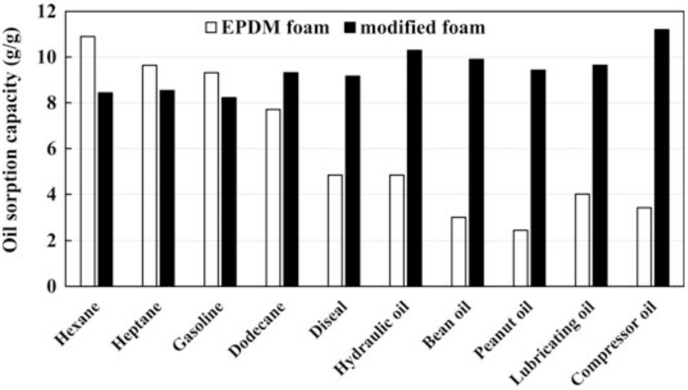


Fig. 12.28 The oilsorption capacity of ethylene propylene diene monomer (EPDM) foam rubber and modified one for different organic solvents with various viscosities. (Modified after Liu and Kang2018)

weight. The squeezing was chosen as oil desorption method. The results of sorption/desorption processes showed that the modified ethylene propylene diene monomer foam rubber had the stable oilsorption capacity after 20 cycles. From the cyclic compression stress–strain measurements it was proved that trichloromethylsilane improved the mechanical strength of the ethylene propylene diene monomer foam rubber.

Magnetic Sorbents

Recently, iron-oxide-based magnetic materials have attracted researchers' interest in applying them as oilsorbents. Oiladsorption ability, biocompatibility, and magnetic property are the significant advantages of these materials. While, agglomeration and oxidization of uncovered iron oxide restrict their application. To protect them from these problems, forming shell on the surface of ferromagnetic nanoparticles has been suggested by researchers.

To produce ferromagnetic nanoparticles, there are some current methods. In coprecipitation method, iron salts react in basic media without oxygen. Functional materials and surface active agents can be improved by this technique to avoid agglomeration and oxidization of naked iron oxide nanoparticles. The pH value, type of iron salts, ratio of Fe (III) to Fe (II) ratio and temperature influence their shape, size, and the magnetic property.

Coprecipitation method is conventional but has a significant problem. In this method, the pH value is high and affects the structural integrity of iron oxide nanoparticles. While, thermal decomposition method can produce monodispersed iron oxide nanoparticles with high quality. The organometallic compounds and surfactants are applied to achieve ferromagnetic nanoparticles in high reaction

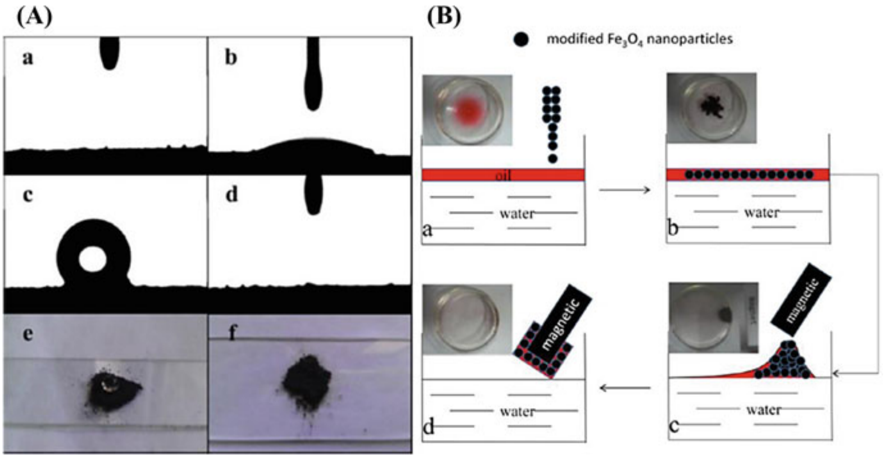


Fig. 12.29 (**a**) The behavior of water and oil droplets on the surface of (a, b) uncovered iron oxide and (c–f) polymer covered iron oxide, (c, e) water droplet, and (d, f) oil droplet. (**b**) The floatation ability and facile removal process of modified iron oxide by external magnetic field. Reprinted with permission of (Application of magnetic adsorbents based on iron oxide nanoparticles for oil spillremediation: A review, Qiao et al., Elsevier)

temperature of about 200–300 °C. The obtained iron oxide nanoparticles from this method only dissolve in nonpolar solvents.

On the other hand, in hydrothermal method, chemical reactions occur at high temperature and vapor pressure (hydrothermal conditions) in an aqueous phase. The temperature, reactant concentration, and time of process are the significant conditions of this method, which affect the size, shape, structure, and saturation magnetization of the iron oxide nanoparticles.

The microemulsion method involves dispersed aqueous phase (water) as nanodroplets, whereafter surfactant molecules surround them in an organic phase (oil). These nanodroplets influence the shape and size of iron oxide nanoparticles. This method provides the iron oxide nanoparticles with size range of 3.5 ± 0.6 nm.

The ION based-magnetic sorbents have the preferred properties that make them appropriate as oilsorbents. The water contact angle is one of the important parameters that show the wettability of surface. Figure 12.29a illustrates the behavior of water and oil droplets on the naked iron oxide and coated iron oxide with polymer. Polymer-coated iron oxides possess higher hydrophobicity and oleophilicity than the naked ones. The ability of oilsorption and repelling of water by iron oxide nanoparticles can be improved by coating their surface.

The modified iron oxide nanoparticles could also stay on the surface of oil/water mixture due to their lower density than water, buoyancy ability, and hydrophobic coat. The floatation ability and facile removal of modified iron oxide nanoparticles in sorption process are shown in Fig. 12.29b. The polymer-modified Fe_3O_4nanoparticles float after being added to the system and finally are recycled by an external magnetic field. The ferromagnetic property of Fe_3O_4nanoparticles makes them appropriate for grafting these nanoparticles to other oilsorbents for easy and quick reusability after sorption. Then ultrasonic washing treatment was used as reuse method and indicated the reusability of magnetic sorbents.

Coating with organic and inorganic compounds, inserting iron oxide into the fiber and membrane and other porous materials, and combining with activated carbon are the familiar and useful techniques for protection and improvement of naked iron oxide. The organic materials like surfactants, polymers, macro-molecules, and biomolecules could physically or chemically passivate the iron oxide nanoparticles. Oleic acid as a surfactant uses the chemical precipitation to coat the ferrite. The –COOH group of oleic acid reacts with the Fe atoms and its hydrophobic tail fabricates a nonpolar coat. The sorption efficiency of oleic molecule-Fe_3O_4 hybrid nanomaterials was reported at about 95 wt% for crude oil. The appropriate surface area, density, and chemical stability make the polymeric materials excellent coating materials. The rich functional group of polymer is connected to iron oxide nanoparticles by ligand exchange reaction. According to reported literature, polymer coated with polyvinylpyrrolidone could adsorb oil 100%. The starch, chitosan, and alginic acid are the common macromolecules that are used to modify iron oxide due to their biodegradability, high stability in various pHs, and nontoxicity. Moreover, the protein as biomolecule has good performance in ferrite modification. Nevertheless, the organic coating materials have some disadvantages like leaching by acidic solution, low intrinsic stability at higher temperature, and negative effect of thick shell on the saturation magnetization.

Inorganic materials such as silica, metal oxide, and carbon were used to improve the stability of uncovered iron oxide nanoparticles. The carbon covered iron oxide enhances the chemical and thermal stability of modified iron oxide. The water angle contact of carbon-coated magnetic nanoparticles was reported near superhydrophobic structure (> 150°). But silica-coated magnetic nanoparticles have a significant sorption capacity and reusability. The inorganic-coated iron oxide nanoparticles processes have not been developed and understood completely.

As mentioned in Sect. 1.5.2.1, electrospinning is a facile method to produce nanofibers, especially magnetic nanofibers like polystyrene/Fe_3O_4, polyvinyl alcohol/Fe_3O_4, polyacrylonitrile/Fe_3O_4, and polyvinyl pyrrolidone/Fe_3O_4. High oleophilicity, selective adsorption, quick removal, and high saturation magnetization value are the advantages of this type of nanofibers. Other porous sorbents like aerogels, foams, and sponges can be modified by magnetic nanoparticles to achieve higher sorption capacity and easy collection.

Activated carbon is applied as inorganic oil sorbent due to its high specific surface area and porosity. The magnetic activated carbon has the desirable benefits of activated carbon and the magnetic property of magnetic materials (Qiao et al. 2019). Table 12.10 presents the summary of magnetic sorbents' properties and their sorption capacities. Although there are many different methods to fabricate magnetic sorbents, still this field needs more investigation.

Zhu et al. (2010) used a thermal decomposition method to coat Fe_3O_4nanoparticles with a carbon layer and modified the surface of as-prepared nanoparticles with polysiloxane layers to achieve superhydrophobic and

Table 12.10 Comparison of magnetic properties and oilsorption capacity of different magnetic oilsorbents. WCA: water contact angle

Magnetic sorbent	Functional material	Synthesis method	Saturation magnetization (emu/mg)	WCA (rad)	Application	uptake
Fe_3O_4@oleic acid (OA)	OA	Microemulsion	0.01657	–	Crude oil (co)	95 wt%
Fe_3O_4@sodium oleate (SO)	SO	Co-precipitation (co-p)	0.04940	2.71	Engine oil (Eo)	–
Fe_3O_4@Quaternized chitosan (QC)	QC	Modification of sorber and grafting reaction	0.0305	–	Emulsified oil	90%
Magnetic (M) compound resin	Gelatin glue	Suspension Polymerization	–	–	Kerosene	100%
M-collagen-SPION	Collagen	Heat treatment	–	–	Eo	2 g/g
Fe_3O_4@Polysttyrene (PS)	Styrene (St) and sodium dodecyl Sulfonate (SDS)	Emulsion Polymerization	0.03462/0.06125	2.46–2.67	Diesel oil (do) Lubricating oil (Lo)	3 g/g
Fe_3O_4@P (St/Divinylbenzene (DVB)) @ P(methyl methacrylate (MMA)/St/DVB)	Methyl Tablemethacrylate	Hydrothermal	–	2.46	Do	3.63 g/g
Fe_3O_4@polyvinyl pyrrolidone (PVP)	PVP	Modification of polyol Hydrothermal	–	–	Co MC252 oil	~100%
Fe_3O_4@sulfonated asphaltene (SAS)	SAS	Co-p	0.075–0.092	–	Co	90%
Fe_3O_4@C	Iron containing metal	Pyrolysis	0.026–0.049	2.50	Oil Hydrocarbon	40 g/g

(continued)

Table 12.10 (continued)

Magnetic sorbent	Functional material	Synthesis method	Saturation magnetization (emu/mg)	WCA (rad)	Application	uptake
Polysiloxane(PSx)-covered Fe_3O_4@C	Terephthalic acid and PSx	Thermal Decomposition	–	2.84	Lo	3.8 g/g
Fe_3O_4@SiO_2	Tetraethyl orthosilicate	Template approach	0.0583	2.60	Lo Salad oil Edible oil Do	11.51 g/g
Fe_3O_4/PS	PS	Electrospinning	0.014	–	Edible oil	~100%
M-foams	PTFE-PU foams	Adsorption	–	2.79	Mineral oil	13 g/g
M-cellulose aerogel	Cellulose aerogel	Incorporation	–	–	Paraffin oil	28 g/g
M-sponge	Sponge	Polymerization	–	2.45	Eo Co	9.9–20.3 g/g
M-P(St-DVB) foams	P(St-DVB) foams	High internal phase emulsions	–	2.62	Do	24.5–57.6 g/g
Fe_3O_4–carbon nanotubes (CNT) sponges	CNT sponges	Chemical vapor deposition	–	2.44	Do Gasoline	99%
M-carbon	Coconut/palm	Co-p	0.015	–	Premium oil Used oil Palm oil	9.33 g/g and 80%

Modified after Qiao et al. (2019)

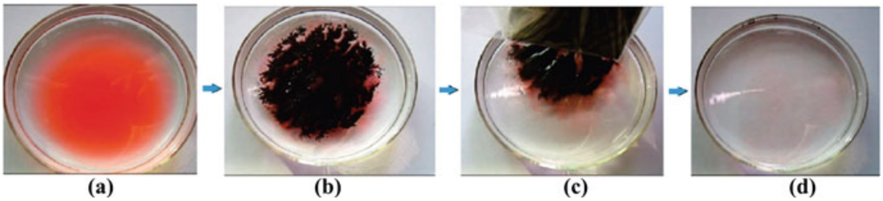


Fig. 12.30 Oilsorption and sorbent removal processes of polysiloxane-coated Fe_3O_4nanoparticles with a carbon layer (Fe2O3@C) for lubricating oil under magnetic field. Reprinted with permission of (Fast and selective removal of oils from water surface via highly hydrophobic core–shell Fe2O3@C nanoparticles under magnetic field, Zhu et al., ACS Publications)

superoleophilic properties. The modified nanoparticles had varying size range from 30 to 200 nm. The results demonstrated that the water contact angle on the bed of modified Fe_3O_4nanoparticles with a carbon layer (162.9°) is greater than that of the bed of pristine Fe_3O_4nanoparticles with a carbon layer, while the lubricating oil droplet quickly spreads.

The presented results emphasize the superhydrophobic and -oleophilic properties of polysiloxane-coated Fe_3O_4nanoparticles with a carbon layer. The behavior of modified Fe_3O_4nanoparticles with a carbon layer in corrosive media for long time showed its stability and kept the superhydrophobicity and water contact angle. Another interesting property of modified Fe_3O_4nanoparticles with a carbon layer was their unsinkable property, which was considerable in both surface (water and oil) and in the mixture under vigorous agitation conditions.

Figure 12.30 shows the removal process of lubricating oil from water by modified Fe_3O_4nanoparticles with a carbon layer. The lubricating oil formed a layer on the surface of water (Fig. 12.30 a, red: oil), then added modified Fe_3O_4nanoparticles with a carbon layer quickly adsorbed the oil (Fig. 12.30 b, up to 3.70 times of its weight), which is greater than the value adsorbed by the pristine Fe_3O_4nanoparticles with a carbon layer (2.18 times of its weight). Finally, oil-loaded nanoparticles were collected by the external magnetic field with strength of 0.35 T (Fig. 12.30 c).

The collected nanoparticles could be reused by ultrasonic washing in ethanol. These sorbents kept their thermal stability and superhydrophobicity after washing. Only, the water contact angle changed slightly after each reuse cycle (Fig. 12.31), but was still above 150°. Therefore, polysiloxane-coated Fe_3O_4nanoparticles with a carbon layer can be selected as strong oil sorbent even in agitation and corrosive conditions.

In another study, the hydrothermal synthesized Fe_3O_4nanoparticles were coated by poly(Styrene/Divinylbenzene) (hydrothermal sample) and modified with poly (Methyl methacrylate/Styrene/Divinylbenzene) (modified sample) (Gu et al. 2014). These modified nanoparticles were also floatable, thermal stable, and corrosion resistant. The SEM images showed the greatest smooth surface for modified sample.

The water contact angles of hydrothermal and modified samples emphasized their high hydrophobicity. They used three kinds of oil to investigate the oilsorption behavior of as-prepared nanoparticles, such as diesel, salad, and lubricating oils.

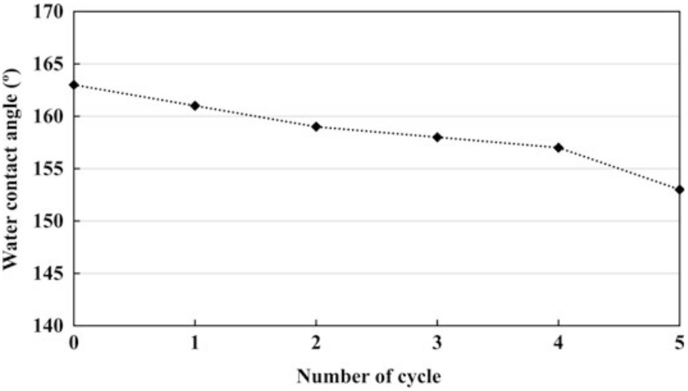


Fig. 12.31 Change of water contact angle (°) of polysiloxane-coated Fe_3O_4nanoparticles with a carbon layer during reuse cycles. (Modified after Zhu et al. 2010)

The modified sample quickly spread on the oil/water mixture surface and sorbed the oil and also prevented the distribution of spilled oil. In addition, the effect of removal time in sorption capacity of hydrothermal and modified samples was considered. The results indicated that the maximum uptake capacity of both nanoparticles was observed at 30 s for diesel. After that the oilsorption capacity did not change by increasing removal time. In all experiments, the capacity of modified sample was greater than that of the hydrothermal sample. The modified sample sorbed 3.63, 4.26, and 9.41 g/g of thin diesel, salad, and lubricating oil, respectively. While, the hydrothermal sample sorbed 2.37 g/g thin diesel. Moreover, the oil uptake capacity of modified sample was greater for viscous oil. To investigate the reusability of modified sample, the water contact angles and oilsorption capacities were measured during ten reuse cycles (Fig. 12.32). As a result, this kind of magnetic modification prepares a facile method to fabricate high hydrophobic magnetic oilsorbents.

Zhou et al. (2019) designed a superhydrophobic polyurethane@Fe_3O_4@polystyrene sponge with great sorption and good reuse property. Iron oxide nanoparticles and polystyrene were attached on the polyurethane sponge surface. The modified sponge was collected with the external magnetic field after oilsorption and recovered by a negative pressure system. The modified sponge did not have some disadvantages of common polyurethane sponge like tedious production and fragility. Figure 12.33 illustrates the fabrication process of modified (polyurethane@Fe3O4@polystyrene) sponge and water contact angles during preparation, which shows high superhydrophobicity of as-prepared sponge. The water contact angle was the greatest for modified sponge (151.3°).

Various kinds of organic solvents and oils were selected to investigate the sorption performance of modified sponge. The results showed the oilsorption capacity was about 24–105 times of as-prepared sponge's weight, which was influenced by viscosity and density of contaminants (Fig. 12.34).

It is obvious that the modified sponge shows greater sorption capacity compared to other superhydrophobic sponges. The reusability of as-prepared sponge was

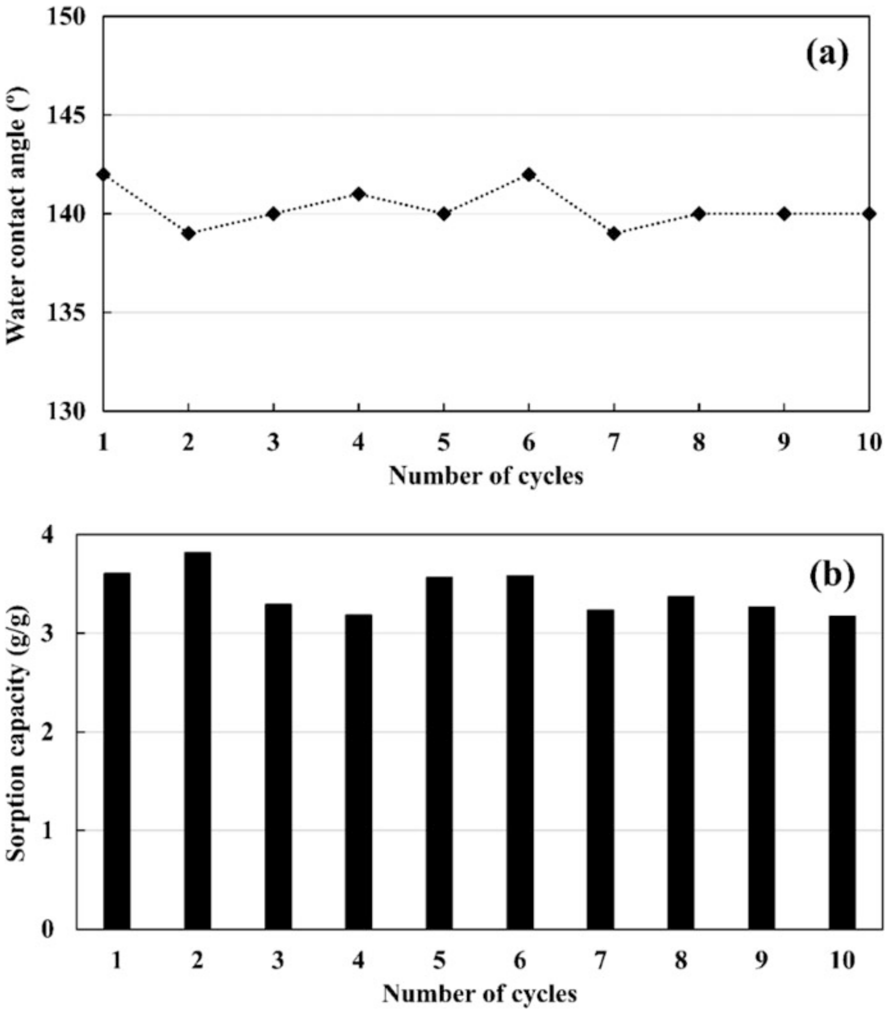


Fig. 12.32 (**a**) water contact angle of the Fe_3O_4nanoparticles modified with poly(MMA/St/DVB) (modified sample) and (**b**) oilsorption capacity of modified sample, for diesel oil during separation cycles. *MMA* Methyl methacrylate, *St* Styrene, *DVB* Divinylbenzene. (Modified after Gu et al. 2014)

investigated by squeezing process for diesel, castor oil, toluene, and chloroform. The adsorption capacities were above 90% of initial capacity and the sponge's weight decreased 5% after 20 reuse cycles. The water contact angles were 151 and 143.6° at initial and final cycles for diesel. Therefore, polyurethane@Fe_3O_4@ polystyrene sponge has excellent ability in cleaning up spilled oil. As a result, synthetic sorbents can be used for various kinds of oil and have excellent hydrophobic and oleophilic properties, but biodegradability is an important disadvantage.

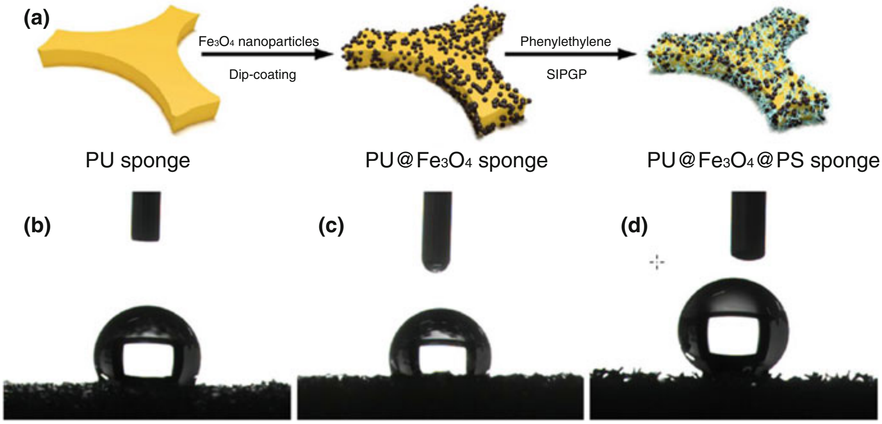


Fig. 12.33 (**a**) The preparation of PU@Fe_3O_4@PS sponge and water contact angles for (**b**) PU sponge, (**c**) PU@Fe_3O_4 sponge, and (d) PU@Fe_3O_4@PS sponge. PU: polyurethane and PS: polystyrene. Reprinted with permission of (Design of Recyclable Superhydrophobic PU@ Fe3O4@ PS Sponge for Removing Oily Contaminants from Water, Zhou et al., ACS Publications)

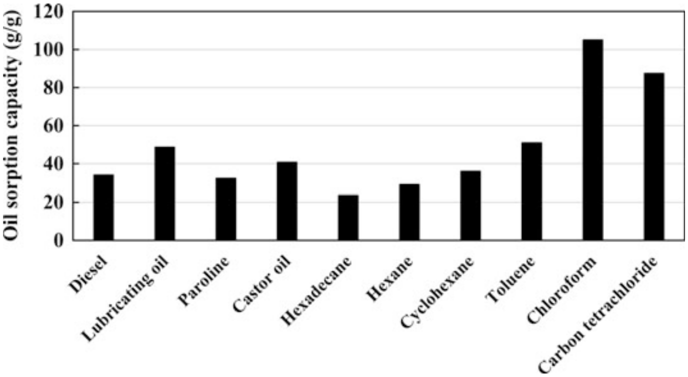


Fig. 12.34 Oilsorption capacity of PU@Fe_3O_4@PS sponge for various organic solvents and oils. PU: polyurethane and PS: polystyrene. (Modified after Zhou et al. 2019)

12.5.3 Inorganic Products

Inorganic materials are not able to sorb oil in the natural form. Hence, their structure should be improved to fabricate hydrophobic sorbents.

Perlite

One mineral porous material is perlite with porosity of about 45–55%. If this material is quickly heated at 700–1200 °C, its volume will increase to 8–15 times.

The expanded perlite possesses excellent buoyancy ability, low density, and high porosity (>90%). Therefore, the expanded perlite has all the popular properties of an oil sorbent.

The fatal problem is that this mineral material is not hydrophobic for the oilsorption process. Treating with polysilicons makes the expanded perlite hydrophobic and is appropriate for selective oilsorption. In oilsorption processes, the expanded perlite spreads over the polluted water and sorbs the oil; finally, it is removed from the water surface by pumping.

Roulia et al. (2003) used three sizes of expanded perlite as a carrier of emulsifiers. They produced modified expanded perlite by adding expanded perlite to an emulsifier solution. The effect of grain size of the expanded perlite was investigated on the heating oil and watersorption capacities. In all sizes, watersorption capacity of expanded perlite was greater than its sorption for oil. Among Among 0-2.5 mm (A), 0-4 mm (B) and 1-5 mm (C) particle size, group A had the greatest water and oil uptakes.

Figure 12.35 shows the effects of different sizes of the expanded perlite, oil/water ratio, and soaked-perlite on the sorption percentage. According to Fig. 12.35 a, d, and e, the watersorption capacity of the expanded perlite is again greater than that of its oilsorption capacity, about 1.8 times. In the case of b (Fig. 12.35 b), first, perlite was added to water and after that oil was added, but still oilsorption was ~30%.

They suggested that oil and water may be sorbed at different sites and oilsorption capacity of the expanded perlite did not exceed 45%. The hydrogen bonds of Si-OH and Si-O groups with water were considered as a possible mechanism for watersorption of the expanded perlite. On the other hand, mechanical adsorption and van der Waals forces cause sorption of the oil molecules. Then, the expanded perlite was modified by various emulsifiers. Table 12.11 presents the amount of emulsion adsorbed for different perlite samples.

The spread of modified perlite over the spilled oil showed that the emulsifier molecules dispersed the oil and perlite, simultaneously (in laboratory conditions). The light perlite particles, which adsorbed more emulsion, moved on the surface and spread quickly over it and acted as an adsorber of the emulsion formed. In the experiments, the lowest oilsorption capacity was observed for the hydrophobic perlite (with silicon). Therefore, the silicon and emulsifiers were not compatible. The modified expanded perlite may be appropriate for calm and rough sea conditions because of the quick sorption action and no agitation required.

Fly Ash

Many industries produced a lot of fly ash annually, which was released into the atmosphere in the past. Nowadays, air pollution control laws prevent their release. Therefore, fly ash is collected and used in many industries like the cement industry. This low cost and ample waste is generally spherical in shape with size range of 0.5–300 μm. The main chemical compositions of fly ash are SiO_2, Al_2O_3, Fe_2O_3, MgO, TiO_2, and sometimes CaO. Recently, fly ash has attracted a lot of attention for

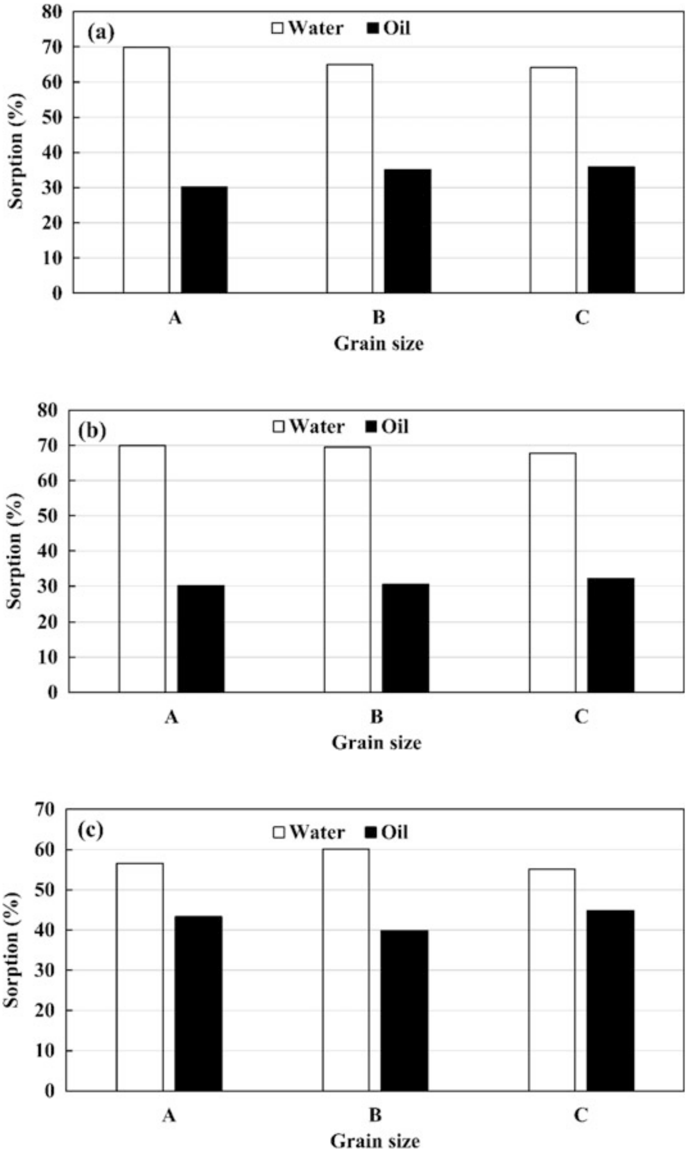
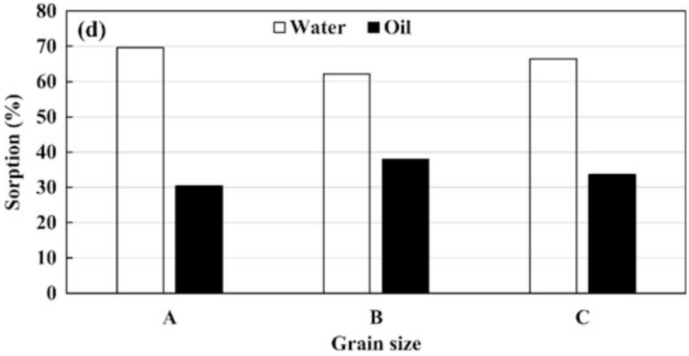


Fig. 12.35 Water and oilsorption capacities (1/kg) of different sizes of the expanded perlite. (**a**) Oil: water = 1:1 (v/v), oil and water were completely mixed before adding perlite. (**b**) Oil: water = 1:1, water and perlite were added together initially (water saturated perlite), and then oil was added to mixture. (**c**) Oil: water = 1:1, at first, the perlite was saturated with oil, then water was added to the mixture. (**d**) Oil: water = 3:7, oil and water were completely mixed before adding perlite. (**e**) Oil: water = 7:3, oil and water were completely mixed before adding perlite. (Modified after Roulia et al. 2003)



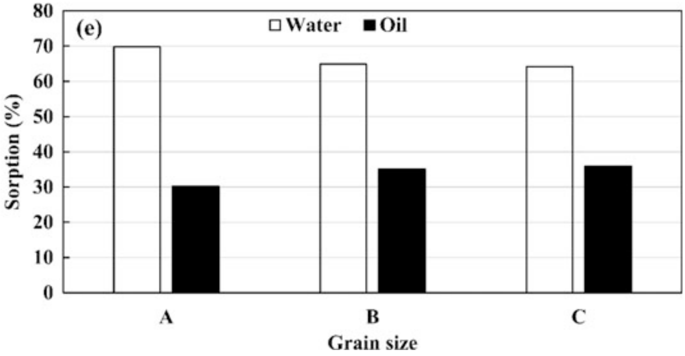


Fig. 12.35 (continued)

Table 12.11 The adsorbed emulsion for various perlite samples

Emulsifier-modified expended (grade size)	Emulsion adsorbed (1/kg perlite)			
	Emulan A[a]	Emulan AF[b]	Lutensol AO3[c]	Lutensol AO5[d]
A (0–2.5 mm)	1.90	1.90	1.70	1.70
B (0–4 mm)	1.75	1.75	1.55	1.55
C (1–5 mm)	1.65	1.65	1.45	1.45
Hydrophobic perlite modified by emulsifiers	0.95	0.95	1.10	1.10
Expanded perlite A (unmodified)	3.90	3.90	3.90	3.90

[a] Oleic acid ethoxylate

[b] Fatty alcohol ethoxylate

[c] $RO(CH_2CH_2O)_3H$, $R = C_{13}C_{15}$ oxo alcohol

[d] $RO(CH_2CH_2O)_5H$, $R = C_{13}C_{15}$ oxo alcohol

Modified after Roulia et al. (2003)

Table 12.12 Some properties of crude oil and fly ash characteristics (Banerjee et al. 2006)

Property/characteristic	Value
Mean particle size of fly ash	47.90 μm
Surface area of fly ash	3.12 m^2/g
Viscosity of crude oil	42.46 cp
Specific gravity of crude oil	0.894 g/cm^3

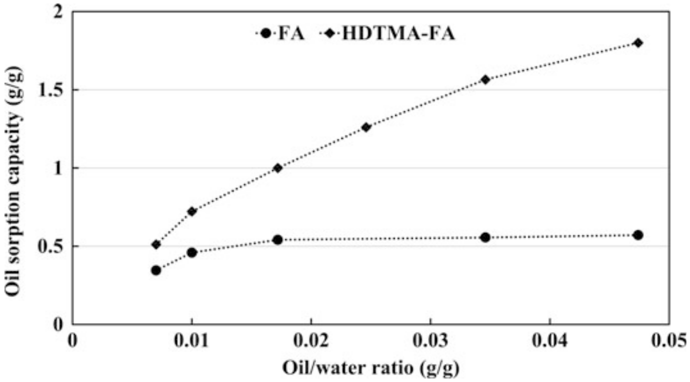


Fig. 12.36 The oilsorption capacity of fly ash (FA) and modified fly ash by hexadecyltrimethylammonium (HDTMA-FA) for different ratios of oil/water. (Modified after Banerjee et al. 2006)

use in oilsorption processes as a sorbent. Fly ash has hydrophilic surface, which must be improved for use as sorbent.

Banerjee et al. (2006) modified fly ash by hexadecyltrimethylammonium as a cationic surfactant. Then, they investigated the ability of modified fly ash for the uptake of crude oil (Arabian light) and weathered crude oil. Some properties of crude oil and fly ash are provided in Table 12.12.

They treated the hydrophobic fly ash by hexadecyltrimethylammonium cation, $[(CH_3)_3NC_{16}H_{33}]^+$, to make organophilic fly ash. Moreover, the oil uptake of modified fly ash was compared with wood shavings. The modification of fly ash was performed with the following reaction:

$$\text{Si-OH} + \text{Br}\left[(\text{CH}_3)_3\text{NC}_{16}\text{H}_{33}\right] \rightarrow \text{Si-O-N}\left[(\text{CH}_3)_3(\text{C}_{16}\text{H}_{33})\right] + \text{HBr} \qquad (12.1)$$

where the hydroxyl group of fly ash reacts with cation $[(CH_3)_3N(C_{16}H_{33})]^+$.

The scanning electron microscope images of fly ash and modified fly ash revealed that the modification with hexadecyltrimethylammonium cation changed the surface roughness of fly ash and the surface of modified fly ash was smoother than that of fly ash. For different ratios of oil/water, the oilsorption results of fly ash and modified fly ash (Fig. 12.36) indicated that the oil uptake of fly ash was lower than that of modified fly ash due to its SiO polar group that reacts with water and nonpolar organic material cannot compete with it.

While the hydrophobic tail ($C_{16}H_{33}$) of modified fly ash causes it to sorb oil and enhances the oilsorption capacity, the oilsorption capacity of wood shavings was greater than that of the modified fly ash. But the oilsorption capacity of modified fly ash increased by partition mechanism; whereas wood shavings very quickly sorbed water and severely decreased its oil uptake. In addition, the contact time impact on the oil uptake of fly ash and modified fly ash was demonstrated. It was revealed that the highest oilsorption capacity was observed in the first 5 min, which reduced the possibility of oil dispersal into sea.

To study the impact of light oil fraction in crude oil, samples were selected with various ratios of kerosene to crude oil (1:4, 3:2, and 4:1). The crude oilsorption capacity of modified fly ash increased from 1550 to 1690 mg/g by increasing the amount of kerosene in crude oil, while the crude oilsorption capacity of fly ash decreased (515 to 480 mg/g). This is due to increased water insolubility in kerosene as compared to crude oil.

Weathered oil-contaminated seawater was obtained during the stimulation of photooxidation and microbial degradation process of 100 ml crude oil in 10 L of seawater. The sorption results of dissolved organic carbon from weathered oil-contaminated seawatersorption by use of fly ash and modified fly ash showed a higher dissolved organic carbon sorption capacity for modified fly ash compared to fly ash. When the dissolved organic carbon concentration (mg/L) was increased, the amount of sorbed dissolved organic carbon was enhanced; While, the polypropylene sorbent does not have satisfactory performance for weathered oil-contaminated seawatersorption.

They also suggested the Freundlich sorption model in the following form, according to the crude oil and dissolved organic carbon sorption results of fly ash and modified fly ash:

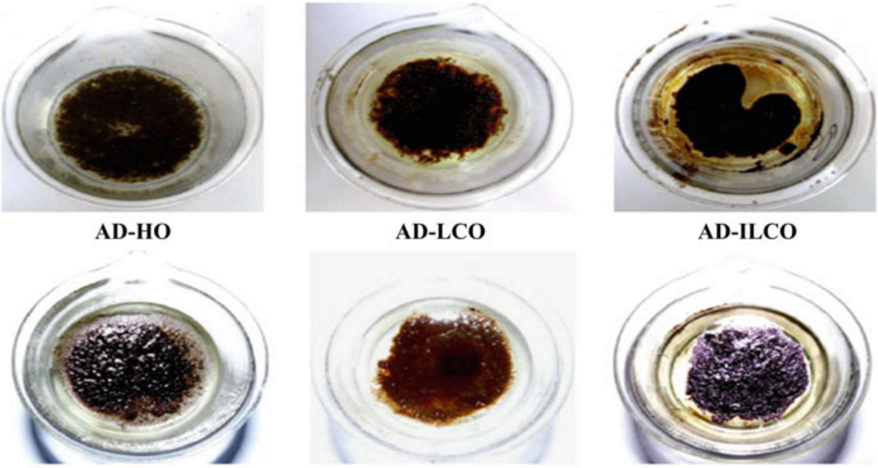
$$C_s = KC_e^{1/n} \tag{12.2}$$

where C_s and C_e are the equilibrium-sorbed concentration of the solute (mg/g) and the equilibrium aqueous concentration of the solute (mg/L), respectively. Also, K and n refer to the Freundlich isotherm constants. Table 12.13 represents the

Table 12.13 Freundlich isotherm constants for the sorption of crude oil and dissolved organic carbon. DOC: dissolved organic carbon, FA: fly ash and HDTMA-FA: modified fly ash by hexadecyltrimethylammonium

	Crude oil		Weathered oil (DOC)	
	FA	HDTMA-FA	FA	HDTMA-FA
K (mg/g)	41.11	57.54	0.063	0.218
1/n	0.239	0.298	0.773	0.901

Modified after Banerjee et al. (2006)



AD-HO AD-LCO AD-ILCO

AD-SO-HO AD-SO-LCO AD-SO-ILCO

Fig. 12.37 Comparison of oil uptake behavior of AD and SO-modified AD with ratio of HCFA: SO = 1: 0.004 for HO, LCO, and ILCO.SO: Sodium oleate, *AD* Ca-rich sample, *HCFA* high calcium fly ash, *HO* heating oil, *LCO* light crude oil and *ILCO* Iranian light crude oil. Reprinted with permission of (Surface modification of high calcium fly ash for its application in oil spill cleanup, Karakasi and Moutsatsou, Elsevier)

Freundlich parameters for uptake of crude oil and dissolved organic carbon. The Freundlich isotherm constants for the sorption of crude oil and dissolved organic carbon by both sorbents indicated that the crude oil sorbed greater than the dissolved organic carbon from weathered oil-contaminated seawatersorption.

In another study, high calcium fly ash from lignite combustion in electric power plants was utilized as oil sorbent (Karakasi and Moutsatsou 2010). Particle size, porosity, buoyancy ability and hydrophobicity are notable characteristics for oil spill processes. For this purpose, an oil spill was simulated by artificial ocean water and three different oils: heating oil, light crude oil, and Iranian light crude oil. To investigate the effect of high calcium fly ash composition on the oilsorption capacity, Ca-rich and Si-rich samples of high calcium fly ash were used. Sodium oleate, $C_{17}H_{33}COONa$ was selected as a surface active agent (surfactant) for modification of high calcium fly ash, and the effect of this agent on the sorption behavior of high calcium fly ash was investigated. The oilsorption capacities of high calcium fly ash were 0.7–0.9 and 0.5–0.6 g/g for Ca-rich and Si-rich samples, respectively (in dry media during 24 h). The oil was adsorbed in the high calcium fly ash pores and formed a semi-solid phase with high calcium fly ash. Figure 12.37 compares the oil uptake of Ca-rich sample and modified Ca-rich sample (with sodium oleate) for heating oil, light crude oil, and Iranian light crude oil.

As seen from Fig. 12.37, the light crude oil and Iranian light crude oil made more cohesive semi-solid phase than light viscous oil, heating oil. In addition, The Ca-rich and Si-rich samples of high calcium fly ash had different oilsorption behaviors due to greater hydrophobicity of Si-rich sample than the Ca-rich sample. But Ca-rich

Table 12.14 Comparison of oil uptake (g/g) of AD, M, and SO-modified AD in dry media for three different oils after 15 min and 24 h

	HO		LCO		ILCO	
HCFA Samples	15 min	24 h	15 min	24 h	15 min	24 h
AD	1.1	0.9	0.9	0.8	1.4	0.7
AD-SO	1.1	0.8	1.0	0.7	1.7	0.9
M	0.6	0.5	0.5	0.5	0.7	0.6

Modified after Karakasi and Moutsatsou (2010)

AD Ca-rich sample, *M* Si-rich sample, *SO* Sodium oleate, *HCFA* high calcium fly ash, *HO* heating oil, *LCO* light cycle oil, *ILCO* Iranian light crude oil

sample expanded in the presence of water (due to its free CaO content) and then trapped oil in its structure; as a result, the sample showed better sorption behavior than the Si-rich sample. Moreover, modified Ca-rich sample had no notable difference with nonmodified Ca-rich sample in oilsorption performance. Table 12.14 summarizes the oil uptake of Ca-rich, Si-rich, and modified Ca-rich samples in dry media for three different oils after 15 min and 24 h.

The effect of CaO content Ca-rich sample appeared in the uptake capacity at different high calcium fly ash: sodium oleate mass ratios. In low mass ratio of high calcium fly ash: sodium oleate = 1: 0.004, the more calcareous high calcium fly ash had excellent oilsorption efficiency, while the less calcareous high calcium fly ash had much higher mass ratio of high calcium fly ash: sodium oleate = 1: 0.5. This is explained by the CaO conversion to calcite and calcium oleate during modification, which enables high calcium fly ash to retain oil tightly.

Clay

The possibility of adsorbing and hosting molecules, fixed and interchangeable charges, nonmetric particle size, layered construction, possibility of tailored surface and interlayer chemical modification, among others are the unique properties of clays and clay minerals. Clay is hydrophilic in nature and contains some metal oxides and SiO_2. The clay mineral surface can be modified by some materials and surfactants for adsorbing organic compounds.

Carmody et al. (2007) used the ion exchange method to produce organophilic clays or organo-clay by use of various surfactants like octadecyltrimethylammonium bromide ($C_{21}H_{46}NBr$), dodecyldimethylammonium bromide ($C_{22}H_{48}BrN$), and di (hydrogenated tallow) dimethylammonium chloride (tallow). In this method, ions exchange with organic cation for creating a hydrophobic or organophilic surface and enhance organic removal capacity. Sodium in Wyoming Na-montmorillonite was used for ion exchange in this study. The diesel, hydraulic oil, and engine oil were used to evaluate the oilsorption behavior of organo-clay. The effects of the used material and surfactant were also investigated on the sorption capacity.

The oil uptake of modified organo-clays is presented in Table 12.15 and compared with other sorbents. It is obvious that the sorption capacity of organo-clay

Table 12.15 Oilsorption capacities of various modified organo-clays and other sorbents for diesel, hydraulic oil, and engine oil

Sorbent	Diesel sorption capacity (g/g)	Hydraulic sorption capacity (g/g)	Engine sorption capacity (g/g)	Watersorption capacity (g/g)
Organo-clay sorbent				
Swy-2, 1 CEC, ODTMA (SD1)	1.2	1.4	1.6	0.3
Bentonite, 1.5 CEC, DDDMA (BD1)	3.5	2.2	2.1	0.2
Swy-2, 1.5 CEC, DDDMA (SD2)	5.2	3.6	3.6	0.2
Bentonite, 1.5 CEC, tallow (BT1)	3.1	1.3	1.3	0.2
Swy-2, 1.5 CEC, tallow (ST1)	7.2	2.2	2.1	0.2
Other sorbent				
Pelletized grain, cotton-based (GC)	1.0	1.4	1.5	4.1
Milled wood, cellulose fibers (WF)	2.1	2.9	2.8	2.5
Organic/mineral powder (OM)	1.0	1.3	1.3	2.9
Cellulose/mineral powder (CM)	0.9	1.2	1.4	2.4
Organic/zeolite powder (OZ)	0.8	1.2	1.0	3.2
Organic with pecan nut shells/mineral powder (PM)	1.5	3.0	3.4	2.6
Zeolite (Z)	0.6	0.9	0.9	1.0
Sand (S)	0.2	0.3	0.3	0.3

Modified after Carmody et al. (2007)
CEC cation exchange capacity, *DDDMA* dodecyldimethylammonium, *ODTMA* octadecyltrimethylammonium, *Swy-2* Sodium in Wyoming Na

depends on the materials and surfactants used for surface modification. The sorption capacities of organo-clay increased when dodecyldimethylammonium and tallow were used as surfactants. This is due to their two long carbon chains, C_{18}, which provide more sites for oilsorption. The greatest oilsorption capacities were achieved for sodium in Wyoming Na, 1.5 cation exchange capacity, dodecyldimethylammonium and sodium in Wyoming Na, 1.5 cation exchange capacity, tallow because of the effect of clay's cation exchange capacity (cation exchange capacity = 1.5) on surfactant formation between the clay layers and modification with Na-montmorillonite.

According to the proposed multi-criteria decision-making analysis, the top five preferred sorbents for oilsorption are placed in the following order:

Dodecyldimethylammonium > tallow > milled wood, cellulose fibers > pelletized grain, cotton-based > Bentonite, 1.5 cation exchange capacity, dodecyldimethylammonium. Bentonite, 1.5 cation exchange capacity, tallow, Sodium in Wyoming Na, 1 cation exchange capacity, octadecyltrimethylammonium, organic/mineral powder, organic/zeolite powder, organic with pecan nut shells/mineral powder, and cellulose/mineral powder have the middle performance in oilsorption processes. The least preferred sorbents are zeolite and sand. The proposed multi-criteria decision-making analysis was combined from PROMETHEE and GAIA methods, which ranked the sorbents based on sorption capacity, cost factor, retention capacity, hydrophilicity, environmental factors, ease of use, biodegradability, and oil emulsion sorption capacity. The results demonstrated that the organo-clays are able to clean up oil spilled because of their high sorption capacity, retention capacity, and hydrophobicity. However, their cost, biodegradability, and reusability have a negative effect on the applications of these sorbents.

Carbon-Based Sorbents

Recently, carbon-based sorbents have attracted the attention of researchers because of their suitable surface area, excellent mechanical properties, large pore volumes, and good chemical stability. They also have high ability to sorb oil because of their porous structures. Graphite, grapheme, and activated carbon are used alone to remove spilled oil or improve other materials for this purpose. The carbon-based sorbents with superhydrophobic and superoleophilic surfaces can be produced by various methods.

Activated carbons are produced from raw source like wood, coconut shell, and charcoal. High surface area, porous structure, and acceptable surface reactivity have made them an appropriate strong sorbent to remove organic pollutants from water surfaces. These sorbents are used in powdered activated carbon and granular activated carbon forms. They are widely used in oilremediation processes, although less information is available on the mechanism of their adsorption. Fulazzaky (2011) investigated mass transfer resistance by activated carbon and developed the current mathematical models. In addition, this study emphasized the impact of porosity, nature of the raw source for activated carbons production, surface characters, molecular structure, and molecular weight on the sorption ability.

In another study, Fulazzaky and Omar (2012) examined the sorption ability of granular activated carbons (used in the block filter) to remove oil and grease from steam water and determined their accumulation rate and adsorption capacity. Finally, numerical models were developed for dynamic uptake of oil and grease. Oil and grease concentration, space of pores and accumulation time were selected as variables to improve the linear equations. The oil and grease concentrations before and after crossing the block filter with granular activated carbons were 5.7–101.2 and 0.0–0.1 mg/L in steam water, respectively. These results showed excellent behavior of block filter to uptake oil and grease contaminant. Figure 12.38 compares oil and

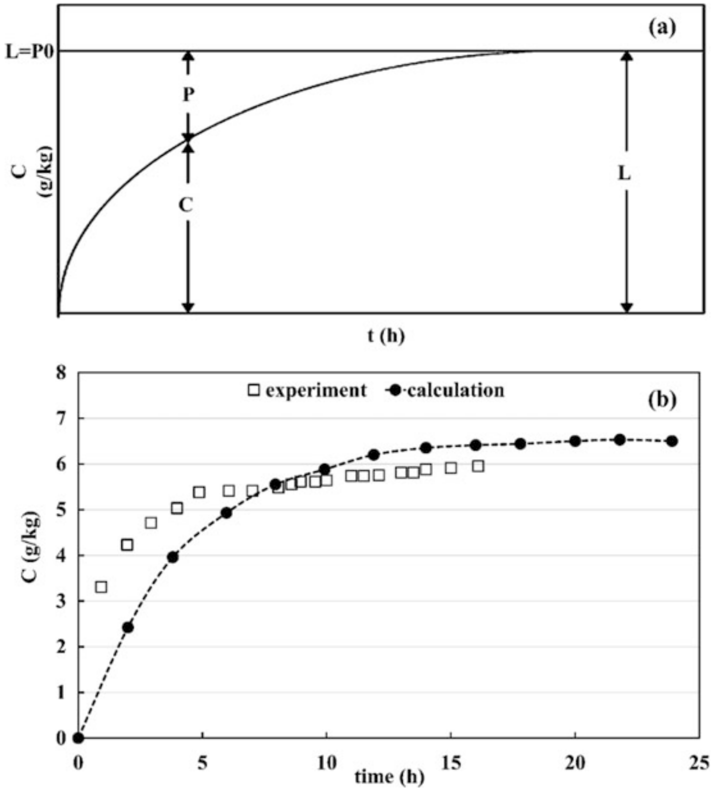


Fig. 12.38 (**a**) The theory, (**b**) experiment and calculation of OG accumulated in the BF. C (g/kg): amount of OG accumulated in the BF, L (g/kg): final uptake of the BF, P (g/kg): filled space of the BF by OG, P_0 (g/kg): total existing space of the BF before any accumulation of OG and t (h): accumulation time. OG: oil and grease and BF: block filter with granular activated carbons. (Modified after Fulazzaky and Omar2012)

grease accumulation in the block filter from the theory, experiment, and calculation. The curves show a good agreement between the obtained results from experiments and improved model. The capacity of the block filter to uptake oil and grease was 6.53 g oil and grease per kg granular activated carbons from steam water for accumulation rate of 0.23 g/ (kg h).

Activated carbon can be used to improve the sorption capacity of other oilsorbents. For this purpose, Keshavarz et al. (2016) modified the surface of polyurethane foam by different amounts of activated carbon to increase its oil removal efficiency from water. Activated carbon 0.5, 1, 2, and 3 wt% were used for impregnation of polyurethane foam. The results showed that the toughness and thermal resistance were improved by grafting of activated carbon on the foam surface. In addition, the oilsorption capacity increased while watersorption capacity decreased in all cases. Table 12.16 presents the oil removal efficiency of these sorbents. The optimal performance was observed for the polyurethane foam with

Table 12.16 Oil removal yield of initial and improved foam in different initial amounts of oil. AC: activated carbon and PU: polyurethane

			Modified PU foam by AC			
Initial oil (g)	Removal yield	Initial PU foam	0.5 wt%	1 wt%	2 wt%	3 wt%
5	Yield%	29.66	37.87	45.29	46.32	50.12
10	Yield%	40.29	52.15	52.61	57.59	60.39
20	Yield%	70.66	76.54	79.45	83.80	85.21
30	Yield%	75.85	92.10	93.93	94.85	95.91
50	Yield%	90.61	96.24	97.79	98.41	99.09
80	Yield%	99.02	97.99	99.38	100.0	100.0

Modified after Keshavarz et al. (2016)

Table 12.17 The comparison of the oilsorption capacity of the blank PU foam and 1 wt% AC surface-modified PU foam with some reported sorbents

Sorbent	Oils	Maximum uptake (g/g)
Carbonized pith bagasse	Gas oil	25.5
Natural wool fibers	Engine oil	5.56
Exfoliated graphite	Wasted engine oil	13.2
Nonwoven polypropylene	Light crude oil	9
Macroporous organogel	Crude oil	18.2
Blank PU foam	Light crude oil	20.38
Modified PU foam with 1 wt% AC	Light crude oil	27.15

Modified after Keshavarz et al. (2016)

1 wt% of activated carbon on its surface. This sorbent adsorbed up to 27.15 g/g for 30 g initial amount of oil.

They also compared the oilsorption capacity of the modified polyurethane foam with other reported sorbents (Table 12.17) to emphasize the excellent ability of the modified polyurethane foam to remove oil. The optimum sorbent achieved was 85% of the initial uptake of the modified polyurethane foam after four cycles of chemical regeneration, which shows its good reusability.

The activated carbon-based amendments are applied widely for in situ subsurface remediation of oilcontaminants. The combination adsorption and degradation is the base mechanism for oil removal in activated-carbon-based remedial technology. The effectiveness and persistence of contaminant degradation are less known in activated carbon-based remedial technologies. The uncertainty and the impacts of the specific amendment methods on the evaluation of treatment performance have caused this technology to be considered an emerging technology for oil removal. Fan et al. (2017) presented the first independent analysis of the activated-carbon-based remedial technology to improve its current understanding in the remediation industry. They emphasized that the adsorption and degradation occur at the same time in activated-carbon-based remedial technologies and focused on the effects of adsorption on degradation. The adsorption process enhances the contact time between oil pollutant and degradation reagents and concentrates the pollutant inside the pore

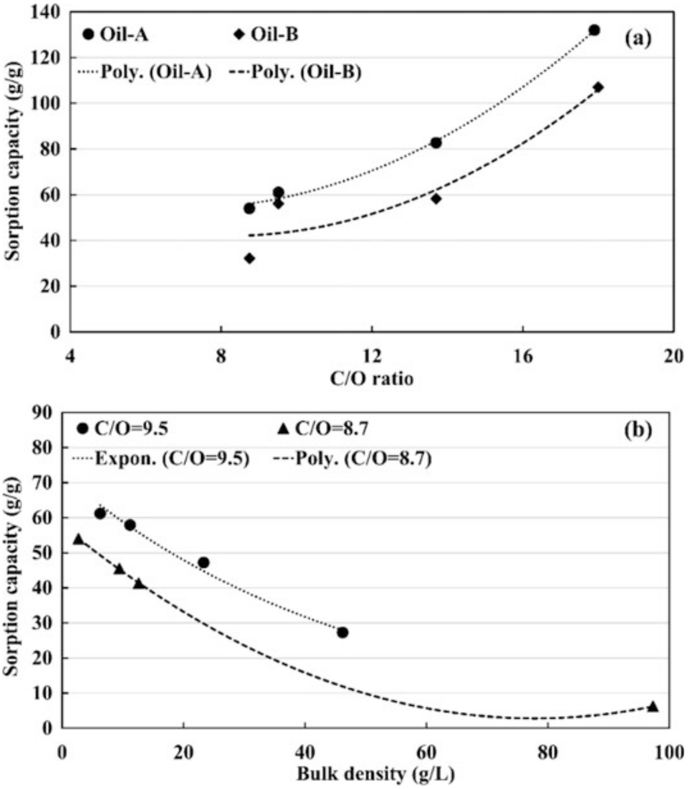


Fig. 12.39 The effects of (**a**) C/O ratio for $\rho_{ave} = 4.3$ g/L and (**b**) bulk density on the oilsorption capacity of TGR. C/O: carbon/oxygen and TGR: thermally reduced graphene. (Modified after Iqbal and Abdala2013)

structure of activated carbon. But the rates of adsorption are faster than that of degradation, thus it is difficult to collect certain evidence about degradation process.

Graphene and graphite are the other carbon-based oilsorbents, which are classified as high sorption capacity sorbents. Graphene has a two-dimensional structure, which can be fabricated by mechanical and chemical methods (Gupta and Tai 2016). Different types of graphene adsorbents are reported, which have high adsorption capacity.

Iqbal and Abdala (2013) investigated the ability of thermally reduced graphene for oil removal process. They fabricated thermally reduced graphene by thermal exfoliation of graphite oxide and used API crude oil and API oil as oil contaminant. The sorption capacity, the oil recovery, and recyclability of these sorbents were studied. The highest capacity (131 and 108 g/g for API crude and API oils) was observed for thermally reduced graphene sample (density of 3 g/L) and carbon-oxygen (C/O) ratio of 17.9. Figure 12.39 shows the changes of oilsorption capacity with different C/O ratios and bulk densities.

According to the results, thermally reduced graphene hydrophobicity increased by increasing the C/O ratio, while thermally reduced graphene sorption capacity decreased by increasing bulk density. Furthermore, thermally reduced graphene sorption capacity was higher for lower viscosity oil. Thermally reduced graphene capacity also depends on the total pore volume. An increase in the total pore volume increases the sorption capacity. The large pores (>50 nm) had a significant effect on the increase in sorption capacity.

The results of recovery process with vacuum filtration showed that the filtration time enhanced with increasing the number of recovery cycle and oil viscosity. In addition, the sorption capacity decreased with recycling of the thermally reduced graphene because of retaining or uncovering the amount of oil during recycling and decreasing of pore volume during filtration and compression processes. A significant reduction of sorption capacity was observed after the second cycle. During six cycles, the sorption capacities of API crude oil are greater than those of API oil because of its greater viscosity. Furthermore, some types of graphene with high sorption capacity are reported, like spongy graphene with sorption capacity of 20–86 times its own weight and reduced graphene by natural phenolic acids with sorption capacity of 15–61 times its own weight (Gupta and Tai 2016).

Graphite is fabricated with the accumulation of graphene sheet (ten or more) by van de Waals forces. The exfoliated graphite fabricates with the graphite by chemical, mechanical, and thermal methods. The exfoliated graphite is a porous material with higher volume, lower density, and higher specific surface area than graphite (Chung 2016). Therefore, the exfoliated graphite can be selected as an oil sorbent.

Toyoda et al. (1998) found that exfoliated graphite was able to uptake the heavy oil and it was collected from the water surface easily. The maximum sorption capacity of exfoliated graphite for heavy oil was reported to be more than 80 times its own weight. They also succeeded to recover about 80% of the sorbed oil. Three types of oil with various viscosities and specific gravities were used. Table 12.18 gives the sorption results of these three kinds of oil. The uptake of oil A was greater than that of oil B and its sorption process was faster due to its lower viscosity. The

Table 12.18 Comparison of oilsorption capacity of exfoliated graphite (EG) for different oils

Weight of heavy oil (oil per 1 g of EG)	Oil A (heavy oil) (specific gravity: 0.8640 g/cm ^{3}, viscosity: 4 poise)	Oil B (heavy oil) (specific gravity: 0.9449 g/cm ^{3}, viscosity: 350 poise)	Oil C (crude oil) (specific gravity: 0.8259 g/cm ^{3}, viscosity: 4 poise)
40	O	O	O
60	O	O	O
75	O	O	O
80	O	Δ	(O)
86	O	X	Δ
98	(O)	X	X
105	Δ	X	X

Modified after Toyoda et al. (1998)

O complete sorption, *Δ* trimming by transparent oily materials, *X* not complete sorption

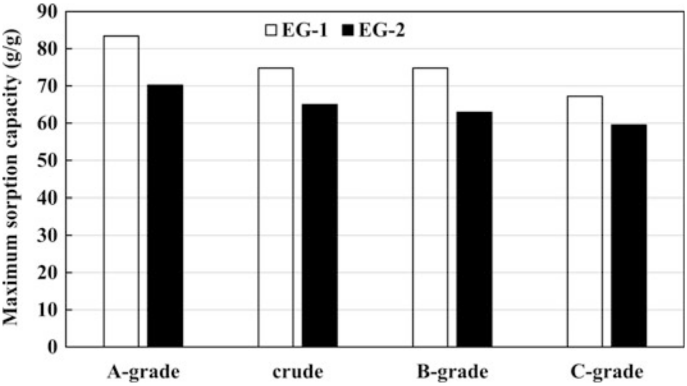


Fig. 12.40 The maximum sorption capacities of EG-1 (bulk density: 6 kg/m^3, total pore volume: 2.3 × 10^{-2} m^3/kg) and EG-2 (bulk density: 10 kg/m^3, total pore volume: 2.0 × 10^{-2} m^3/kg) for A-Grade (specific gravity: 864 kg/m^3, viscosity: 0.4 kg/m.s), crude (specific gravity: 825 kg/m^3, viscosity: 0.4 kg/m.s), B-grade (specific gravity: 890 kg/m^3, viscosity: 27 kg/m.s), and C-grade (specific gravity: 949 kg/m^3, viscosity: 35 kg/m.s) oils at 25 °C. EG: exfoliated graphite. (Modified after Toyoda and Inagaki2000)

sorption rate of oil A was similar to oil C but the maximum sorption capacity of oil C was similar to oil B. These results showed the exfoliated graphite can be used as effective oil sorbent.

In another study, Toyoda and Inagaki (2000) investigated the effect of bulk density of oil on the sorption behavior of exfoliated graphite. The highest uptakes of two types of the exfoliated graphite are shown in Fig. 12.40 for different oils.

According to the results, up 70 g of oilsorption was obtained for 1 g of exfoliated graphite-1, while the sorption capacity of exfoliated graphite-2 was slightly lower than that of exfoliated graphite −1 (about 70 g/g). For high viscous heavy oils (B-grade and C-grade), the sorption capacities were lower than the values for A-grade because of their higher viscosity. Moreover, the effects of temperature and viscosity were determined on the maximum sorption capacity by exfoliated graphite-1. The maximum sorption capacities increased by increasing temperature and decreasing viscosity (except for crude oil). The crude oil had a different behavior so that the crude sorption capacity decreased with increasing viscosity in viscosity greater than 1 kg/m.s and below 0.5 kg/m.s.

The highest sorption time was observed for A-grade oil with exfoliated graphite-1. In addition, the sorption capacities decreased with increasing bulk density and decreasing pore volume of exfoliated graphite samples. A compression or suction filtration was used to recover sorbed oil, and recovery rate was estimated at about 60–70%. These results clearly emphasized the ability of exfoliated graphite for oil removal, but investigation of the effect of other properties and development of the understanding of their sorption mechanism were suggested.

Graphite can improve the sorption capacity of other materials as oilsorbents. Hu et al. (2013) added graphite to the pure isobutylene-isoprene rubber (IIR) cryogel to increase its oil removal ability. They reported the modification method of isobutylene-isoprene rubber 1751 by graphite and explained its sorption properties. The maximum sorption capacities were 17.8, 21.6, and 23.4 g/g for crude oil, diesel, and lubricant oil, respectively. The modified isobutylene-isoprene rubber showed reusability after 30 cycles and the sorption capacity had no significant change during reuse by centrifugation. In addition, this modified isobutylene-isoprene rubber was able to sorb the organic solvents like benzene, toluene, xylene, hexane, heptane, and cyclohexane.

To improved graphite, Ding et al. (2014) presented an improved expanded graphite with magnetic particles for oil uptake. They added magnetic particles to expanded graphite by the blended calcination method. The expanded graphite can float on the water surface because of its low density. Adding magnetic particles can improve expanded graphite's application in oil removal processes especially in oil recovery. The sorption capacity of expanded graphite with magnetic particles was 35.72 g/g for crude oil at the first time of sorption and sorbed oil recovered about 80% of its initial value.

Carbon aerogels, graphene or carbon nanotubes-coated sponges, carbon nanotube forests, graphene foams or sponges, carbon coatings, porous carbon nanoparticles, and carbon fibers are other carbon-based materials, which can be used as oilsorbents. Table 12.19 summarizes the best performances of various carbon-based sorbents.

Other Mineral Powders

The possibility of using superhydrophobic and oleophilic calcium carbonate powder selectively for oilsorption was laboratory investigated by Arbatan et al. (2011). They improved the calcium carbonate powder with fatty acid to achieve a superhydrophobic and oleophilic surface. The sorption capacity of this porous sorbent was examined for diesel oil and crude oil.

Comparison between scanning electron microscope images of calcium carbonate crystal before and after treatment revealed that the modified crystal had a rougher surface because of treatment erosion. The results of contact angles of treated powder indicated that the fatty acid-treated-calcium carbonate powder sorbed oil, while water cannot penetrate into the mass powder (Fig. 12.41).

Figure 12.42 also shows the oil separation process from water by use of treated-calcium carbonate powder, qualitatively. As one can see, the as-prepared powder sorbed the diesel oil and oil-loaded powder could be recovered, effortlessly.

In addition, the adsorption efficiencies of treated calcium carbonate powder of varied oil /water mixtures were studied and the results are prepared in Table 12.20. The mixtures with light weight of water had lower oilsorption efficiency for both oilcontaminants. But low amount of water in the separation process is preferred. An environmentally friendly, low-cost, easy surface modification and excellent oilsorption behavior make an appropriate superhydrophobic calcium carbonate powder for cleaning up spilled oil.

Table 12.19 Summaries of the excellent sorption behavior of various carbon-based sorbents

Sorbent	Materials	Method	Density (mg/cm^3)	Water contact Angle (°)	Sorption capacity (g/g)	Method of extraction	References
Carbon nanotubes (CNT)	1,2-dichlorobenzene, ferrocene powder	Chemical vapor deposition (CVD)	5–10	156	80–180	Mechanical	Gupta and Tai (2016)
CNT	1,2-dichlorobenzene, acetonitrile, p-phenylenediamine	Hydrothermal followed by purification, drying and treating, diazotization Reaction	–	140.8	346–1190 wt %	Heat treatment	Sun et al. (2014)
CNTs-coated sponges	PU sponge, Tris–HCl, CNTs, ODA, anhydrous ethanol	Self-polymerization	–	158	22–35	Mechanical	Gupta and Tai (2016)
CNT sponges	Ferrocene catalyst precursor, 1,2-Dichlorobenzene carbon source	CVD	7.5	–	92.3	–	Zhu et al. (2013)
Graphene	Graphene oxide, pyrrole	Hydrothermal followed by freeze drying and annealing	2.1 ± 0.3	–	200–600	–	Gupta and Tai (2016)
Graphene coated sponges	Melamine sponge, PDMS, graphene	Dip coating	11.3	162	54–165	Mechanical squeezing	Gupta and Tai (2016)
Graphene/carbon nanotube	Flake graphite powder, $NaNO_3$, $KMnO_4$, H_2SO_4, HNO_3, HCl, H_2O_2	Hummers method	–	–	0.232 (saturated adsorption capacity)	–	Huang et al. (2019)
Carbon aerogel	Bacterial cellulose pellicles	Freeze-drying followed by pyrolysis	4–6	128.64	106–312	Distillation, direct combustion	Gupta and Tai (2016)
Carbon aerogel	Cellulose microfibrils	Freeze-drying followed by pyrolysis	10	149	50–87	Immerse into ethanol	Meng et al. (2015)

Graphene–CNTs aerogel	GGO, CNTs	Freeze-drying followed by chemical reduction	0.16–22.4	132.9	215–913	Mechanical or heating	Gupta and Tai 2016)
Polyimide/graphene aerogel	Natural graphite powder, H_2SO_4, $NaNO_3$, $KMnO_4$, HCl, H_2O_2, PMDA, ODA, DMA, TEA	Hummer’s method	–	136	22.94–37.44	Squeezing	Ren et al. (2019)
Graphite	Natural graphite, H_2SO_4, HNO_3, $KMnO_4$ or $FeCl_3$	Thermal expansion of H_2SO_4–graphite intercalation compound	3.9–25.7	–	2.4–9.7 L/ 100 g absorbent	–	Gupta and Tai (2016)
Carbon soot sponge	Ethylene, oxygen, and melamine sponges	Combustion flame method followed by dip-coating	–	144	25–80	Heating	Gupta and Tai (2016)
Melamine-derived carbon sponges	Melamine foams, sodium bisul te copolymer,	Electric furnace heating followed by pyrolysis	6.7	150	93	Compression	Stolz et al. (2016)
Carbon nanofibers/ carbon foam composite	CLR, THF, polyurethane (PU) foam slabs	Template synthesis of carbon foam and CCVD treatment	–	140	15–28	–	Gupta and Tai (2016)
Carbonaceous nanoparticles modified polyurethane foam	Carbonaceous nanoparticles, PU foam	Ultrasonication	–	127.6	50–121	–	Gupta and Tai (2016)
Hollow carbon beads	Polysulfone, N-methyl-2-pyrrolidone, tetraethyl orthosilicate, cetyltrimethylammoniumbromide, sodium hydroxide	Simple phase inversion method and subsequent carbonization	200	148	50–55% of their own volume	Heat treatment	Gupta and Tai (2016)
Hollow carbon fibers	Cotton balls	Pyrolysis in nitrogen	–	150	32–77	Mechanical	Wang et al. (2013)

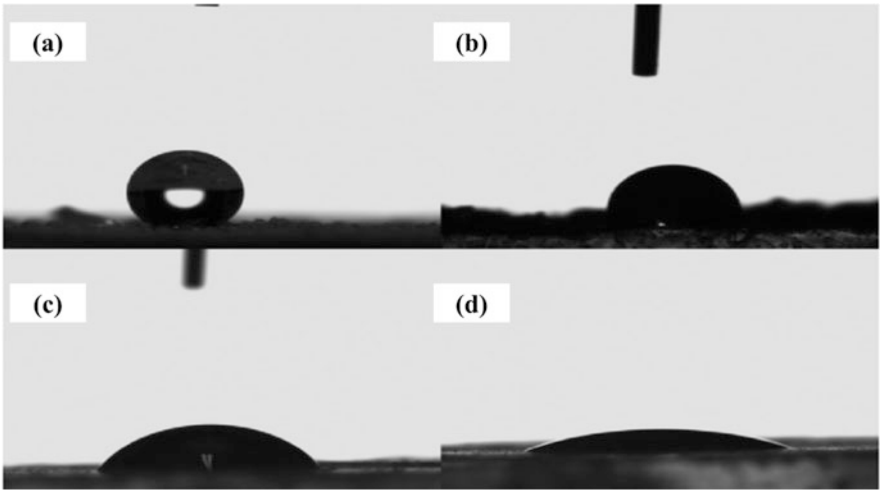


Fig. 12.41 (**a**) A water droplet on the fixed powder on a glass slide using a thin layer of glue, contact angle (CA) = 152°, (**b**) a water droplet on a flat piece of fatty-acid-treated natural calcite crystal, CA = 93°, (**c**) a diesel oil droplet on the treated flat piece of calcite crystal, CA = 42° and (**d**) a crude oil droplet on the treated flat piece of calcite crystal, CA = 25 °C. Reprinted with permission of (Superhydrophobic and oleophilic calcium carbonate powder as a selective oil sorbent with potential use in oil spill cleanups, Arbatan et al., Elsevier)

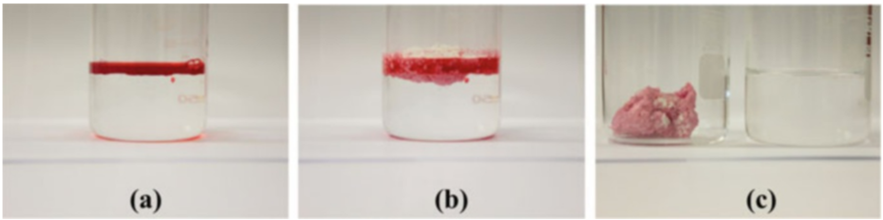


Fig. 12.42 Oil–water mixture: (**a**) before addition, (**b**) after addition, and (**c**) after separation of powder; 10 g of diesel oil (red) was added to 90 g water, then 10 g of as-prepared sorbent was added to the mixture. Reprinted with permission of (Superhydrophobic and oleophilic calcium carbonate powder as a selective oil sorbent with potential use in oil spill cleanups, Arbatan et al., Elsevier)

Table 12.20 The oilsorption efficiency (%) for diesel and crude oils for different oil/water ratios

Oil/water ratio (w/w)	Diesel oil–water	Crude oil–water
1:100	99.6	99.5
1:50	99.2	99.1
1:20	98.7	98.9
1:5	98.5	98.2
1:1	98.3	98.1

Modified after Arbatan et al. (2011)

Incorporating nanoparticles by some materials with low surface energy in sol–gel technique has been suggested to produce a superhydrophobic surface, as a cost-effective method. The SH surfaces are generally self-cleaning and oleophilic. Nevertheless, improvement of their oleophilicity is very important in order to use them in practical applications like cleaning up spilled oil. Lakshmi et al. (2012) modified silica nanoparticles with perfluoroalkylmethacrylic copolymer to fabricate a sol–gel nanocomposite coating. The wetting property of different coatings like sol–gel, perfluoroalkylmethacrylic copolymer, sol–gel-perfluoroalkylmethacrylic copolymer, sol–gel-silica and sol–gel-perfluoroalkylmethacrylic copolymer-silica coating was compared with each other by determining water contact angle, ethylene glycol contact angle, and lubricant oil contact angle.

The water contact angle of the perfluoroalkylmethacrylic copolymer coating (108.2°) was greater than that of sol–gel coating (89.0°). With incorporating of perfluoroalkylmethacrylic copolymer to the sol–gel coating (sol–gel-perfluoroalkylmethacrylic copolymer coating), the water contact angle decreased to 97.3°. While, after incorporating of fumed silica in the sol–gel and sol–gel-perfluoroalkylmethacrylic copolymer mixtures, the water contact angle of sol–gel-silica and sol–gel-perfluoroalkylmethacrylic copolymer-silica were 155° and 158°, respectively. The results of organic contact angle measurements indicated that ethylene glycol and oil contact angle of perfluoroalkylmethacrylic copolymer coating was greater than those of sol–gel and sol–gel-perfluoroalkylmethacrylic copolymer coating. The greatest amounts of ethylene glycol and oil contact angles were observed for sol–gel-perfluoroalkylmethacrylic copolymer-silica (13.2 wt% of perfluoroalkylmethacrylic copolymer), 146.7 and 113.3°, respectively.

The effect of perfluoroalkylmethacrylic copolymer concentration in the coating of sol–gel-perfluoroalkylmethacrylic copolymer-silica was investigated on the water contact angle, ethylene glycol, and oil contact angles (Fig. 12.43). According to the

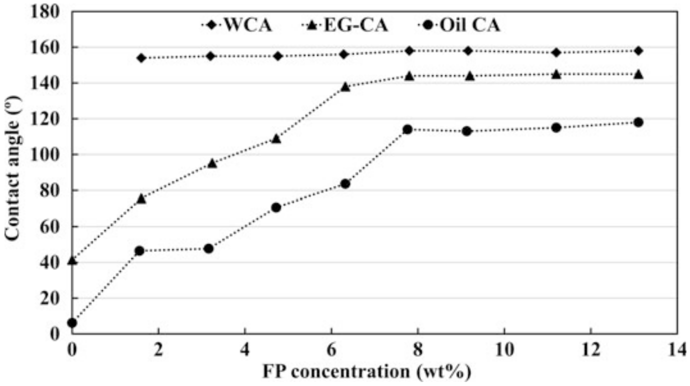


Fig. 12.43 Effect of FP concentration in the coating of MT-CS-FP-silica on the WCA, EG-CA, and oil CA. FP: perfluoroalkylmethacrylic copolymer, MT-CS-FP: sol–gel-FP, WCA: water contact angle, EG-CA: ethylene glycol contact angle and CA: contact angle. (Modified after Lakshmi et al. 2012)

obtained results, the water contact angle does not change by increasing the perfluoroalkylmethacrylic copolymer concentration in the coating of sol–gel-perfluoroalkylmethacrylic copolymer-silica and remains about 155°. While, ethylene glycol and oil contact angles enhance by increasing the perfluoroalkylmethacrylic copolymer concentration and reach the greatest value for 7.8 wt%, whereafter they are approximately constant.

The results indicated that the increased oleophobicity is due to the perfluoroalkylmethacrylic copolymer effects on the surface energy (decreases that) and the random distribution of silica on the surface roughness. Therefore, low concentration of the perfluoroalkylmethacrylic copolymer can fabricate the superhydrophobic (water contact angle >150°) and superoleophilic (oil contact angle <10°) surfaces.

The sliding angle is another parameter for measuring superhydrophobicity of surface (<10°). The water sliding angle was <2° for all coatings, whereas in all perfluoroalkylmethacrylic copolymer concentrations, the sliding angle value decreased for ethylene glycol (>90° to 20°) and did not change for oil (>90°). The reported method for fabrication of superhydrophobic and oleophobic sol–gel nanocomposite coatings is low cost and feasible. The authors suggested this method can be used for glass, metal, and other composites with various shapes. Moreover, this method needs fluorine less than the other reported methods.

In summary, Table 12.21 compares the sorption or removal performance of various tools or sorbents of remediation technology for oil spills. To select the best one, the effective parameters of oil spill control should be considered. The effects of water conditions, wind conditions, current, tides, and atmospheric conditions were investigated on oil cleanup (Al-Majed et al. 2012).

In conclusion, inorganic adsorbents can be used for spilled oil removal and have the same sorption capacity as synthetic sorbents. These sorbents are less expensive, readily available, and buoyant; nevertheless, it is necessary to improve their structure for using them as spilled oil adsorbents.

12.6 Part II: Bioremediation Technology

12.6.1 Bioremediation: Definition, Advantages, and Disadvantages

In bioremediation, microorganisms degrade chemical materials and metabolize them in order to restore the quality of environment. The aim is accelerating the natural treatment process as well as producing by-products like H_2O, CO_2 and heat by microorganisms via assimilating the organic molecules to cell biomass (Atlas 1995). For marine oil spill, the ubiquitous microorganisms in the oil spill location degrade hydrocarbons. Microorganisms degrade paraffinic and aromatic hydrocarbons with different degradation rates. The easiest degradation hydrocarbons are alkanes with a

Table 12.21 Sorption or removal performance of different tools and sorbents for oilremediation technology

Sorbent or tool	Type of oil	Maximum sorption capacity (g/g) or removal efficiency (%)	References
Oleophilic drum skimmer	HydroCal 300	Recovery rate ~25 L/min	Broje and Keller (2007a)
Octadecyltrichlorosilane modified 3D-printed oil skimmer	Hexadecane Gasoline Corn oil Mineral oil	90%	Yan et al. (2016)
Hydrocarbon-based herder	Alaska north slope crude	90%	Buist et al. (2011)
Corexit 9500 dispersant	Total petroleum hydrocarbons	67.3%	Zahed et al. (2010)
Nochar A 650 solidifier	South Louisiana crude oil	70%	Delaune et al. (1999)
Waste-set #3200 ® and Rubberizer solidifiers	Arabian light crude Prudhoe Bay crude Intermediate fuel oil 180	80% 80% 60%	Sundaravadivelu et al. (2016b)
Milkweed Cotton Polypropylene web Milkweed/polypropylene	Light crude oil	~40 g/g ~35 g/g ~12 g/g ~28 g/g	Choi and Cloud (1992)
Nonwoven wool fiber	SN 150 oil	~15 g/g	Radetić et al. (2003)
Silk-floss	Crude heavy-oil	85 g/g	Annunciado et al. (2005)
Poly propylene nonwoven	Light crude oil Gas oil no.1 Gas oil no.2 Heavy crude oil	8.26 g/g 7.6 g/g 8.46 g/g 9.12 g/g	Bayat et al. (2005)
Polyvinyl chloride-polystyrene fibers Polystyrene (PS) fibers Composite polystyrene–polyurethane (PU) mat	Engine oil	149 g/g 113.87 g/g 64.40 g/g	Sarbatly et al. (2016)
Electrospun composite PS–PU fibers	Engine oil Sunflower seed oil	~65 g/g ~48 g/g	Lin et al. (2013)
Electrospun polystyrene nanofiber membrane	Diesel	100%	Lee et al. (2013)
Modified sponge	Lubricating oil	~20 g/g	Zhu et al. (2011)

(continued)

Table 12.21 (continued)

Sorbent or tool	Type of oil	Maximum sorption capacity (g/g) or removal efficiency (%)	References
Nanofibrillated cellulose-based aerogel	–	139–356 g/g	Liu et al. (2016)
Methyltrimethoxysilane based silica aerogels	Heavy crude oil Light crude oil	16.7 g/g 13.7 g/g	Mahani et al. (2018)
TiO_2–sodium alginate composite aerogels	Soybean oil	~100%	Dai et al. (2019)
Modified foam rubber	Compressor oil	~12 g/g	Liu and Kang (2018)
Magnetic composite resin PS/Fe_3O_4 fibrous Fe_3O_4–carbon nanotubes (CNT) sponges Fe_3O_4@SAS	Kerosene Edible oil Diesel oil and gasoline Crude oil	100% ~100% 99% 90%	Qiao et al. (2019)
Modified Fe_3O_4@C nanoparticles	Lubricant	3.8 g/g	Zhu et al. (2010)
Modified magnetic polymer nanoparticles	Salad oil Lubricating oil	4.26 g/g 9.41 g/g	Gu et al. (2014)
PU@Fe_3O_4@PS sponge	Various oils	24–105 times of its own weight	Zhou et al. (2019)
Emulsifier-modified expanded perlite	Heating oil	~45%	Roulia et al. (2003)
Modified organo fly ash	Arabian crude oil	1.8 g/g	Banerjee et al. (2006)
Modified high calcium fly ash	Heating oil Light crude oil Iranian light crude oil	1.1 g/g 1 g/g 1.7 g/g	Karakasi and Moutsatsou (2010)
Organo clay	Diesel oil	7.2 g/g	Carmody et al. (2007)
Granular activated carbon (GAC) block filter	Oil and grease	6.53 g/kg GAC	Fulazzaky and Omar (2012)
Activated carbon modification of PU foam PU foam	Light crude oil	27.15 g/g 30.38 g/g	Keshavarz et al. (2016)
Thermally reduced graphene	Crude oil	300 g/g	Iqbal and Abdala (2013)
Exfoliated graphite	Crude oil	~85 g/g	Toyoda and Inagaki (2000)
Graphite/isobutylene-isoprene rubber	Lubricant oil	23.4 g/g	Hu et al. (2013)

(continued)

Table 12.21 (continued)

Sorbent or tool	Type of oil	Maximum sorption capacity (g/g) or removal efficiency (%)	References
Magnetic expanded graphite	Crude oil	35.72 g/g	Ding et al. (2014)
Modified calcium carbonate powder	Diesel oil Crude oil	99.6% 99.5%	Arbatan et al. (2011)

chain of 10–26 carbons and aromatic hydrocarbons with low molecular weight. High-molecular-weight aromatic hydrocarbons and branched alkanes are two classes of hydrocarbons difficult to biodegrade (Atlas and Cerniglia 1995). The main genera of fungi and bacteria for oil degradation are listed in Table 12.22.

In aquatic systems, the dominant hydrocarbon degraders are bacteria. In marine environment, the concentration of oil and bioavailability of nutrients, the extent to which the natural biotreatment has already taken place and time affect the biodegradation of an oil spill (Zahed et al. 2010). To grow the hydrocarbon-degraders, nutrients like phosphorus and nitrogen, which are always found in marine environment with low concentrations, are necessary. However, the natural attenuation does not proceed with a noticeable rate because of the scarcity of nutrients (Atlas and Bartha 1973). Moreover, high concentration of oil causes a remarkable lag phase in around 2–4 weeks into its bioremediation process. Microorganisms normally need at least 1 week to acclimatize to the environment and the completion of bioremediation process takes months and years (Zahed et al. 2010). To improve the rate of the natural biodegradation, addition of dispersants and fertilizers (biostimulation), and insemination of contaminated seawater with hydrocarbon-degrading microorganisms are essential. Although there is a competition between the indigenous and the inoculated microorganism because of the vast distribution of fungi and bacteria, screening the microorganism from the polluted sites and inoculating them to the polluted seawater is a way for seawater bioremediation. Bioaugmentation cannot be an effective way for oil spill bioremediation (Venosa et al. 1991). The application of fertilizers such as nitrogen and phosphorous nutrient supplements for oil-contaminated seawater is effective but with low efficacy for the bioremediation of severely degraded oil (Bragg et al. 1994; Zahed et al. 2010). Surfactants or dispersants improve the oil bioavailability to hydrocarbon degraders and the success of their application was reported in the study of Zahed et al. (2010). Some studies have been performed on the eutrophication caused by adding phosphorus and nitrogen to the water. According to the work of Bragg et al. (1994) and Atlas and Cerniglia (1995), applying fertilizer has not caused the eutrophication and no critical toxicity has been found for the sensitive species. Always the resisting nonbiodegradable components of oil remain as asphaltic residues and can coat and suffocate marine life. During bioremediation technology, hydrocarbons biota toxicity is removed from the contaminated site.

Table 12.22 Major genera of oil-degrading bacteria and fungi

Microorganism	Degradable compounds
Bacteria	
Pseudomonas spp.	4-chlorobenzoate
Brachybacterium	
Janibacter	Polycyclic hydrocarbon
Flavobacterium	Chlorophenols
Nocardia spp.	4-chlorobenzoate
Mycobacterium	Pyrene, polycyclic hydrocarbon, Diesel, phenanthrene
Arthrobacter spp.	Phenanthrene, methyl-tert-butyl ether,
	Tert-amyl methyl ether, ethyl-tert-butyl ether
Dietzia	n-C12 to n-C38 alkane components
Brevebacterium	Oil, Asphaltenes
Rhodococcus	Hexadecane, polychlorinated-biphenyl,
	Polycyclic hydrocarbon, trichloroethane
Fungi	
Fusarium	Tert-butyl alcohol and methyl-tert-butyl ether
Aspergillus	Pyrene, Benzo(a)pyrene
Candida	Toluene
Trichoderma	Phenanthrene
Phanerochaete	Benzo [a] pyrene, phenanthrene, and fluorine
Mortierella	2, 4-Dichlorophenol
Trichoderma harzianum	Naphthalene *Aspergillus fumigatus*
Aspergillus spp.	Crude oil
Cunninghamella elegans	Phenanthrene
Aspergillus Niger	n-hexadecane Penicillium sp
Cunninghamella elegans	Pyrene
Aspergillus ochraceus	Benzo [a] pyrene, Trametes versicolor
Aspergillus sp. RFC-1	Different PHs
Penicillium sp. RMA1 and RMA2	Crude oil

Modified after Al-Hawash et al. (2018); Dave and Ghaly (2011)

An analysis at an international level was performed by Quintella et al. (2019) for bioremediation technology based on strengths, weaknesses, opportunities, and threats. They reported that the bioremediation is growing for water (53%), soils (36%), and sludge (11%) yearly and at nearly constant rates. Predominantly, bacteria (57%), enzymes (19%), fungi (13%), algae (6%), plants (4%), and protozoa are the bioremediation agents and the oils (38%), metals (21%), organic waste (21%), polymers (10%), food (5%), cellulose (5%), and biodiesel are the main pollutants. Basically, the final aim of remediation methods is providing the net benefits for environment. Selection of each response method depends on conditions of sea and weather; the kind of oil, biological, physical, and economical characteristics of the spilled site; depth of water; the season and effectiveness of cleanup; concentration of oil spilled; and the rate of spillage (Dave and Ghaly 2011). The most effective response to the oil spill with much decreased cost is a combination of physical, chemical, and biological treatments. Recently, Villela et al. (2019) have reported an analysis of the patent documents in bioremediation, which use microorganisms to clean seawater. According to their report, China, Russia, and USA have various temporal deposit profiles dictated by their historical, political, and economic regulations. In their list of countries, which have patent applications, China has the first place with 152 deposits followed by Russia with 133 and then USA with 48. Among 500 patent documents considered in this study, 368 patents presented a description of oil degradation exclusively by bacteria, 24 by yeasts and fungi, 32 by mixed consortia, 1 using a microalgal strain, and 1 by archaea. The major microbial genera are Pseudomonas with 114 patents, Bacillus with 75, and Rhodococcus with 60.

Metabolic Processes of Bioremediation

The first level of the organic compound metabolism is use of the substrate, which serves as an electron donor for microbial growth and acts as a source of energy and carbon. When the nature of the molecular structure, which induces the essential catabolic enzymes, cannot provide the energy and carbon, co-metabolism to site-treatment of xenobiotics is required to be applied. The term co-metabolism refers to the metabolism of a material that cannot act as a source of energy, carbon, and essential nutrient. The essential nutrients are provided only in the presence of a primary (enzyme inducing) material (Boopathy 2000). The term aerobic process refers to the metabolic activities involving oxygen as a reactant. The two primary enzymes employed during mineralization and transformation of xenobiotics by aerobic organisms are dioxygenases and monooxygenases. Aerobic bacteria like *Alcaligenes, Pseudomonas*, *Mycobacterium, Sphingomonas*, and *Rhodococcus* have ability to treat pollutants. These microbes degrade hydrocarbons including alkanes and polycyclic aromatic compounds as well as pesticides. When an activity of an organism involves other molecules besides oxygen, the process is anaerobic. Anaerobic microbes apply electron acceptors like iron, nitrate, manganese, carbon dioxide and sulfate based on their availability and the dominant redox conditions. Use of anaerobic bacteria for biotreatment of polychlorinated biphenyls in sediments of river, dechlorination of the solvent chloroform, and trichloroethylene has been attracting much interest (Lovley 1995). In conclusion it can be said that the oxidation–reduction reactions play important role in bioremediation.

The Classes of Bioremediation

Bioremediation techniques are divided into two classes: in situ and ex situ. In ex situ technology, the treatments involve the physical removal of the polluted materials from contaminated site and transporting them to another site (Azubuike et al. 2016), while in situ technology is involved with treatment of the polluted materials at the site of contamination (Boopathy 2000). Therefore, excavation and its extra cost are not required. It does not disturb the structure of the soil. However, the important challenges of in situ techniques are the on-site installation of some complicated equipment and cost of design to increase the activity of microbes during bioremediation (Jain et al. 2011). The type and the quality of the contaminants, the type and the environmental situation of the contaminated site, and the cost of treatment determine the best treatment method (Khan et al. 2004). It is also required that before selecting the best method, a thorough investigation of the properties of the contaminated site be conducted. This process is important especially for in situ remediation since the performance of the treatment process is more complicated for monitoring and controlling through treatment than the ex situ remediation process (Morgan and Watkinson 1992). Achieving uniform remediation throughout the treatment is an important challenge for in situ treatment. In situ bioremediation methods were successfully applied to treat many contaminants like hydrocarbons in crude oils (Kim et al. 2014). To achieve successful in situ bioremediation, the important environmental conditions include the moisture content, status of electron acceptor, pH, availability of nutrient and temperature (Philp and Atlas 2005). Transferring the bioremediation methods, which have been tested in laboratory with good results to the field is the specific challenge of in situ bioremediation. The ex situ technology needs shorter time to treat than in situ technology and because of the ability to monitor, homogenize, and screen, it provides more uniformity of treatment. It can be used for a wide range of pollutants and is controlled easily. However, ex situ technology needs excavation that requires more cost and engineering for equipment. The base of the ex situ methods is the cost of treatment, type of contaminant, degree of pollution, depth of pollution, geographical location, and geology of the contaminated site. Philp and Atlas (2005) have described the performance criteria to select the ex situ method. In situ bioremediation includes bioventing, biosparging, permeable reactive barrier, intrinsic bioremediation, bioslurping, and phytoremediation. In conclusion, both in situ and ex situ technologies are beneficial in bioremediation; however, the type and the quality of the pollutants, the type and the medium of the contaminated site, and the cost of treatment determine the effective treatment method.

Bioventing

The method, which is also called soil vacuum extraction (Boopathy 2000), increases the bioremediation and the activity of indigenous microorganisms in order to microbial transformation of contaminants to safe state (Philp and Atlas 2005), using controlled airflow to deliver oxygen to the unsaturated zone (Azubuike et al. 2016). It is useful to remove the oily phase contaminants above the water table. Undissolved subsurface contaminants which get biodegraded contact with the oxygenated air. Appearance of CO_2 in an extraction well, which is near the contamination points but above the water table shows the biological activity. In comparison with the use of electron acceptors such as nitrates and hydrogen peroxide, bioventing is a cheaper technique and has obtained popularity especially to restore the sites contaminated by light spilled products (Höhener and Ponsin 2014).

Biosparging

In this method, air is injected with pressure below the water table in order to increase the concentration of oxygen in groundwater and enhance the rate of biotreatment using natural microorganisms. Biosparging increases the contact between soil and groundwater as a result of increasing the mixing in the saturated zone. The advantage of this method is that the installation of the small-diameter air injection points is easy with low cost and therefore the design and construction of the system is flexible.

Phytoremediation

In this method, plants are used to remove pollutants from water and soil via physical, biological, chemical, biochemical, and microbiological interactions. Depending on the contaminant, the types of phytoremediation include rhizofiltration, phytoextraction, phytovolatilization, phytodegradation, phytostabilization, rhizodegradation, and hydraulic control (Mahajan and Kaushal 2018; Yadav et al. 2018; Muthusaravanan et al. 2018). The factors to select a plant as a phytoremediator are: the required time to obtain the desired level of cleanliness of root system, toxicity of contaminant for plant, rate of plant growth, site monitoring, resistance of plant against disease and pests (Lee 2013). Based on the study of Miguel et al. (2013), the treatment by plants involves the uptake, displacement from roots to shoots accomplished by xylem flow, and accumulation in shoot (Azubuike et al. 2016). Moreover, accumulation and replacement are dependent on partitioning and transpiration between neighbor tissues and xylem sap, respectively. However, the process can be different based on the nature of pollution and type of plant. Most plants that grow in the contaminated site perform phytoremediation very well. Thus, the efficiency of phytoremediation method depends on the optimization of treatment by indigenous plants that grow in contaminated site by biostimulation or bioaugmentation using exogenous or endogenous plant rhizobacteria (Azubuike et al. 2016). Also, plant growth-promoting rhizobacteria is a factor that might play an important role in phytoremediation. It increases the biomass production and the ability of plants to tolerate the undesirable soil situations (Yancheshmeh et al. 2011; De-Bashan et al. 2012). Based on the study of Grobelak et al. (2015), the plant root growth, plant height, and plant stem growth increased when *Festuca ovinia L. and Brassica napus L. subsp. napus* were inoculated with exogenous plant growth-promoting rhizobacteria through germination of seeds, 14 days after plant growth, therefore protect the plants and seeds inhibition in heavy metal contaminated soil. Mesa et al. (2015) investigated phytoremediation of polluted site by metal with *Spartina maritime* in a similar way. They concluded that bioaugmentation with endogenous rhizobacteria increased metal accumulation and enhanced metal

Table 12.23 Some plants with phytoremediation potential

Plant (References)	Kind of pollutant	Initial concentration	% removal	Mechanism of removal
Dracaena reflexa Dadrasnia and Agamuthu (2013)	Diesel	1–5 wt%	90–98	Rhizodegradation
Ludwigia octovalvis Almansoory et al. (2015)	Gasoline	2078×10^2 mg/kg total petroleum hydrocarbons	~94	Biosurfactant enhanced rhizodegradation
Rizophora mangle Moreira et al. (2013)	Total petroleum hydrocarbons	33215.16 mg/kg	87	Phytostimulation and Phytoextraction
Sparganium sp. Gregorio et al. (2013)	Polychlorinated biphenyls	6.260 ± 9.3 10^{-3} μg/g	~92	Biostimulated Rhizodegradation
Phragmites australis Gregorio et al. (2014)	Polycyclic aromatic hydrocarbons	229.67 ± 15.56 μg/g	58.5	Rhizodegradation
Aegiceras corniculm Chen et al. (2015)	Brominated diphenyl ethers (BDE-47)	5 $\mu g g^{-1}$dw	58	Biostimulated degradation
Luffa acutangula Ignatius et al. (2014)	Fluoranthene and Anthracene	50 mg/kg	50–100	Phytostimulation[a]

[a] Hypothetical, needs further investigation
Modified after Azubuike et al. (2016)

removal as well as plant subsurface biomass. Table 12.23 lists various plant species that participate in phytoremediation of different pollutions (Azubuike et al. 2016).

Wang et al. (2012) and Kuiper et al. (2004) described other plants with phytoremediation potentials. One of the advantages of phytoremediation is phytomining, a process to use plants for remediating the polluted site by precious metals for bioaccumulating in plants and recovering after treatment. Other advantages include low cost, low installation and maintenance cost, large-scale operation, leaching of metal, prevention of erosion, protection of the structure of soil, and environmentally friendly (Khan et al. 2004; Van Aken 2009). There are some factors like contaminant concentration, depth of roots, longer treatment time, toxicity for plant, bioavailability to plant, and slow plant growth rate that restrict use of phytoremediation (Vangronsveld et al. 2009; Kuiper et al. 2004). There also is a probability that accumulated toxic pollutions transfer along the food chain. Some human interventions are required to enhance the capacity of phytoremediation because the plant–microbiome interactions are not adequate for a successful phytoremediation to CO_2 and H_2O is another disadvantage (Lee 2013). To understand and determine factors with a major role for beneficial microbiota assembly degrading PGP (plant-growth promoting) along with phytoremdiation processes, a competition-driven model for the interaction between rhizosphere and microbiome was proposed by Thijs et al. (2016). To ensure that the pathogenic microbial populations and opportunistic are controlled in the contaminated sites to increase the ability of enhanced phytoremediation processes using PGP microbes, some strategies are determined. These are including root exudate interference, disturbance, selection of plant in performance of microbiome, and feeding of the supply lines are determined to ensure that pathogenic microbial populations and opportunistic are controlled in polluted sites for increasing the ability of enhanced phytoremediation processes using PGP microbes. Since the plant–microbiome interaction is not adequate for a successful phytoremediation, to enhance the capacity of phytoremediation some human interventions are required. Some approaches to enhance phytoremediation have been reported by Wenzel (2009) and Schwitzguebel (2015).

Mechanisms of Phytoremediation

The mechanism of phytoremediation and its yield depend on the properties of the contaminated site and the type of pollution as well as bioavailability (Cunningham et al. 1996). For phytoremediation there are several ways. A root system where the main mechanisms to prevent toxicity are found primarily uptakes the pollutions. Here we have listed the mechanisms to treat soil, sediments, and water with impact on the mobility, volume, or toxicity of pollutants. There is overlap or similarities between some of the mechanisms.

Phytoextraction

In phytoextraction, which is also called phytoaccumulation, the plant roots uptake the translocation of metal pollutants from the soil to the aboveground parts of the plants (Yadav et al. 2018; Muthusaravanan et al. 2018). The method is inexpensive with a permanent removal of pollution. The mechanism depends mainly on the plant to grow fast, eradicate metals, tolerate their high concentrations, and accumulate high amounts in their shoots (Mahajan and Kaushal 2018; Brennan and Shelley 1999).

Rhizofiltration

This is applicable to remove metals or inorganic compounds from surface of water, groundwater, and wastewater. Rhizofiltration includes the uptake or precipitation into roots or the solution surrounding the roots. It is similar to phytoextraction but it is applicable for water than soil. The tobacco, sunflower, rye, Indian mustard, corn, and spinach have shown the potential to treat the contaminated waters by lead. Among them, sunflower has the greatest potential (Mahajan and Kaushal 2018). The plant should have substantial amount of surface area and high capacity to accumulate and tolerate the significant amount of pollutions. The ideal plant needs low cost to maintain, can grow in submerged situation, has the minimum secondary waste, and involves easy handling (Yahav et al. 2018).

Phytovolatilization

In this mechanism, the contaminants are adsorbed from the soil into the body of the plant to transform them into volatile products. Finally, the volatile degradation form is transpired with water vapor from the leaves, stems or other parts of plant, which the pollutants cross before attaining the leaves (Muthusaravanan et al. 2018). The method is applicable for contaminated soil, sediment, and water. The metal contaminants such as mercury, volatile organic materials like trichloroethene, and volatile forms of inorganic chemicals such as selenium and arsenic can be treated by phytovolatilization (Yadav et al. 2018; Muthusaravanan et al. 2018).

Phytostabilization

Plants immobilize pollutants of groundwater and soil through absorption and accumulation by precipitation or roots in the rhizosphere (the root zone of plants). The processes via reducing the mobility of the pollutant prevent migration to the groundwater and it in turn decreases metal bioavailability in the food chain (Muthusaravanan et al. 2018). Phytostabilization is useful to treat lead, cadmium, arsenic, zinc, chromium, and copper, and takes advantage of the soil chemical and environmental changes induced by the presence of the plant (Yadav et al. 2018). The mechanism is highly effective and treats a broad variety of contaminations. Additional resolution of phytostabilization includes the stabilization of waste and decreasing the next complications, hydraulic control, and reducing erosion via wind and water (Yadav et al. 2018).

Phytodegradation

In phytodegradation, which is also referred to as phytotransformation (Trap et al. 2005), either complex organic compounds are degraded to simple molecules or they are incorporated into the tissues of plant. First, the contaminants are taken up by the plants and then they are broken down by plants utilizing enzymes (Yadav et al. 2018). The enzymes are dehalogenase, peroxidase, oxygenase, nitrilase, phosphatase, and nitroreductase (Jabeen et al. 2009). Because the heavy metals are nonbiodegradable, this mechanism is limited to treat organic pollutions.

Hydraulic Control

In this mechanism, plant (tree) is used to control the movement of pollutions from the polluted site through groundwater. Large amount of water is utilized by trees with long roots and therefore they act as pumps to pull out the water. So the pollutions are absorbed along with water in this process (Muthusaravanan et al. 2018). Hydraulic control has been reported in some plants (reader is referred to the Table 12.6 of Muthusaravanan et al. 2018).

Rhizodegradation

In rhizodegradation, which is also referred to as rhizosphere bioremediation, the breakdown of pollutions occurs within the rhizosphere or plant root zone. It is carried out using fungi and bacteria (Yadav et al. 2018). Microorganisms are widespread in the rhizosphere since the plants exude enzymes, amino acids, sugars, and other compounds, which are effective to stimulate bacterial growth. It has been observed (Zhang et al. 2010) that the fungal and microbial degradation is stimulated by releasing of enzymes/exudates in the root zone of plant. The ideal performance depends on the association between plants and microorganisms in the rhizosphere, concentration of pollutions, the temperature, pH, texture and nutrition of soil, and rate of metabolism of microorganism (Yadav et al. 2018).

Permeable Reactive Barrier

The method is often maintained as a physical technique to treat the pollution in groundwater due to its mechanism and design to remove contaminants (Thiruvenkatachari et al. 2008); however, it has been reported that one of the mechanisms of contaminants removal in permeable reactive barrier methods is the biological reaction, which includes degradation, precipitation, and sorption (Obiri-Nyarko et al. 2014). Apart from the proposed alternative terms like passive bioreactive barrier, biological permeable reactive barrier, and bioenhanced permeable reactive barrier to accommodate the biotreatment or biotechnological aspects of this method, the microorganisms' role is mainly to enhance rather than an independent biotechnology (Azubuike et al. 2016; Philp and Atlas 2005). Generally, permeable reactive barrier is an in situ technique to treat the polluted groundwater with heavy metals and chlorinated compounds. Xin et al. (2013) reported biodegradation with 84.7–97.8% efficiency for ethylbenzene, p-xylene, toluene, and benzene with bioaugmented (Pseudomonas sp. and Mycobaterium sp.) permeable reactive barrier. The inherent gradient of contaminated water causes its flow through the barrier, thus the contaminants are trapped and enter a series of reactions that result in clean water from the flow (Obiri-Nyarko et al. 2014; Thiruvenkatachari et al. 2008). An ideal barrier is reactive enough to trap pollutions, allow water to flow, and penetrate but prevent the penetration of contaminants, passive with little energy input, low cost, accessible, and available easily (De Pourcq et al. 2015). The efficiency of the method is related to the kind of media that is affected by the kind of contaminant, health effect, biogeochemical conditions, cost, mechanical stability, hydrogeological conditions, and environmental effect (Liu et al. 2015). Today, combining permeable reactive barrier with other methods like electrokinetics to treat the different kinds of contaminants has attracted great attention (García et al. 2014; Mena et al. 2015). Mena et al. (2015) and Ramırez et al. (2015) reported 30% diesel removal and 39% decrease in biodegradable fractions of diesel where biopermeable reactive barrier was combined with electrokinetics to treat the contaminated soils by diesel after 14 days, respectively. Folch et al. (2013) observed 97% decay of Orange G dye in a man-made aquifer in laboratory standard when a fungus was applied as a biological barrier. They reported that the fungus can be used as a barrier (permeable reactive barrier) in natural aquifers. When a permeable reactive barrier was applied to treat the contaminated groundwater by chlorinated solvents, the main constraint was the carbonate precipitated in the iron zone rather than the velocity precise measurement of groundwater. For the performance of permeable reactive barrier, maintaining barrier reactivity and preserving the permeability of barrier are crucial for its success and can be achieved via retaining the suitable size distribution of particles (Vogan et al. 1999; Mumford et al. 2014). The most critical challenges in this method are decrease in barrier reactivity, zero-valent iron, inability to use the method on contaminated site for some recalcitrant compounds, reduction of porosity, and chlorinated hydrocarbons. Polyhydroxybutyrate as a biodegradable polymer showed a slow-release nutrient capability (carbon capacity) and can improve the biological activity as a barrier and enhance the treatment of chlorinated compounds (Baric et al. 2014). Some studies (Henderson and Demond 2007) have showed that change in climate conditions can make a complicated hydrogeological site characterization and flaws of design can decrease the success of this method. The improved designs of permeable reactive barrier and developed cost-effective techniques for site characterization enhance the efficiency of the method (Gibert et al. 2013). Moreover, to remove the challenges like lack of permeability under the given geological situations, which are related to using of zero-valent iron, the use of iron sulfide (FeS) barrier is useful (Henderson and Demond 2007).

Natural Attenuation

Natural attenuation, which is called intrinsic bioremediation, is an in situ biotreatment method that includes passive treatment of contaminated sites, through an absence of external forces (human intervention). The technique involves both anaerobic and aerobic processes to biodegrade pollutions including those of recalcitrants (Azubuike et al. 2016). The lack of external force means that the method is not costly as compared to other in situ methods. Based on the US National Research Council, there are some challenges including proof of pollutions loss from polluted sites, proof according to the analyses to show that the isolated microorganism from polluted sites has the inherent potentials for biodegrading or transforming the present pollutions at that polluted site, and proof of realization of biodegradation potentials on-site (Philp and Atlas 2005). Adetutu et al. (2015) studied chlorinated compounds and compared the efficiency different bioremediations including natural attenuation to dechlorination of polluted groundwater by trichloroethene. They found a good decrease in the concentration of trichloroethene, less than stipulated by the US Environmental Protection Agency. Moreover, biodegradation is the principal mechanism of contaminant removal during natural attenuation. The disadvantage of this method is that the intrinsic bioremediation takes more time to get the aimed concentration level of contaminants. It was also reported that it does not result in enough removal of polycyclic aromatic hydrocarbons and the corresponding decrease in contaminated soil eco-toxicity (García et al. 2014).

Bioslurping

Bioslurping combines soil vapor extraction, bioventing, and vacuum-enhanced pumping to treat groundwater and soil via indirect preparing of O_2 and stimulation of biodegradation. The method is not appropriate to treat low permeable soil; however, it is cost-effective because of lesser content of groundwater after operation, so the costs of storage, treatment, and disposal are minimized (Gidarakos and Aivalioti 2007). The major challenges of this in situ technique (Philp and Atlas, 2005) are the fluctuating water table and the need to establish a vacuum on a deep and high-permeable site.

Ex situ bioremediation includes land farming, windrows, bioreactors, and biopiles.

Land Farming

One of the simplest bioremediation techniques with less equipment and low cost requirement is land farming. This can be an ex situ or in situ technique depending on the site of treatment. Pollutant depth plays a major role in whether the method carried out is ex situ or in situ. In this method, the contaminated soil is commonly excavated and/or tilled; however, the kind of bioremediation is obviously specified by the site of remediation. Whenever the excavated contaminated soil is remediated on-site, it is classified as in situ and in other cases it is ex situ. It has been showed that bioremediation can proceed without excavation if a contaminant lies <1 m below the ground surface, while contaminant lying >1.7 m must be carried to ground surface to enhance efficiency of biotreatment (Nikolopoulou et al. 2013). Land farming system can be used in any climate and location. The method is very easy to implement and design, can treat a large volume of contaminated soils with the minimum of environmental impact and required energy as well as low capital input (Maila and Colete 2004). Some limitations of the technique are big operating space, decrease in the activities of microbes because of undesirable environmental situations, further cost because of excavation, as well as decreased efficacy in inorganic contaminant removal (Maila and Colete 2004). Land farming technique is not appropriate to treat soil contaminated with toxic volatiles because of its mechanism of contaminant removal (volatilization) and design and especially in high-temperature (tropical) climate regions. The limitations are that the farming-based biotreatment can be time-consuming with less success in comparison with other ex situ bioremediation methods.

Windrows

It is based on turning of piled contaminated soil periodically, in order to enhance biotreatment by improving the degradation activities of native microorganisms and transient hydrocarbonoclastic bacteria. The periodic turning and addition of water increase uniformity of pollutant distribution, aeration, nutrients, and microorganism activity, increasing the bioremediation rate, which is done through biotransformation, mineralization, and assimilation (Azubuike et al. 2016).

Bioreactors

Bioreactor is a vessel that converts raw materials to particular product(s) via different biological reactions. The various bioreactors include batch, sequencing batch, fed-batch, continuous, and multistage. Market economy and capital expenditure are the two factors in choosing the operating mode. In a bioreactor, the situation provides cell natural process via mimicking and retaining its natural environment. It provides the optimum conditions to grow. Contaminated samples such as dry matter or slurry can be fed into a bioreactor. One of the important advantages of bioreactor-based bioremediation is outstanding control of bioprocess parameters including pH, temperature, agitation rates, substrate and inoculum concentrations, and aeration rates. Control and manipulating the process parameters in a bioreactor provides the possibility to enhance the biological reactions and thus effectively reduce the bioremediation time. Other factors that can limit the bioremediation process like controlled bioaugmentation, increased contaminant bioavailability, addition of nutrient, and mass transfer (collision between contaminant and microbes) can efficiently be performed in a bioreactor; thus, the bioreactor-based biotreatment can be more effective. The method can be applied to treat water or soil contaminated by volatile organic compounds, including benzene, toluene, ethylbenzene, and xylenes (Azubuike et al. 2016).

Biopiles

This method is used to treat surface contaminated with hydrocarbons and is a combination of land farming and composting. Biopiles provide an appropriate medium for indigenous aerobic and anaerobic microorganisms. Biopile-mediated remediation treats aboveground piling of excavated contaminated soil with aeration and nutrient amendment to improve biotreatment via enhancing microorganism activity. This method has some components including irrigation, aeration, leachate collection systems, nutrient, and a remediation bed. The ex situ method is widely used because of constructive features such as cost-effectiveness that enables efficient biodegradation when temperature, nutrient, and aeration are well controlled. This special ex situ method is being used increasingly (Whelan et al. 2015) because of its constructive features like cost-effectiveness that provides successful biodegradation on the condition that temperature, aeration, and nutrient are well controlled. Using biopiles helps to limit volatilization of contaminants with low molecular weight. The method is effectively used to treat environments in extreme situations like very cold regions (Gomez and Sartaj 2014; Dias et al. 2015). It has been observed that the concentration of hydrocarbons decreases up to 71% and the structure of bacteria changes during 50 days following preremediation of polluted soil before the formation of biopile and then biostimulation using fishmeal (Dias et al. 2015). Sieving and aeration of polluted soil before the processing are the important factors in the efficiency of biopiles (Delille et al. 2008). In order to increase the bioremediation process in a biopile construction, bulk agents like dust, saw, straw, bark or wood chips, and other organic compounds can be used (Rodrıguez-Rodrıguez et al. 2010). Conserving space is the advantage of biopile systems in comparison with other ex situ bioremediation methods.

Factors Influencing Bioremediation

Indigenous microorganisms like bacteria, yeast, and fungi (*Talaromyces*, *Cunninghamella*, *Aspergillus*, *Amorphotheca*, *Penicillium*, *Fusarium*, *Neosartorya*, *Paecilomyces*, *Graphium*) provide a reliable method to remove the exterior contaminants like crude oil (Haritash and Kaushik 2009; Ghanavati et al. 2008; *Deshmukh* et al. 2016). In the study by Lee et al. (2015), biodegradation of ligninolytic fungi was investigated. They proved that in the lignin system there are major enzymes like peroxidases, lignin, phenol oxidases, manganese-dependent peroxidases, and hydrogen peroxide-producing enzymes that can degrade hydrocarbons. Many researches have studied the influence of the different environmental factors on biodegradation of hydrocarbons in crude oil (Cooney et al. 1985). The poor biodiversity of local microbes, availability of microorganisms, which is limited in the environment, shortage of local specialized microbes with supplementary substrate properties (Ron and Rosenberg 2014), accessibility of hydrocarbons-degrading organism, chemical composition of the hydrocarbons, biological activity optimization, pH, electron acceptors, energy sources (electron donors), inhibitory substrates or metabolites, temperature, nutrients, and oxygen are the factors that affect hydrocarbonsbiodegradation. For success, microorganisms should improve their catabolic activities to convert the pollutants via developing their metabolic capability by genetic changes, induction of special enzymes and electric enrichment of microorganism. Crude oilhydrocarbons include aromatics, resins (carbazoles, pyridines, sulfoxides, amides, and quinolines), asphaltenes (esters, ketones, phenols, fatty acids, and porphyrins), and aliphatics (Al-Hawash et al. 2018), and their degradation is influenced mainly by their nature and amount. In the marine environment, the maximum degradation rate is in a temperature range of 15–20 °C, while this range in freshwater is 20–30 °C (Al-Hawash et al. 2018). Leaked crude oilhydrocarbons in water are spread by wind and waves and can form emulations. In the absorption of hydrocarbons by microorganisms, formation of emulations is a main factor. As a short list, the biological factors affecting bioremediation are accessibility of hydrocarbons-degrading organism, local specialized microbes with supplementary substrate properties, inhibitory substrates or metabolites, and nutrients. In addition, the chemical and physical factors are chemical composition of the hydrocarbons, pH, electron acceptors, electron donors, temperature, and oxygen.

Temperature

Temperature is a significant factor that affects bioremediation via its effect on the chemical and physical compositions of contaminants (Zhang et al. 2019). The activity of enzymes and the degradation rate are reduced at low temperatures (Bisht et al. 2015). At high temperature from 30 to 40 °C, the hydrocarbon metabolism reaches the maximum level (Al-Hawash et al. 2018). The ranges of temperature with the greatest rate of degradation are 30–40, 15–20, and 20–30 °C in soil, marine, and freshwaterenvironments, respectively (Al-Hawash et al. 2018).

Oxygen

One of the factors to limit the rate of crude oilhydrocarbons degradation is the concentration of oxygen (Von Wedel et al. 1988). According to the report of Haritash and Kaushik (2009), anaerobic degradation of crude oilhydrocarbons using microorganisms can be at insignificant rates. Based on the study of McNally et al. (1998), the aerobic biodegradation of crude oilhydrocarbons is higher than their anaerobic biodegradation. For the catabolism of all aromatic and aliphatic and cyclic materials by microorganisms, substrate oxidation by oxygenases is a key step in the biodegradation process.

Nutrients

Nutrients including nitrogen, phosphorus, and iron in some cases have an important role in successful biodegradation and act as a limiting factor for this process (Atlas 1995). Carbon can be provided from organic materials. Oxygen and hydrogen can be supplied from H_2O (Kalantary et al. 2014). Oil spills in freshwater and marine environment increase the amounts of carbon and reduces the phosphorus and nitrogen levels and thus affects biodegradation. There are low levels of nitrogen and phosphorus in marine environments. Moreover, nutrients cannot be provided by wetlands since there is a high nutrients demand by plants. Therefore, adding nutrients is essential to increase the biodegradation of pollutants (Hesnawi and Adbeib 2013). It should be noted that the extra nutrients concentration can inhibit the biodegradation activity. Mineki et al. (2015) investigated the degradation of polycyclic aromatic hydrocarbons by Trichoderma/Hypocrea applying pyrene as a source of carbon. The strains growth and pyrene-degrading efficiency were increased in comparison with the control sample after 1 and 2 weeks of incubation when 0.1% of lactose or 0.1% of sucrose and 0.02% of yeast extraction were added.

Salinity

In estuarine sediments, there is a positive relation between polycyclic aromatic hydrocarbons mineralization rate and salinity (Kerr and Capone 1988). Some studies have reported that the evaporation of salt ponds shows that the rate of hydrocarbon metabolism is highly reduced with increased salinity range of 3.3–28.4% because of a general decline in the rate of microbial metabolism (Al-Hawash et al. 2018). Salinity has an important effect on biodegradation and bioremediation processes; it affects the diversity and growth of microbes and has a harmful effect on the activity of some principal enzymes in the degradation of hydrocarbons (Qin et al. 2012; Ebadi et al. 2017).

pH

The pH must be considered to improve biological treatment methods. Catalytic reaction balance, cell membrane transport, and activities of enzyme are influenced by the environmental pH (Bonomo et al. 2001). Many of the heterotrophic bacteria grow in a neutral to alkaline pH compared to the pH of many aquatic ecosystems (Jain et al. 2011). The acidity of soil can widely vary between pH 2.5 and 11 in alkaline deserts. Generally, bacteria and fungi prefer almost neutral pH; however, fungi can bear the acidic pH. The microbial mineralization of octadecane and naphthalene occurs at pH of 6.5 (Al-Hawash et al. 2018). It has been reported that the highest level of crude oilbiodegradation in water by *Pseudomonas aeruginosa* is at pH = 8.0. Moreover, the highest rate of biodegradation in an oil sludge sample is at pH 7.8 (Al-Hawash et al. 2018).

Activity of Water

In terrestrial ecosystems, the treatment of hydrocarbons can be limited due to the available water for metabolism and growth of microbes. In oil sludge, the optimal biodegradation is in 30–90% water saturation (Al-Hawash et al. 2018). The growth and movement of microorganism are directly influenced by availability of water.

Microbial Community

The main factor that contributes to biodegradation is availability of yeast, bacteria, fungi, and some algae that catabolize pollutants. Hydrocarbons in crude oil are the source of food for microorganisms that may be available in high levels near the sites contaminated by oils like crude oil: ports, oil fields, shipping lanes, gas stations, seeps, and other facilities.

Bioavailability

The effect of the microbial, physical, and chemical factors on the extent and rate of biodegradation is defined as bioavailability. It refers to the amount of a soil contaminant that is transformed and taken up using microorganisms. Other factors like the extent of hydrocarbons deterioration, microbial community, and pH may be widely influenced by the limitations in the hydrocarbons bioavailability. The bioavailable component of the hydrocarbons is the accessible part to microorganism (Semple et al. 2003). Hydrocarbonorganic pollutants have little water solubility and therefore they are stable to chemical biological and photolytic breakdown. The reducing of bioavailability with time is often referred to as weathering or aging. It may result from the chemical oxidation reactions incorporating pollutants into natural organic materials, slow diffusion into very small pores and absorption into organic materials as well as the formation of semi-rigid films close to non-aqueous-phase liquids with a good stability toward non-aqueous-phase liquids-water mass transfer (Boopathy 2000). Using of food-grade surfactants that enhance the availability of pollutants for microbial degradation overcomes bioavailability problems (Boopathy et al. 1998). Table 12.24 lists all the main factors affecting bioremediation.

Degradation Mechanism of Crude Oil Hydrocarbons

Most organic contaminants need aerobic conditions for a rapid and complete degradation. The primary intracellular organic contaminant attack takes the form of oxidation and activation. The key enzymatic catalyst by oxygenates and peroxidases needs integration of oxygen. The key degradation pathways transform organic contaminants in intermediates of the main intermediary metabolism. The biosynthesis of cell biomass occurs from the central precursors metabolites like the succinate, pyruvate, and Acetyl-CoA. The essential saccharide for various biosynthesis and growth is synthesized using gluconeogenesis. Crude oilhydrocarbons treatment can be performed by a specific enzyme system, attaching microbial cell to substrates and biosurfactant production (Rahman et al. 2003). Cytochrome P450 hydroxylases, which is isolated form Candida species like *C. maltose, C. tropicalis* and *Candida apicola* attends in the biodegradation of chlorinated compounds and other materials (Van Beilen and Funhoff 2007). The system of extracellular enzymes in *Aspergillus* spp., isolated from crude oil contaminated soil, efficiently treats crude oil (Zhang et al. 2016). The efficiency of anthracene degradation of ligninolytic and non-ligninolytic fungi was studied by Jové et al. (2016). They reported less efficiency of anthracene degradation for *Irpex lacteus* and *Pleurotus ostreatus* than those for *Phanerochaete chrysosporium*. As a conclusion, aerobic situations provide the best medium for a quick and complete degradation of organic pollutants.

Table 12.24 Main factors affecting bioremediation

Microbial
Growth until critical biomass is reached Mutation and horizontal gene transfer Enzyme induction Enrichment of the capable microbial populations Production of toxic metabolites
Substrate
Too low concentration of contaminants Chemical structure of contaminants Toxicity of contaminants Solubility of contaminants
Environmental
Depletion of preferential substrates Lack of nutrients Inhibitory environmental conditions
Biological aerobic vs. anaerobic process
Oxidation/reduction potential Availability of electron acceptors Microbial population present in the site
Physico-chemical bioavailability of pollutants
Equilibrium sorption Irreversible sorption Incorporation into humic matters
Growth substrate vs. co-metabolism
Type of contaminants Concentration Alternate carbon source present Microbial interaction (competition, succession, and predation)
Mass transfer limitations
Oxygen diffusion and solubility Diffusion of nutrients Solubility/miscibility in/with water

Modified after Boopathy (1998)

Case Studies on Oil Bioremediation

Case 1: North Sea

Oil contamination in the North Sea was investigated by Carpenter (2018) over several decades. For many decades, high amount of oil contamination was introduced into the North Sea. The sea contaminants were the cause of much pollution and death of seabirds continuously from the early years of the twentieth century (Dunnet et al. 1987). Carpenter (2018) reviewed the legislation of oil pollution in the North Sea from 1954 to 2009 (reader is referred to the Table 12.1 of Carpenter (2018)). The article presents data on trades in contaminants from ships and oil illustrations. Many actions and measures have resulted in reduction of oil introduced into the North Sea. More than two decades, the annual total number of oil leakage in the sea have denied from all sources. In this region, in 1999, the ratio of reported slicks by flight hours was 22×10^{-2} and it decreased to 4×10^{-2} in 2010. This study indicates that international cooperation is required to reduce the marine contamination and lead to a cleaner environment.

Case 2: Northern Gulf of Mexico

Liu et al. (2017) studied the environmental factors that have effect on the oil-degrading bacterial populations in the Northern Gulf of Mexico in both the deep and surface waters. Their purpose was investigation of the roles of nutrients, temperature and initial bacterial community to select the oil degraders via a series of incubation experiments in the Gulf of Mexico. Pyrosequencing and gas chromatography-mass spectrometry have applied to analyze the bacterial community and residual oil, respectively. The results indicated that temperature has a key role to select the oil-degrading bacteria. Nutrients and the initial community also have the important effects on the enhancement of hydrocarbon-degrading bacterial communities. Additional analysis revealed that temperature, initial community, oil and water chemistry explained 57%, 19%, 14%, and 10% of the variation observed, respectively.

Case 3: Arctic Seawater

McFarlin et al. (2014) studied the biodegradation of dispersed oil in Arctic seawater at −1 °C. Biodegradation in cold regions is a slow process and the degree of its success depends on the properties and fate of oil spilled, and major microbial and environmental limitations. Understanding the impact of oil in Arctic seawater is an important factor to consider since offshore gas and oil exploration expands in the Arctic. The purpose of the article was to study the chemical loss due to bioremediation of crude oil at Alaska North Slope that happens in the water column after successful dispersion of a surface oil slick. They measured mineralization and biodegradation in mesocosms containing Arctic seawater collected from the Chukchi Sea, Alaska and incubated at −1 °C. Indigenous microorganisms treated the weathered as well as fresh oil over 60 days, with oil losses ranging from 46% to 61%, up to 11% mineralization. Their study indicated that the indigenous microorganisms to Arctic seawater have ability to perform extensive biodegradation of physically and chemically dispersed oil at an environmentally relevant temperature (−1 °C) in the absence of additional nutrients. They concluded that the biodegradation of oil in Arctic seawater is extensive at −1 °C.

Case 4: Rich Savannah of Palogue, Upper Nile Area-Southern in Sudan

Ecological benefits of biotreatment of oil-polluted water in Rich Savannah of Palogue, Upper Nile Area-Southern in Sudan were investigated by Elredaisy (2010). The article reviewed the ecological benefits of bioremediation to treat the oil-polluted water and how far it could benefit Sudan, supported by various world experiences. They obtained valuable results by the Reed Bed *Phragmites australis* that degrades hydrocarbons, produces clean water, and is appropriate for forestry development and recovery of natural fauna after decades of military conflict. They concluded that community awareness is necessary and a national strategy is required for further adaptive techniques toward environment conservation.

Case 5: Wastewater in Egypt

Biodegradation of industrial wastewater contaminated by oil in Egypt was studied by El-Borai et al. (2016) using bacterial consortium immobilized in various kinds of carriers. They examined the effectiveness of some carriers and immobilization methodology for some samples of hydrocarbon-degrading strains. Adsorbing cells on a sponge resulted in optimal efficiency of hydrocarbon removal for some cultures compared with free cells. Comparison of a designed bacterial consortium with individual cultures indicated that the highest percentage of crude oil degradation was seen in a mixed culture (81.70% removal efficiency), 1.083 times higher than that recorded for *Bacillus brevis* (75.42%). The use of a fixed bed bioreactor for biotreatment of crude oil by bacteria held on sponge cubes indicated that the highest percentage of crude oil degradation was seen in a mixed culture (87.53%), followed by individual cultures of *Pseudomonas aeruginosa* KH6 (82.97%), providing insight for biotreatment using immobilized bacterial consortia within bioreactors. Degradation in both aromatic and aliphatic hydrocarbons was observed significantly from adsorbed mixed culture on sponge. Gas Chromatography-Mass Spectrometry was used to analyze the results. Applying simulation strategy for oily wastewater sample recommended the combination of bioaugmentation and biostimulation methods, which obtained 92.17% and 91.30% removal efficiencies in a bioreactor packed with sponge or polyethylene, respectively. Thus, the tested strains can be employed for industrial effluent treatment and remediation of natural contaminated areas.

Case 6: Nitex Textiles in Serbia

Marić et al. (2015) studied enhanced in situ bioremediation of contaminated groundwater at Nitex textiles, Serbia. This study aimed to provide an insight into the enhanced in situ bioremediation used for remediation of groundwater contaminated by hydrocarbons. Before the application of this remediation method, the source of groundwater pollution – an underground storage tank and polluted sediments – was removed from the unsaturated zone. The hydraulic conductivity characterization of the site was used to prove the hydraulic feasibility of this remediation. A combination of biostimulation and bioaugmentation within the closed bipolar system (one extraction and two injection wells) was applied to enhance the in situ bioremediation. For biostimulation, nutrients were added and for stimulation of oxidation processes, H_2O_2 was injected into the aquifer. The injection of a zymogenous consortium of isolated hydrocarbon-degrading microorganisms from the polluted groundwater was used for bioaugmentation/reinoculation. The obtained average extraction capacity in their study was 0.5 L/s, with an average injection capacity of 0.25 L/s per well. By evaluating the changes in the content of total chemoorganoheterotrophic and hydrocarbon-degrading microorganisms as well as total hydrocarbon, the efficiency of the remediation method was measured. The number of total chemoorganoheterotrophic and hydrocarbon-degrading microorganisms started to increase after bioaugmentation and biostimulation. Then the hydrocarbon concentration decreased in the groundwater from an initial 6.8 to 0.5 mg/L at the end of the biotreatment. The used remediation method was very effective in treating the contaminated groundwater.

Case 7: Southern Mediterranean

Bioremediation of Southern Mediterranean oil-polluted sites was investigated by Daffonchio et al. (2013). The intense maritime traffic of oil tankers and high number of oil extractive and refining sites through the basin coasts cause the Mediterranean Sea to be at a very high risk of oil contamination. There are severe regulations adapted by all Mediterranean countries to reduce the contamination resources and great attention has been paid to biotreatment feasibility studies for the most critical contaminated sites. Many studies have also discussed its serious polluted sites. Analyses of the scientific studies indicates that the international research has neglected the Southern Mediterranean side. Many researches in the Mediterranean Sea were performed in contaminated sites of the Northern side of the basin. Recently, the EU-funded research project ULIXES has been assigned to investigate the bioremediation potential of the south of the Mediterranean Sea. The targets of ULIXES are four main contaminated sites on the coastlines of Morocco, Jordan, Tunisia, and Egypt including seashore sands, lagoons, and oil refinery contaminated sediments. A cooperation of 12 Southern Mediterranean and European partners aims to plug the present gap of information to develop novel bioremediation processes for these contaminated sites with poor investigation. This study focuses on unraveling, categorizing, cataloguing, exploiting, and managing the ecology and diversity of microorganisms thriving in the contaminated sites. Isolation of new microorganisms with the ability to degrade hydrocarbon and a series of state-of-the-art “meta-omics” techniques are the baseline tools to extend our information on biodegradation ability mediated by microorganisms under various environmental settings and to design the new site-tailored bioremediation methods.

The common remediation methods are physical, chemical, thermal, and biological methods. Table 12.25 compares the advantages and disadvantages of all the methods.

The criteria for evaluation of the methods, the definitions, and the assigned scores based on the advantages and disadvantages of the methods are listed in Table 12.26.

Table 12.27 provides the final comparative results of the methods. The results of the analysis based on the oil spill response methods indicated the highest score (73) for bioremediation. Economic and the environmentally friendly properties of bioremediation are its two important advantages and its main limitations are time-consuming treatment, low response of microbes to high concentrations, the biodegradability of limited hydrocarbons, influenced by the environmental factors, and the heterogeneity of marine oil spill (Dave and Ghaly 2011).

For in situ burning, score 59 was obtained, but it cannot be used for all the areas of oil spill. Score 55 was for booms and skimmers that are useful for all kinds of oils but their efficiency is highly dependent on the conditions of sea and weather. Score 54 was obtained for dispersants, which are always applied to bioremediation processes.

As a conclusion and according to the information of Table 12.25 and the scores discussed in Table 12.27, bioremediation can be the best choice if the situation is appropriate for its performance. However, to have the best efficiency, a combination of all the methods provides the highest level of remediation.

12.7 Conclusions

Oil-polluted water has harmful effects on marine life and human health. Immediate action is required to remove oil spills. The choice of an appropriate removal method depends on the site conditions, limitations of the method, and environmental considerations.

Physical methods are eco-friendly but these are expensive and time-consuming methods requiring a large number of personnel and equipment and are not feasible in harsh sea conditions and brush or broken ice conditions. In situ burning methods produce a large amount of secondary pollutants like CO_2, which may have irreparable effects on marine life. Therefore, these methods are not recommended at any time. Chemical agents can be used to improve other removal methods like skimmers, while some types such as dispersant agents break the oil components and oil recovery is impossible in such conditions.

Sorbents have excellent sorption and recovery performance because of their high sorption capacity, porous structure, low density, high specific surface area, oleophilicity, and reusability. Synthetic and modified inorganic sorbents have greater oilsorption capacity than natural sorbents. Nevertheless, secondary pollution is a major disadvantage. On the other hand, natural sorbents have no significant resistance during reuse cycles. Therefore, composition of natural or inorganic and synthetic sorbents can modify the defects of both types of sorbents.

Table 12.25 Comparison of advantage and disadvantage of physical, chemical, thermal, and bioremediation

Kind of treatment	Disadvantage	Advantage
Physical treatment		
Booms	Costly	All types of oil
	Labor-intensive	Recovery of oil possible
	Complex	
	Including oil Other technologies must be applied	
	Efficient in considered weather conditions	
Skimmers	Costly	All types of oil
	Labor-intensive	Inflammable
	Complex	Recovery of oil possible
	Collected oil Additional treatment is needed	
	Efficient in considered weather conditions	
	Clogging is possible with floating debris	
	Maintenance is needed	
	Oil recovery should be before emulsified	
Adsorbents	Costly	All types of oil moderate
	Labor-intensive	Effective as ultimate cleanup
	Considered weather conditions	Step
	Dispose with regulation required	Simple
	A challenge is biodegradability with a synthetic sorbents	No maintenance required
	A challenge is sinkage in water with natural adsorbents	Synthetic sorbents made of polypropylene and oleophilic properties
Chemical treatment		
Dispersants	No oil recovery	All weather conditions
	Nonspreading, Not effective on highly viscous	Quick
	Not effective on waxy oil	Successful for wide range of oil
	The localized and temporary increase in amount of oil in water concentration that could have an effect on the surrounding marine life	The degradation of the oil by natural processes is accelerated
	An effect on the surrounding marine life If dispersion is not reached other response method	Advanced formulations have reduced the previous concern about toxicity
	Effect may be reduced on less dispered oil	Less manpower needed
		Less expensive and mechanical methods
Solidifiers	No practical application	All weather conditions
	Large amount required	Quick
	Not effective	

(continued)

Table 12.25 (continued)

Kind of treatment	Disadvantage	Advantage
	Selected oil	
	No oil recovery	
Thermalremediation		
	No oil recovery	Effective
	Worry about flashback and secondary fires	Quick
	Emit many hydrocarbons-related compounds to air environment	Requires minimal but some specialized equipment
	Considered oil	Less manpower needed
	Threaten for human, surrounding recourse and marine life	Cost-effective
	Initial product is less viscous than burn residue	
	Advisable on area covered with snow or ice	
	Advisable on open water area	
Bioremediation		
	No oil recovery	All weather conditions
	Selected oils	Less manpower needed
	Less capacity of microbes to survive against oil pollutants	Cost-effective
	Depends on the indigenous	Mineralize oil to CO_2 and H_2O
	The presence of microorganisms at the site	
	Dependent on nutrient, available at the polluted site	

Modified after Dave and Ghaly (2011)

Table 12.26 The criteria to evaluate the treatment methods for marine oil spill

Criteria	Definition	Score
Cost	Relatively inexpensive	15
Efficiency	95–99% removal	20
Time	Removes contaminant within days	15
Oil recovery	Chances of oil recovery	5
Impact on marine life	No health risks involved with method	10
The need for further treatment	No further treatment required	5
Weather	Favorable for application of method	10
Level of difficulty	Easy to maintain and operate	10
Effect on physical/chemical characteristic of oil	No changing in physical and/or chemical characteristic of oil	5
Reliability	The method works the majority of the time	5

Modified after Dave and Ghaly (2011)

Table 12.27 Assessment of marine oil spillremediation methods

	Physical methods			Chemical methods			
Criteria	Skimmers	Booms	Adsorbents	Dispersants	Solidifiers	In situ Burning	Bioremediation
Cost	7	7	8	8	7	10	12
Weather	5	5	4	8	8	5	10
Oil recovery	4	4	1	0	1	0	0
Impact on marine life	9	9	9	5	5	3	9
Level of difficulty	2	2	2	5	4	5	8
Efficiency	10	10	10	13	7	17	18
Time	10	10	8	8	8	13	7
Reliability	2	2	2	3	2	3	4
The need for further treatment	1	1	1	4	0	3	5
Effect on physical and chemical characteristics of oil	5	5	0	0	0	0	0
Total score	55	55	45	54	42	59	73

Modified after Dave and Ghaly (2011)

It seems that carbon-based sorbents that are modified by magnetic nanoparticles have the best sorption behavior among remediation methods. Further research on the production and improvement of these types of sorbents is recommended.

Among all the remediation techniques, bioremediation has attracted great attention thanks to its advantages and acceptable performance. In bioremediation, microorganisms degrade and metabolize chemical substances in order to recover the environment quality. Its aim is to accelerate the intrinsic bioremediation process via assimilating the organic compounds to cell biomass and produce by-products like CO_2, H_2O, and heat by microorganisms. The specie of microorganisms introduced in the system depends on the process design, environmental conditions, and the plant operation mode.

Different aspects of bioremediation investigated in ten different locations including North Sea, Northern Gulf of Mexico, Nile River, Arctic seawater, Rich Savannah of Palogue, Upper Nile Area-Southern in Sudan, wastewater in Egypt, Nitex textiles in Serbia, Southern Mediterranean, Antarctic sea-ice and Gulf of Gdansk (Southern Baltic Sea) in Poland were studied and the obtained results have been mentioned.

As a result, increasing the oil contaminated waters require an urgent attention to conduct the related researches in order to improve the clean up technologies. The bioremediation is a special useful technique that has an acceptable efficiency. Its efficiency can be increased by some methods or by being combined with other techniques.

References

Adebajo MO, Frost RL, Kloprogge JT, Carmody O, Kokot S (2003) Porous materials for oil spill cleanup: a review of synthesis and absorbing properties. J Porous Mater 10(3):159–170. https://doi.org/10.1023/A:1027484117065

Adetutu EM, Gundry TD, Patil SS, Golneshin A, Adigun J, Bhaskarla V, Aleer S, Shahsavari E, Ross E, Ball AS (2015) Exploiting the intrinsic microbial degradative potential for field-based in situ dechlorination of trichloroethene contaminated groundwater. J Hazard Mater 300:48–57. https://doi.org/10.1016/j.jhazmat.2015.06.055

Al-Hawash AB, Dragh MA, Li S, Alhujaily A, Abbood HA, Zhang X, Ma F (2018) Principles of microbial degradayion of petroleum hydrocarbons in the environment. Egypt J Aquat Res 44:71–76. https://doi.org/10.1016/j.ejar.2018.06.001

Al-Majed AA, Adebayo AR, Hossain ME (2012) A sustainable approach to controlling oil spills. J Environ Manag 113:213–227. https://doi.org/10.1016/j.jenvman.2012.07.034

Almansoory AF, Hasan HA, Idris M, Abdullah SRS, Anuar N (2015) Potential application of a biosurfactant in phytoremediation technology for treatment of gasoline-contaminated soil. Ecol Eng 84:113–120. https://doi.org/10.1016/j.ecoleng.2015.08.001

Amin A, Naik ATR, Azhar M, Nayak H (2013) Bioremediation of different waste waters - a review. CJFAS 7(2):7–17. https://doi.org/10.5707/cjfas.2013.7.1.7.17

Annunciado TR, Sydenstricker THD, Amico SC (2005) Experimental investigation of various vegetable fibers as sorbent materials for oil spills. Mar Pollut Bull 50:1340–1346. https://doi.org/10.1016/j.marpolbul.2005.04.043

Arbatan T, Fang X, Shen W (2011) Superhydrophobic and oleophilic calcium carbonate powder as a selective oil sorbent with potential use in oil spill clean-ups. Chem Eng J 166(2):787–791. https://doi.org/10.1016/j.cej.2010.11.015

Arulazhagan P, Vasudevan N, Yeom I (2010) Biodegradation of polycyclic aromatic hydrocarbon by a halotolerant bacterial consortium isolated from marine environment. Int J Environ Sci Technol 7(4):639–652. https://doi.org/10.1007/BF03326174

Atlas RM (1995) Petroleum biodegradation and oil spill bioremediation. Mar Pollut Bull 31:178–182. https://doi.org/10.1016/0025-326X(95)00113-2

Atlas RM, Bartha R (1973) Stimulated biodegradation of oil slicks using oleophilic fertilizers. Environ Sci Technol 7:538–541. https://doi.org/10.1021/es60078a005

Atlas RM, Cerniglia CE (1995) Bioremediation of petroleum pollutants-diversity and environmental aspects of hydrocarbon biodegradation. Bioscience 45:332–338. https://doi.org/10.2307/1312494

Azubuike CC, Chikere CB, Okpokwasili GC (2016) Bioremediation techniques–classification based on site of application: principles, advantages, limitations and prospects. World J Microbiol Biotechnol 32:180–198. https://doi.org/10.1007/s11274-016-2137-x

Banerjee SS, Joshi MV, Jayaram RV (2006) Treatment of oil spills using organo-fly ash. Desalination 195(1–3):32–39. https://doi.org/10.1016/j.desal.2005.10.038

Baric M, Pierro L, Pietrangeli B, Papini MP (2014) Polyhydroxyalkanoate (PHB) as a slow-release electron donor for advanced in situ bioremediation of chlorinated solvent-contaminated aquifers. New Biotechnol 31:377–382. https://doi.org/10.1016/j.nbt.2013.10.008

Bayat A, Aghamiri SF, Moheb A, Vakili-Nezhaad GR (2005) Oil spill cleanup from sea water by sorbent materials. Chem Eng Technol 28(12):1525–1528. https://doi.org/10.1002/ceat.200407083

Bisht S, Pandey P, Bhargava B, Sharma S, Kumar V, Sharma KD (2015) Bioremediation of polyaromatic hydrocarbons (PAHs) using rhizosphere technology. Braz J Microbiol 46 (1):7–21. https://doi.org/10.1590/S1517-838246120131354

Bonomo R, Cennamo G, Purrello R, Santoro A, Zappala R (2001) Comparison of three fungal laccases from Rigidoporus lignosus and Pleurotus ostreatus: correlation between conformation changes and catalytic activity. J Inorg Biochem 83(1):67–75. https://doi.org/10.1016/S0162-0134(00)00130-6

Boopathy R (2000) Factors limiting bioremediation technologies. Bioresour Technol 74:63–67. https://doi.org/10.1016/S0960-8524(99)00144-3

Boopathy R, Manning J, Kulpa CF (1998) A laboratory study of the bioremediation of 2,4,6-trinitrotoluene-contaminated soil using aerobic anaerobic soil slurry reactor. Water Environ Res 70:80–86. https://doi.org/10.2175/106143098X126919

Bragg JR, Prince RC, Harner EJ, Atlas RM (1994) Effectiveness of bioremediation for the Exxon Valdex oil spill. Nature 368:413–418. https://doi.org/10.1038/368413a0

Brennan MA, Shelley ML (1999) A model of the uptake, translocation, and accumulation of lead (Pb) by maize for the purpose of phytoextraction. Ecol Eng 12:271–297. https://doi.org/10.1016/S0925-8574(98)00073-1

Broje V, Keller AA (2007a) Effect of operational parameters on the recovery rate of an oleophilic drum skimmer. J Hazard Mater 148(1–2):136–143. https://doi.org/10.1016/j.jhazmat.2007.02.017

Broje V, Keller AA (2007b) Interfacial interactions between hydrocarbon liquids and solid surfaces used in mechanical oil spill recovery. J Colloid Interface Sci 305(2):286–292. https://doi.org/10.1016/j.jcis.2006.09.078

Brooksbank AM, Latchford JW, Mudge SM (2007) Degradation and modification of fats, oils and grease by commercial microbial supplements. World J Microbiol Biotechnol 23(7):977–985. https://doi.org/10.1007/s11274-006-9323-1

Buist I, McCourt J, Potter S, Ross S, Trudel K (1999) In situ burning. Pure Appl Chem 71:43–65. https://doi.org/10.1351/pac199971010043

Buist I, Potter S, Nedwed T, Mullin J (2011) Herding surfactants to contract and thicken oil spills in pack ice for in situ burning. Cold Reg Sci Technol 67(1–2):3–23. https://doi.org/10.1016/j.coldregions.2011.02.004

Cammarota MC, Teixeira GA, Freire DMG (2001) Enzymatic pre-hydrolysis and anaerobic degradation of wastewaters with high fat contents. Biotechnol Lett 23:1591–1595. https://doi.org/10.1023/A:1011973428489

Carmody O, Frost R, Xi Y, Kokot S (2007) Adsorption of hydrocarbons on organo-clays—implications for oil spill remediation. J Colloid Interface Sci 305(1):17–24. https://doi.org/10.1016/j.jcis.2006.09.032

Carpenter A (2018) Oil pollution in the North Sea: the impact of governance measures on oil pollution over several decades, Hydrobiologia, 1–19, https://doi.org/10.1007/s10750-018-3559-2

Castro A, Iglesias G, Carballo R, Fraguela J (2010) Floating boom performance under waves and currents. J Hazard Mater 174(1–3):226–235. https://doi.org/10.1016/j.jhazmat.2009.09.040

Chen J, Zhou HC, Wang C, Zhu CQ, Tam NF-Y (2015) Short-term enhancement effect of nitrogen addition on microbial degradation and plant uptake of polybrominated diphenyl ethers (PBDEs) in contaminated mangrove soil. J Hazard Mater 300:84–92. https://doi.org/10.1016/j.jhazmat.2015.06.053

Choi HM, Cloud RM (1992) Natural sorbents in oil spill cleanup. Environ Sci Technol 26(4):772–776. https://doi.org/10.1021/es00028a016

Choi H-M, Kwon H-J, Moreau JP (1993) Cottton nonwovens as oil spill cleanup sorbents. Text Res J 63(4):211–218. https://doi.org/10.1177/004051759306300404

Chung D (2016) A review of exfoliated graphite. J Mater Sci 51(1):554–568. https://doi.org/10.1007/s10853-015-9284-6

Clayton C (2005) Chemical and physical properties of petroleum. Pet Geol 10:248–260. https://doi.org/10.1016/B0-12-369396-9/00246-X

Cooney J, Silver S, Beck E (1985) Factors influencing hydrocarbon degradation in three freshwater lakes. Microb Ecol 11(2):127–137. https://doi.org/10.1007/BF02010485

Cunningham SD, Anderson TA, Schwab PA, Hsu FC (1996) Phytoremediation of soils contaminated with organic pollutants. Adv Agron 56:55–114. https://doi.org/10.1016/S0065-2113(08)60179-0

Dadrasnia A, Agamuthu P (2013) Diesel fuel degradation fromcontaminated soil by dracaena reflexausing organic wastesupplementation. J Jpn Petrol Inst 56:236–243. https://doi.org/10.1627/jpi.56.236

Daffonchio D, Ferrer M, Mapelli F, Cherif A, Lafraya A, Malkawi HI, Yakimov MM, Abdel-Fattah YR, Blaghen M, Golyshin PN, Kalogerakis N, Boon N, Magagnini M, Fava F (2013) Bioremediation of southern Mediterranean oil polluted sites comes of age. New Biotechnol 30(6):743–748. https://doi.org/10.1016/j.nbt.2013.05.006

Dai J, Tian Q, Sun Q, Wei W, Zhuang J, Liu M, Cao Z, Xie W, Fan M (2019) TiO_2-alginate composite aerogels as novel oil/water separation and wastewater remediation filters. Compos Eng 160:480–487. https://doi.org/10.1016/j.compositesb.2018.12.097

Daling PS, Strøm T (1999) Weathering of oils at sea: model/field data comparisons. Spill Sci Technol Bull 5:63–74. https://doi.org/10.1016/S1353-2561(98)00051-6

Dave D, Ghaly AE (2011) Remediation Technologies for Marine oil Spills: a critical review and comparative analysis. Am J Environ Sci 7(5):423–440. https://doi.org/10.3844/ajessp.2011.423.440

De Pourcq K, Ayora C, García-Gutiérrez M, Missana T, Carrera J (2015) A clay permeable reactive barrier to remove Cs-137 from groundwater: column experiments. J Environ Radioact 149:36–42. https://doi.org/10.1016/j.jenvrad.2015.06.029

De-Bashan LE, Hernandez J-P, Bashan Y (2012) The potential contribution of plant growth-promoting bacteria to reduce environmental degradation—a comprehensive evaluation. Appl Soil Ecol 61:171–189. https://doi.org/10.1016/j.apsoil.2011.09.003

Delaune R, Lindau C, Jugsujinda A (1999) Effectiveness of “Nochar” solidifier polymer in removing oil from open water in coastal wetlands. Spill Sci Technol Bull 5(5–6):357–359. https://doi.org/10.1016/S1353-2561(99)00081-X

Delille D, Duval A, Pelletier E (2008) Highly efficient pilot biopiles for on-site fertilization treatment of diesel oil contaminated sub-Antarctic soil. Cold Reg Sci Technol 54:7–18. https://doi.org/10.1016/j.coldregions.2007.09.003

Deshmukh R, Khardenavis AA, Purohit HJ (2016) Diverse metabolic capacities of fungi for bioremediation. Indian J Microbiol 56(3):247–264. https://doi.org/10.1007/s12088-0160584-6

Dias RL, Ruberto L, Calabró A, Balbo AL, Del Panno MT, Mac Cormack WP (2015) Hydrocarbon removal and bacterial community structure in on-site biostimulated biopile systems designed for bioremediation of diesel-contaminated Antarctic soil. Polar Biol 38:677–687. https://doi.org/10.1007/s00300-014-1630-7

Ding X, Wang R, Zhang X, Zhang Y, Deng S, Shen F, Zhang X, Xiao H, Wang L (2014) A new magnetic expanded graphite for removal of oil leakage. Mar Pollut Bull 81(1):185–190. https://doi.org/10.1016/j.marpolbul.2014.01.056

Dunnet GM, Samiullah Y, Stone DP, Tasker ML (1987) Seabirds and North Sea oil. Philos Trans R Soc Lond B Biol Sci 316:513–524. https://doi.org/10.1098/rstb.1987.0036

Ebadi A, Khoshkholgh Sima NA, Olamaee M, Hashemi M, Ghorbani Nasrabadi R (2017) Effective bioremediation of a petroleum-polluted saline soil by a surfactant-producing Pseudomonas aeruginosa consortium. J Adv Res 8(6):627–633. https://doi.org/10.1016/j.jare.2017.06.008

El-Borai AM, Eltayeb KM, Mostafa AR, El-Assar SA (2016) Biodegradation of Industrial Oil-Polluted Wastewater in Egypt by Bacterial Consortium Immobilized in Different Types of Carriers. Pol J Environ Stud 25:1901–1909. https://doi.org/10.15244/pjoes/62301

Elredaisy SMA (2010) Ecological Benefi ts of bioremediation of oil contaminated water in rich Savannah of Palogue, Upper Nile Area-Southern Sudan. J Bioremediat Biodegradation 1:103–110. https://doi.org/10.4172/2155-6199.1000103

Fan D, Gilbert EJ, Fox T (2017) Current state of in situ subsurface remediation by activated carbon-based amendments. J Environ Manag 204:793–803. https://doi.org/10.1016/j.jenvman.2017.02.014

Folch A, Vilaplana M, Amado L, Vicent R, Caminal G (2013) Fungal permeable reactive barrier to remediate groundwater in an artificial aquifer. J Hazard Mater 262:554–560. https://doi.org/10.1016/j.jhazmat.2013.09.004

Fulazzaky MA (2011) Determining the resistance of mass transfer for adsorption of the surfactants onto granular activated carbons from hydrodynamic column. Chem Eng J 166(3):832–840. https://doi.org/10.1016/j.cej.2010.11.052

Fulazzaky MA, Omar R (2012) Removal of oil and grease contamination from stream water using the granular activated carbon block filter. Clean Technol Environ 14(5):965–971. https://doi.org/10.1007/s10098-012-0471-8

García Y, Ruiz C, Mena E, Villaseñor J, Cañizares P, Rodrigo MA (2014) Removal of nitrates from spiked clay soils by coupling electrokinetic and permeable reactive barrier technologies. J Chem Technol Biotechnol 90:1719–1726. https://doi.org/10.1002/jctb.4488

Ghanavati H, Emtiazi G, Hassanshahian M (2008) Synergism effects of phenoldegrading yeast and ammonia-oxidizing bacteria for nitrification in coke wastewater of Esfahan steel company. Waste Manag Res 26(2):203–208. https://doi.org/10.1177/0734242X07079874

Gibert O, Cortina JL, De Pablo J, Ayora C (2013) Performance of a field-scale permeable reactive barrier based on organic substrate and zero-valent iron for in situ remediation of acidmine drainage. Environ Sci Pollut Res 20:7854–7862. https://doi.org/10.1007/s11356-013-1507-2

Gidarakos E, Aivalioti M (2007) Large scale and long term application of bioslurping: the case of a Greek petroleum refinery site. J Hazard Mater 149:574–581. https://doi.org/10.1016/j.jhazmat.2007.06.110

Gomez F, Sartaj M (2014) Optimization of field scale biopiles for bioremediation of petroleum hydrocarbon contaminated soil at low temperature conditions by response surface methodology

(RSM). Int Biodeterior Biodegradation 89:103–109. https://doi.org/10.1016/j.ibiod.2014.01.010

Gregorio SD, Azaizeh H, Lorenzi R (2013) Biostimulation of the autochthonous microbial community for the depletion of polychlorinated biphenyls (PCBs) in contaminated sediments. Environ Sci Pollut Res 20:3989–3999. https://doi.org/10.1007/s113560121350-x

Gregorio SD, Gentini A, Siracusa G, Becarelli S, Azaizeh H, Lorenzi R (2014) Phytomediated biostimulation of the autochthonous bacterial community for the acceleration of the depletion of polycyclic aromatic hydrocarbons in contaminated sediments. Biomed Res Int 2014:891630–891641. https://doi.org/10.1155/2014/891630

Grobelak A, Napora A, Kacprzak M (2015) Using plant growth-promoting rhizobacteria (PGPR) to improve plant growth. Ecol Eng 84:22–28. https://doi.org/10.1016/j.ecoleng.2015.07.019

Gu J, Jiang W, Wang F, Chen M, Mao J, Xie T (2014) Facile removal of oils from water surfaces through highly hydrophobic and magnetic polymer nanocomposites. Appl Surf Sci 301:492–499. https://doi.org/10.1016/j.apsusc.2014.02.112

Gupta BS, Edwards JV (2019) Textile materials and structures for topical management of wounds. In: Advanced textiles for wound care. Woodhead Publishing, Cambridge, pp 55–104. https://doi.org/10.1016/B978-0-08-102192-7.00003-5

Gupta S, Tai N-H (2016) Carbon materials as oil sorbents: a review on the synthesis and performance. J Mater Chem A 4(5):1550–1565. https://doi.org/10.1039/C5TA08321D

Haritash A, Kaushik C (2009) Biodegradation aspects of polycyclic aromatic hydrocarbons (PAHs): a review. J Hazard Mater 169:1–15. https://doi.org/10.1016/j.jhazmat.2009.03.137

Hasanuzzaman M, Ueno A, Ito H, Ito Y, Yamamoto Y, Yumoto I, Okuyama H (2007) Degradation of long-chain n-alkanes (C 36 and C 40) by Pseudomonas aeruginosa strain WatG. Int Biodeterior Biodegradation 59(1):40–43. https://doi.org/10.1016/j.ibiod.2006.07.010

Henderson AD, Demond AH (2007) Long-term performance of zerovalent iron permeable reactive barriers: a critical review. Environ Eng Sci 24:401–423. https://doi.org/10.1089/ees.2006.0071

Hesnawi RM, Adbeib MM (2013) Effect of nutrient source on indigenous biodegradation of diesel fuel contaminated soil. APCBEE Proc 5:557–561. https://doi.org/10.1016/j.apcbee.2013.05.093

Höhener P, Ponsin V (2014) In situ vadose zone bioremediation. Curr Opin Biotechnol 27:1–7. https://doi.org/10.1016/j.copbio.2013.08.018

Hu Y, Liu X, Zou J, Gu T, Chai W, Li H (2013) Graphite/isobutylene-isoprene rubber highly porous cryogels as new sorbents for oil spills and organic liquids. ACS Appl Mater Interfaces 5 (16):7737–7742. https://doi.org/10.1021/am303294m

Huang Y, Zhu J, Liu H, Wang Z, Zhang X (2019) Preparation of porous graphene/carbon nanotube composite and adsorption mechanism of methylene blue. SN Appl Sci 1(1):37. https://doi.org/10.1007/s42452-018-0035-6

Hussein M, Amer AA, IIb S (2009) Oil spill sorption using carbonized pith bagasse application of carbonized pith bagasse as loose fiber. Global NEST J 11:440–448. https://doi.org/10.30955/gnj.000539

Ignatius A, Arunbabu V, Neethu J, Ramasamy EV (2014) Rhizofiltration of lead using an aromatic medicinal plant Plectranthus amboinicus cultured in a hydroponic nutrient film technique (NFT) system. Environ Sci Pollut Res 21:13007–13016. https://doi.org/10.1007/s11356-01432041

Iqbal MZ, Abdala AA (2013) Oil spill cleanup using graphene. Environ Sci Pollut R 20 (5):3271–3279. https://doi.org/10.1007/s11356-012-1257-6

Ismail AS, El-Sheshtawy HS, Khalil NM (2019) Bioremediation process of oil spill using fatty-lignocellulose sawdust and its enhancement effect. Egypt J Petrol (In Press). https://doi.org/10.1016/j.ejpe.2019.03.002

Ivshina IB, Kuyukina MS, Krivoruchko AV, Elkin AA, Makarov SO, Cunningham CJ, Peshkur TA, Atlas RM, Philp JC (2015) Oil spill problems and sustainable response strategies through new technologies. Environ Sci-Proc Imp 17(7):1201–1219. https://doi.org/10.1039/C5EM00070J

Jabeen R, Ahmad A, Iqbal M (2009) Phytoremediation of heavy metals: physiological and molecular mechanisms. Bot Rev 75:339–364. https://doi.org/10.1007/s12229-009-9036-x

Jain PK, Gupta VK, Gaur RK, Lowry M, Jaroli DP, Chauhan UK (2011) Bioremediation of petroleum oil contaminated soil and water. RJET 5(1):1–26. https://doi.org/10.3923/rjet.2011.1.26

Jernelöv A (2010) The threats from oil spills: now, then, and in the future. Ambio 39(5–6):353–366. https://doi.org/10.1007/s13280-010-0085-5

Jové P, Olivella MÀ, Camarero S, Caixach J, Planas C, Cano L, De Las Heras FX (2016) Fungal biodegradation of anthracene-polluted cork: a comparative study. J Environ Sci Health A 51 (1):70–77. https://doi.org/10.1080/10934529.2015.1079114

Kalantary RR, Mohseni-Bandpi A, Esrafili A, Nasseri S, Ashmagh FR, Jorfi S, Jafari M (2014) Effectiveness of biostimulation through nutrient content on the bioremediation of phenanthrene contaminated soil. J Environ Health Sci Eng 12(1):143–151. https://doi.org/10.1186/s40201-014-0143-1

Karakasi O, Moutsatsou A (2010) Surface modification of high calcium fly ash for its application in oil spill clean up. Fuel 89(12):3966–3970. https://doi.org/10.1016/j.fuel.2010.06.029

Kerr RP, Capone DG (1988) The effect of salinity on the microbial mineralization of two polycyclic aromatic hydrocarbons in estuarine sediments. Mar Environ Res 26(3):181–198. https://doi.org/10.1016/0141-1136(88)90026-8

Keshavarz A, Zilouei H, Abdolmaleki A, Asadinezhad A, Nikkhah A (2016) Impregnation of polyurethane foam with activated carbon for enhancing oil removal from water. Int J Environ Sci Technol 13(2):699–710. https://doi.org/10.1007/s13762-015-0908-9

Khan FI, Husain T, Hejazi R (2004) An overview and analysis of site remediation technologies. J Environ Manag 71:95–122. https://doi.org/10.1016/j.jenvman.2004.02.003

Kim S, Krajmalnik-Brown R, Kim J-O, Chung J (2014) Remediation of petroleum hydrocarbon-contaminated sites by DNA diagnosis- based bioslurping technology. Sci Total Environ 497:250–259. https://doi.org/10.1016/j.scitotenv.2014.08.002

Kuiper I, Lagendijk EL, Bloemberg GV, Lugtenberg BJJ (2004) Rhizoremediation: a beneficial plant-microbe interaction. MPMI 7:6–15. https://doi.org/10.1094/MPMI.2004.17.1.6

Lakshmi R, Bharathidasan T, Bera P, Basu BJ (2012) Fabrication of superhydrophobic and oleophobic sol–gel nanocomposite coating. Surf Coat Technol 206(19–20):3888–3894. https://doi.org/10.1016/j.surfcoat.2012.03.044

Lee JH (2013) An overview of phytoremediation as a potentially promising technology for environmental pollution control. Biotechnol Bioproc E 18:431–439. https://doi.org/10.1007/s12257-013-0193-8

Lee CM, Kang KH (1997) Prediction of oil boom performance in currents and waves. Spill Sci Technol Bull 4(4):257–266. https://doi.org/10.1016/S1353-2561(98)00022-X

Lee MW, An S, Latthe SS, Lee C, Hong S, Yoon SS (2013) Electrospun polystyrene nanofiber membrane with superhydrophobicity and superoleophilicity for selective separation of water and low viscous oil. ACS Appl Mater Interfaces 5(21):10597–10604. https://doi.org/10.1021/am404156k

Lee H, Yun SY, Jang S, Kim G-H, Kim J-J (2015) Bioremediation of polycyclic aromatic hydrocarbons in creosote-contaminated soil by Peniophora incarnate KUC8836. Biorem J 19 (1):1–8. https://doi.org/10.1080/10889868.2014.939136

Lessard RR, Demarco G (2000) The significance of oil spill dispersants. Spill Sci Technol Bull 6:59–68. https://doi.org/10.1016/S1353-2561(99)00061-4

Lewis A, Trudel BK, Belore RC, Mullin JV (2010) Large-scale dispersant leaching and effectiveness experiments with oils on calm water. Mar Pollut Bull 60(2):244–254. https://doi.org/10.1016/j.marpolbul.2009.09.019

Lin J, Tian F, Shang Y, Wang F, Ding B, Yu J, Guo Z (2013) Co-axial electrospun polystyrene/polyurethane fibres for oil collection from water surface. Nanoscale 5(7):2745–2755. https://doi.org/10.1039/C3NR34008B

Liu H, Kang Y (2018) Superhydrophobic and superoleophilic modified EPDM foam rubber fabricated by a facile approach for oil/water separation. Appl Surf Sci 451:223–231. https://doi.org/10.1016/j.apsusc.2018.04.179

Liu Y, Mou H, Chen L, Mirza ZA, Liu L (2015) Cr(VI)-contaminated groundwater remediation with simulated permeable reactive barrier (PRB) filled with natural pyrite as reactive material: environmental factors and effectiveness. J Hazard Mater 298:83–90. https://doi.org/10.1016/j.jhazmat.2015.05.007

Liu H, Geng B, Chen Y, Wang H (2016) Review on the aerogel-type oil sorbents derived from nanocellulose. ACS Sustain Chem Eng 5(1):49–66. https://doi.org/10.1021/acssuschemeng.6b02301

Liu J, Bacosa HP, Liu Z (2017) Potential environmental factors affecting oil-degrading bacterial populations in deep and surface waters of the northern Gulf of Mexico. Front Microbiol 7:2131–2140. https://doi.org/10.3389/fmicb.2016.02131

Lovley DR (1995) Bioremediation of organic and metal contaminants with dissimilatory metal reduction. J Ind Microbiol Biotechnol 14:85–90. https://doi.org/10.1007/BF01569889

Lu Y, Kun F, Shu Z, Ying L, Chen C, Zhu J, Meltem Y, Mahmut D, Xiangwu Z (2015) Centrifugal spinning: a novel approach to fabricate porous carbon fibers as binder-free electrodes for electric double-layer capacitors. J Power Sources 273:502–510. https://doi.org/10.1016/j.jpowsour.2014.09.130

Lucas Z, MacGregor C (2006) Characterizationand source of oil contamination on the beaches and seabird corpses, Sable Island, Nova Scotia, 1996-2005. Mar Pollut Bull 52:778–789. https://doi.org/10.1016/j.marpolbul.2005.11.023

Lund A, Jonasson C, Johansson C, Haagensen D, Hagström B (2012) Piezoelectric polymeric bicomponent fibers produced by melt spinning. J Appl Polym Sci 126(2):490–500. https://doi.org/10.1002/app.36760

Mackay D, Fraser A (2000) Bioaccumulation of persistent organic chemicals: mechanisms and models. Environ Pollut 111:375–391. https://doi.org/10.1016/S0269-7491(00)00162-7

Mahajan P, Kaushal J (2018) Role of phytoremediation in readucing cadmium toxicity in soil and water. J Toxicol 2018:1–16. https://doi.org/10.1155/2018/4864365

Mahani AA, Motahari S, Mohebbi A (2018) Sol-gel derived flexible silica aerogel as selective adsorbent for water decontamination from crude oil. Mar Pollut Bull 129(2):438–447. https://doi.org/10.1016/j.marpolbul.2017.10.012

Maila MP, Colete TE (2004) Bioremediation of petroleum hydrocarbons through land farming: are simplicity and cost-effectiveness the only advantages? Rev Environ Sci Biotechnol 3:349–360. https://doi.org/10.1007/s11157-004-6653-z

Marić N, Ilić M, Miletić S, Gojgić-Cvijović G, Beškoski V, Vrvić MM, Papić P (2015) Enhanced in situ bioremediation of groundwater contaminated by petroleum hydrocarbons at the location of the Nitex textiles. Serbia, Environ Earth Sci 74:5211–5219. https://doi.org/10.1007/s12665-015-4531-3

McFarlin KM, Prince RC, Perkins R, Leigh MB (2014) Biodegradation of dispersed oil in Arctic seawater at −1 °C. PLoS 9:e84297–e84305. https://doi.org/10.1371/journal.pone.0084297

McNally DL, Mihelcic JR, Lueking DR (1998) Biodegradation of three-and fourring polycyclic aromatic hydrocarbons under aerobic and denitrifying conditions. Environ Sci Technol 32 (17):2633–2639. https://doi.org/10.1021/es980006c

Mena E, Ruiz C, Villasenor J, Rodrigo MA, Canizares P (2015) Biological permeable reactive barriers coupled with electrokinetic soil flushing for the treatment of diesel-polluted clay soil. J Hazard Mater 283:131–139. https://doi.org/10.1016/j.jhazmat.2014.08.069

Meng Y, Young TM, Liu P, Contescu CI, Huang B, Wang S (2015) Ultralight carbon aerogel from nanocellulose as a highly selective oil absorption material. Cellulose 22(1):435–447. https://doi.org/10.1007/s10570-014-0519-5

Mesa J, Rodrı’guez-Llorente JD, Pajuelo E, JMB P, Caviedes MA, Redondo-Go’mez S, Mateos-Naranjo E (2015) Moving closer towards restoration of contaminated estuaries:

bioaugmentation with autochthonous rhizobacteria improves metal rhizoaccumulation in native Spartina maritima. J Hazard Mater 300:263–271. https://doi.org/10.1016/j.jhazmat.2015.07.006

Miguel AS, Ravanel P, Raveton M (2013) A comparative study on the uptake and translocation of organochlorines by Phragmites australis. J Hazard Mater 244:60–69. https://doi.org/10.1016/j.jhazmat.2012.11.025

Mineki S, Suzuki K, Iwata K, Nakajima D, Goto S (2015) Degradation of polyaromatic hydrocarbons by fungi isolated from soil in Japan. Polycycl Aromat Compd 35(1):120–128. https://doi.org/10.1080/10406638.2014.937007

Moreira ITA, Oliveira OMC, Triguis JA, Queiroz AFS, Barbosa RM, Anjos JASA, Reyes CY, Silva CS, Trindade MCLF, Rios MC (2013) Evaluation of the effects of metals on biodegradation oftotal petroleum hydrocarbons. Microchem J 110:215–220. https://doi.org/10.1016/j.microc.2013.03.020

Morgan P, Watkinson RJ (1992) Factors limiting the supply and efficiency of nutrient and oxygen supplements for the *in situ* biotreatment of contaminated soil and groundwater. Water Res 26:73–78. https://doi.org/10.1016/0043-1354(92)90113-I

Motta FL, Stoyanov SR, Soares JB (2018) Application of solidifiers for oil spill containment: a review. Chemosphere 194:837–846. https://doi.org/10.1016/j.chemosphere.2017.11.103

Mullin JV, Champ MA (2003) Introduction/overview to in situ burning of oil spills. Spill Sci Technol Bull 8:323–330. https://doi.org/10.1016/S1353-2561(03)00076-8

Mumford KA, Rayner JL, Snape I, Stevens GW (2014) Hydraulic performance of a permeable reactive barrier at Casey Station, Antarctica. Chemosphere 117:223–231. https://doi.org/10.1016/j.chemosphere.2014.06.091

Muthusaravanan S, Sivarajasekar N, Vivek JS, Paramasivan T, Naushad M, Prakashmaran J, Gayathri V, Al-Duaij OK (2018) Phytoremediation of heavy metals: mechanisms, methods and enhancements. Environ Chem Lett 16:1339–1359. https://doi.org/10.1007/s10311-018-0762-3

Muttin F (2008) Structural analysis of oil-spill containment booms in coastal and estuary waters. Appl Ocean Res 30(2):107–112. https://doi.org/10.1016/j.apor.2008.07.001

Muttin F, 2015 Structural analysis of oil-spill booms, mathematical modelling and numerical simulation of oil pollution problems, Springer, 141–166, https://doi.org/10.1007/978-3-319-16459-5_7

Nikolopoulou M, Pasadakis N, Norf H, Kalogerakis N (2013) Enhanced ex situ bioremediation of crude oil contaminated beach sand by supplementation with nutrients and rhamnolipids. Mar Pollut Bull 77:37–44. https://doi.org/10.1016/j.marpolbul.2013.10.038

Nordvik AB, Simmons JL, Bitting KR, Lewis A, Strom-Kristiansen T (1996) Oil and water separation in marine oil spill clean-up operations. Spill Sci Technol Bull 3:107–122. https://doi.org/10.1016/S1353-2561(96)00021-7

Obiri-Nyarko F, Grajales-Mesa SJ, Malina G (2014) An overview of permeable reactive barriers for in situ sustainable groundwater remediation. Chemosphere 111:243–259. https://doi.org/10.1016/j.chemosphere.2014.03.112

Philp JC, Atlas RM (2005) Bioremediation of contaminated soils and aquifers. In: Atlas RM, Philp JC (eds) Bioremediation: applied microbial solutions for real-world environmental cleanup. American Society for Microbiology (ASM), USA, pp 139–236. https://doi.org/10.1128/9781555817596.ch5

Putatunda S, Bhattacharya S, Sen D, Bhattacharjee C (2019) A review on the application of different treatment processes for emulsified oily wastewater. Int J Environ Sci Technol 16(5):2525–2536. https://doi.org/10.1007/s13762-018-2055-6

Qiao K, Tian W, Bai J, Wang L, Zhao J, Du Z, Gong X (2019) Application of magnetic adsorbents based on iron oxide nanoparticles for oil spill remediation: a review. J Taiwan Inst Chem E 97:227–236. https://doi.org/10.1016/j.jtice.2019.01.029

Qin X, Tang J, Li D, Zhang Q (2012) Effect of salinity on the bioremediation of petroleum hydrocarbons in a saline alkaline soil. Lett Appl Microbiol 55(3):210–217. https://doi.org/10.1111/j.1472-765X.2012.03280.x

Quintella CM, Mata AMT, Lima LCP (2019) Overview of bioremediation with technology assessment and emphasis on fungal bioremediation of oil contaminated soils. J Environ Manag 241:156–166. https://doi.org/10.1016/j.jenvman.2019.04.019

Radetić MM, Jocić DM, Jovančić PM, Petrović ZL, Thomas HF (2003) Recycled wool-based nonwoven material as an oil sorbent. Environ Sci Technol 37(5):1008–1012. https://doi.org/10.1021/es0201303

Rahman K, Rahman TJ, Kourkoutas Y, Petsas I, Marchant R, Banat I (2003) Enhanced bioremediation of n-alkane in petroleum sludge using bacterial consortium amended with rhamnolipid and micronutrients. Bioresour Technol 90(2):159–168. https://doi.org/10.1016/S0960-8524(03)00114-7

Ramırez EM, Jimenez CS, Camacho JV, Rodrigo MAR, Canizares P (2015) Feasibility of coupling permeable bio-barriers and electrokinetics for the treatment of diesel hydrocarbons polluted soils. Electrochim Acta 181:192–199. https://doi.org/10.1016/j.electacta.2015.02.201

Ren R-P, Wang Z, Ren J, Lv Y-K (2019) Highly compressible polyimide/graphene aerogel for efficient oil/water separation. J Mater Sci 54(7):5918–5926. https://doi.org/10.1007/s10853-018-03238-1

Rodrıguez-Rodrıguez CE, Marco-Urrea E, Caminal G (2010) Degradation of naproxen and carbamazepine in spiked sludge by slurry and solid-phase Trametes versicolor systems. Bioresour Technol 101:2259–2266. https://doi.org/10.1016/j.biortech.2009.11.089

Ron EZ, Rosenberg E (2014) Enhanced bioremediation of oil spills in the sea. Curr Opin Biotechnol 27:191–194. https://doi.org/10.1016/j.copbio.2014.02.004

Roulia M, Chassapis K, Fotinopoulos C, Savvidis T, Katakis D (2003) Dispersion and sorption of oil spills by emulsifier-modified expanded perlite. Spill Sci Technol Bull 8(5–6):425–431. https://doi.org/10.1016/S1353-2561(02)00066-X

Sajna KV, Sukumaran RK, Gottumukkala LD, Pandey A (2015) Crude oil biodegradation aided by biosurfactants from Pseudozyma sp. NII 08165 or its culture broth. Bioresour Technol 191:133–139. https://doi.org/10.1016/j.biortech.2015.04.126

Sarbatly R, Krishnaiah D, Kamin Z (2016) A review of polymer nanofibres by electrospinning and their application in oil–water separation for cleaning up marine oil spills. Mar Pollut Bull 106 (1–2):8–16. https://doi.org/10.1016/j.marpolbul.2016.03.037

Schwitzguebel J-P (2015) Phytoremediation of soils contaminated by organic compounds: hype, hope and facts. J Soils Sediments 17:1492–1502. https://doi.org/10.1007/s11368-015-1253-9

Semple KT, Morriss A, Paton GI (2003) Bioavailability of hydrophobic organic contaminants in soils: fundamental concepts and techniques for analysis. Eur J Soil Sci 54(4):809–818. https://doi.org/10.1046/j.1351-0754.2003.0564.x

Shi Y, Li S, Chen H, He M, Shao S (2018) Improved SPH simulation of spilled oil contained by flexible floating boom under wave–current coupling condition. J Fluid Struct 76:272–300. https://doi.org/10.1016/j.jfluidstructs.2017.09.014

Stams AG, Oude ESJ (1997) Understanding and advancing wastewater treatment. Curr Opin Biotechnol 8:328–334. https://doi.org/10.1016/S0958-1669(97)80012-2

Stolz A, Le Floch S, Reinert L, Ramos SM, Tuaillon-Combes J, Soneda Y, Chaudet P, Baillis D, Blanchard N, Duclaux L (2016) Melamine-derived carbon sponges for oil-water separation. Carbon 107:198–208. https://doi.org/10.1016/j.carbon.2016.05.059

Sun H, La P, Zhu Z, Liang W, Yang B, Zhao X, Pei C, Li A (2014) Hydrophobic carbon nanotubes for removal of oils and organics from water. J Mater Sci 49(20):6855–6861. https://doi.org/10.1007/s10853-014-8387-9

Sundaravadivelu D, Suidan MT, Venosa AD, Rosales PI (2016a) Characterization of solidifiers used for oil spill remediation. Chemosphere 144:1490–1497. https://doi.org/10.1016/j.chemosphere.2015.10.030

Sundaravadivelu D, Suidan MT, Venosa AD, Rosales PI, Campo-Moreno P, Conmy RN (2016b) Development of a testing protocol for oil solidifier effectiveness evaluation. Clean Technol Environ 18(4):1141–1150. https://doi.org/10.1007/s10098-016-1107-1

Thijs S, Sillen W, Rineau F, Weyens N, Vangronsveld J (2016) Towards an enhanced understanding of plant–microbiome interactions to improve phytoremediation: engineering the metaorganism. Front Microbiol 7:1–15. https://doi.org/10.3389/fmicb.2016.00341

Thiruvenkatachari R, Vigneswaran S, Naidu R (2008) Permeable reactive barrier for groundwater remediation. J Ind Eng Chem 14:145–156. https://doi.org/10.1016/j.jiec.2007.10.001

Toyoda M, Inagaki M (2000) Heavy oil sorption using exfoliated graphite: new application of exfoliated graphite to protect heavy oil pollution. Carbon 38(2):199–210. https://doi.org/10.1016/S0008-6223(99)00174-8

Toyoda M, Aizawa J, Inagaki M (1998) Sorption and recovery of heavy oil by using exfoliated graphite. Desalination 115(2):199–201. https://doi.org/10.1016/S0011-9164(98)00038-1

Trap S, Kohler A, Larsen LC, Zambrano KC, Karlson U (2005) Phytotoxicity of fresh and weathered diesel and gasoline to willow and poplar trees. J Soils Sediments 1:71–76. https://doi.org/10.1007/BF02987712

Van Aken B (2009) Transgenic plants for enhanced phytoremediation of toxic explosives. Curr Opin Biotechnol 20:231–236. https://doi.org/10.1016/j.copbio.2009.01.011

Van Beilen JB, Funhoff EG (2007) Alkane hydroxylases involved in microbial alkane degradation. Appl Microbiol Biotechnol 74(1):13–21. https://doi.org/10.1007/s00253-006-0748-0

Vangronsveld J, Herzig R, Weyens N, Boulet J, Adriaensen K, Ruttens R, Thewys T, Vassilev A, Meers E, Nehnevajova E, Van der Lelie D, Mench M (2009) Phytoremediation of contaminated soils and groundwater: lessons from the field. Environ Sci Pollut Res 16:765–794. https://doi.org/10.1007/s11356-009-0213-6

Varjani SJ, Upasani VN (2016) Carbon spectrum utilization by an indigenous strain of Pseudomonas aeruginosa NCIM 5514: production, characterization and surface active properties of biosurfactant. Bioresour Technol 221:510–516. https://doi.org/10.1016/j.biortech.2016.09.080

Venosa AD, Haines JR, Nisamaneepong W, Govind R, Pradhan S (1991) Screening of commercial inocula for efficacy in stimulating oil biodegradation in closed laboratory system. J Hazard Mater 28:131–144. https://doi.org/10.1016/0304-3894(91)87012-Q

Vidal G, Carvalho A, Mendez R, Lema JM (2000) Influence of the content in fats and proteins on the anaerobic biodegradability of dairy wastewaters. Bioresour Technol 74:231–239. https://doi.org/10.1016/S0960-8524(00)00015-8

Villela HDM, Peixoto RS, Soriano AU, Carmo FL (2019) Microbial bioremediation of oil contaminated seawater: a survey of patent deposits and the characterization of the top genera applied. Sci Total Environ 666:743–758. https://doi.org/10.1016/j.scitotenv.2019.02.153

Vogan JL, Focht RM, Clark DK, Graham SL (1999) Performance evaluation of a permeable reactive barrier for remediation of dissolved chlorinated solvents in groundwater. J Hazard Mater 68:97–108. https://doi.org/10.1016/S0304-3894(99)00033-3

Von Wedel R, Mosquera J, Goldsmith CD, Hater G, Wong A, Fox T, Hunt W, Paules M, Quiros J, Wiegand J (1988) Bacterial biodegradation of petroleum hydrocarbons in groundwater: in situ augmented bioreclamation with enrichment isolates in California. Water Sci Technol 20:501–503. https://doi.org/10.2166/wst.1988.0335

Wakelin NG, Forster CF (1997) An investigation into microbial removal of fats oils and greases. Bioresour Technol 59:37–43. https://doi.org/10.1016/S0960-8524(96)00134-4

Wang X, Wang Q, Wang S, Li F, Guo G (2012) Effect of biostimulation on community level physiological profiles of microorganisms in field-scale biopiles composed of aged oil sludge. Bioresour Technol 111:308–315. https://doi.org/10.1016/j.biortech.2012.01.158

Wang B, Karthikeyan R, Lu X-Y, Xuan J, Leung MK (2013) Hollow carbon fibers derived from natural cotton as effective sorbents for oil spill cleanup. Ind Eng Chem Res 52(51):18251–18261. https://doi.org/10.1021/ie402371n

Wenzel WW (2009) Rhizosphere processes and management in plantassisted bioremediation (phytoremediation) of soils. Plant Soil 321:385–408. https://doi.org/10.1007/s11104-008-9686-1

Whelan MJ, Coulon F, Hince G, Rayner J, McWatters R, Spedding T, Snape I (2015) Fate and transport of petroleum hydrocarbons in engineered biopiles in polar regions. Chemosphere 131:232–240. https://doi.org/10.1016/j.chemosphere.2014.10.088

Witka-Jeżewska E, Hupka J, Pieniążek P (2003) Investigation of oleophilic nature of straw sorbent conditioned in water. Spill Sci Technol Bull 8(5–6):561–564. https://doi.org/10.1016/S1353-2561(03)00069-0

Xin B-P, Wu C-H, Wu C-H, Lin C-W (2013) Bioaugmented remediation of high concentration BTEX-contaminated groundwater by permeable reactive barrier with immobilized bead. J Hazard Mater 244:765–772. https://doi.org/10.1016/j.jhazmat.2012.11

Yadav KK, Gupta N, Kumar A, Reece LM, Singh N, Rezania S, Khan SH (2018) Mechanistic understanding and holistic approach of phytoremediation: Areview on application and future prospects. Ecol Eng 120:274–298. https://doi.org/10.1016/j.ecoleng.2018.05.039

Yan C, Ji Z, Ma S, Wang X, Zhou F (2016) 3D printing as feasible platform for on-site building oil-skimmer for oil collection from spills. Adv Mater Interfaces 3(13):1–7. https://doi.org/10.1002/admi.201600015

Yancheshmeh JB, Khavazi K, Pazira E, Solhi M (2011) Evaluation of inoculation of plant growth-promoting rhizobacteria on cadmium uptake by canola and barley. Afr J Microbiol Res 5:1747–1754. https://doi.org/10.5897/AJMR10.625

Zahed MA, Aziz HA, Isa MH, Mohajeri L (2010) Effect of initial oil concentration and dispersant on crude oil biodegradation in contaminated seawater. Bull Environ Contam Toxicol 84:438–442. https://doi.org/10.1007/s00128-010-9954-7

Zhang E, Wang B, Wang Q, Zhang S, Zhao B (2008) Ammonia- nitrogen and orthophosphate removal by immobilized Scenedesmus sp., isolated from municipal waste water for potential use in tertiary treatment. Biosour Technol 99:3787–3793. https://doi.org/10.1016/j.biortech.2007.07.011

Zhang X, Xia H, Li Z, Zhang P, Gao B (2010) Potential of four forage grasses in remediation of cd and Zn contaminated soils. Bioresour Technol 101:2063–2066. https://doi.org/10.1016/j.biortech.2009.11.065

Zhang JH, Xue QH, Gao H, Ma X, Wang P (2016) Degradation of crude oil by fungal enzyme preparations from Aspergillus spp. For potential use in enhanced oil recovery. J Chem Technol Biotechnol 91(4):865–875. https://doi.org/10.1002/jctb.4650

Zhang X, Li X, Zhao X, Li Y (2019) Factors affecting the efficiency of a bioelectrochemical system: a review. RSC Adv 9:19748–19761. https://doi.org/10.1039/C9RA03605A

Zhou Y, Zhang N, Zhou X, Hu Y, Hao G, Li X, Jiang W (2019) Design of Recyclable Superhydrophobic PU@ Fe3O4@ PS sponge for removing oily contaminants from water. Ind Eng Chem Res 58:3249–3257. https://doi.org/10.1021/acs.iecr.8b04642

Zhu S-P, Strunin D (2001) Modelling the confinement of spilled oil with floating booms. Appl Math Model 25(9):713–729. https://doi.org/10.1016/S0307-904X(01)00008-7

Zhu S-P, Strunin D (2002) A numerical model for the confinement of oil spill with floating booms. Spill Sci Technol Bull 7(5–6):249–255. https://doi.org/10.1016/S1353-2561(02)00042-7

Zhu Q, Tao F, Pan Q (2010) Fast and selective removal of oils from water surface via highly hydrophobic core− shell Fe2O3@ C nanoparticles under magnetic field. ACS Appl Mater Interfaces 2(11):3141–3146. https://doi.org/10.1021/am1006194

Zhu Q, Pan Q, Liu F (2011) Facile removal and collection of oils from water surfaces through superhydrophobic and superoleophilic sponges. J Phys Chem C 115(35):17464–17470. https://doi.org/10.1021/jp2043027

Zhu K, Shang Y-Y, Sun P-Z, Li Z, Li X-M, Wei J-Q, Wang K-L, Wu D-H, Cao A-Y, Zhu H-W (2013) Oil spill cleanup from sea water by carbon nanotube sponges. Front Mater Sci 7 (2):170–176. https://doi.org/10.1007/s11706-013-0200-1

Chapter 13
Remediation of Organic Pollutants in Water

Gangadharan Dheenadayalan and Rajagopalan Thiruvengadathan

Contents

Abstract In the past few decades, there has been an increase in the production of organic chemicals for their utilization in the fields, such as agriculture, pharma, flame retardants, and personal care products. Many of them are characterized as pollutants due their harmful effects on humans and the environment. Even today, adequate methods are not matured enough to prevent their release from industry into the environment. This is a serious challenge in front of the global community, and the responsibility to save the environment and humans from these hazardous chemicals is enormous. Organic pollutants accumulated into the human body generally lead to various types of carcinogenic effects. So, it is necessary to understand the flow cycle

---

G. Dheenadayalan
Department of Sciences, Amrita School of Engineering, Amrita Vishwa Vidyapeetham, Coimbatore, India
e-mail: d_gangadharan@cb.amrita.edu

R. Thiruvengadathan (✉)
Department of Electronics and Communication Engineering, Amrita School of Engineering, Amrita Vishwa Vidyapeetham, Coimbatore, India
e-mail: t_rajagopalan@cb.amrita.edu

Inamuddin et al. (eds.), *Water Pollution and Remediation: Organic Pollutants*, Environmental Chemistry for a Sustainable World 54,
https://doi.org/10.1007/978-3-030-52395-4_13

of these pollutants in the environment to save ourselves. In this regard, the first part of the chapter focuses on the various sources of organic pollutants, their transport process, and their impact on human health.

The second part of the chapter explores the recent possible solutions reported for removing these organic pollutants from the water. The treatment methods are selected based on their performance efficiency and their feasibility in employing them as remediation technology. The major treatment methods covered in this chapter are adsorption, photocatalytic process, advanced oxidation process, electrochemical methods, and bioremediation. Adsorption using carbon nanospheres are reported with 100% removal efficiency. All the photocatalytic materials covered in this chapter possesses degradation efficiency above 91% for the degradation of organic dyes.

The bioremediation section details the various species of microorganism reported for the degradation of pesticides in the water. Finally, the technological gaps existing in this field to be addressed in near future are highlighted.

Keywords Organic Pollutants · Water · Environment · Remediation · Health · Harmful Effects, Hazardous Chemicals, Human Health · Adsorption · Bioremediation

13.1 Introduction

During the second half of the twentieth century, it has been found that numerous organic contaminants having harmful side effects exist in water bodies. These contaminants enter the water bodies mainly due to industrial and agricultural practices. The usage of organic chemicals in sectors, such as flame retardants, pesticides, pharmaceuticals, personal care products, and textiles has increased after the industrial revolution. This increased consumption of organic chemicals is due to the increase in global population. Most of the synthesized organic compounds still have wide range of applications in human life, but their residues enter the water cycle and pose threats to the environment. So, an organic substance with an elevated risk to harm the environment is referred as organic pollutant.

The first commonly known organic pollutant is dichlorodiphenyltrichloroethane, an organochlorine used as an insecticide to protect crops from damage. Dyes, such as rhodamine B, methylene blue, and acid red, are used in textile industries also contribute as organic pollutant. Effluents from dyeing industry percolate down the soil and even make the ground water colored. Organic pollutants tend to remain in the soil and in the environment for longer years due to their poor biodegradability.

In recent times, many methods have been studied for treating organic pollutants. Some of such methods are absorption/adsorption, biological methods, electrochemical, and photocatalysis. Absorption/adsorption using activated carbon prepared from different precursors is generally reported widely in the literature (Menya et al. 2018; Li et al. 2019). In the biodegradation process, microorganisms, such as bacteria, fungi, algae, and their enzymes, are utilized to degrade and transform the organic pollutant into harmless products. Being a natural process, it is economically favorable (Shaw and Burns 2003). Recently, several articles are reported on the photocatalytic degradation of organic pollutants. Photocatalyst which is responsive to photons generates oxidative species for nonselective oxidation and degradation of organic contaminants (Areerachakul et al. 2019).

13.2 Sources of Various Organic Pollutants

The major source of organic pollutant is the industries which produce and process these chemicals. Mostly, synthesis of organic compounds involves more than one step and, in each step, there may be formation of byproducts. Once the desired product is synthesized, it must be separated from other byproducts and purified using different organic solvents. On the whole, from the starting compound till the final desired product, numerous chemicals are used, and only few chemicals are recycled back or treated before discharge into the environment.

The synthetic organic compounds of different classes, such as pesticides, insecticides, phthalates, phenolic compounds, and nitrogen-containing compounds, are often found as pollutants in water. Halogenated hydrocarbons, such as trichloroethylene, tetrachloroethylene, and 1,1,1- trichloroethane can sweep into the soil and end up in ground water. Even in surface water, lower concentrations of dioxins and polynuclear aromatic hydrocarbons are found. Moreover, disinfection byproducts, such as N-halamines, trihalomethanes, and haloacetic acids, which are produced during disinfection process by the reaction of chlorine and organic materials, are often found in drinking water.

Apart from the organic pollutants discussed above, there are other organic contaminants, which enter the water cycle through human activities. Generally, drugs administered to the patients and the extent of elimination from the human body decide the concentration levels of such residues in waste water. The drug diclofenac prescribed as analgesic and antirheumatic has been detected as one among the most important drug residues in the water cycle (Heberer 2002a, 2002b). The analgesic drug ibuprofen has been detected in sewage effluent plants of countries, such as Spain, France, and Germany (Farré et al. 2001). The cancerogenic and mutagenic antineoplastic agent cyclophosphamide found in the hospital sewage water sample has been analyzed using GC/MS. The concentration ranging from 20 ng L^{-1} to 4.5 μg L^{-1} is found in the sewage water sample (Steger-Hartmann et al. 1997). Kolpin et al. has reported the detection of 29 pharmaceutical residues across 139 rivers and streams in 30 states of the United States (Kolpin et al. 2004). From the reported works, it is well known that the major source of pharmaceutical residues in water is due to the medication given to humans and feed supplements provided for livestocks. The administration of medications to livestocks and humans is considered as one of the main sources of pharmaceutical residues in the environment (Boxall et al. 2004). As of now, more than 100 pharmaceutical residues have been identified in various water bodies (Daughton and Ternes 1999; Heberer 2002a, 2002b; Boxall et al. 2004). Some reports show that these pharmaceutical residues percolate down the soil and even enter the ground water stream, making it unfit for drinking purpose (Heberer 2002a, 2002b).

The herbicide is the other class of organic pollutant, which pollutes the ground water by the release of herbicides from soil surface and further transport through the vadose zone to the aquifer by rain water. These pollutants enter the water cycle due to various agricultural practices adopted for obtaining better yield in crops. The pollutants are carried to various surface water resources by rain water, and their concentration in surface water found to vary depending on the season (Bodur and Bakırdere 2019). The common herbicides found in water bodies are atrazine, terbutylazine, and simazine as well as their metabolites. In recent years, the usage of herbicides has gone down, as there is a strong link found between herbicide usage and their occurrence in surface water.

The major industrial source of organic pollutants that enter water cycle is dyes and detergents. Organic synthetic dyes having wide applications in industries, such as textile, paper, pharmaceutical, food, and cosmetic industries, contribute to a large extent for the entry these chemicals in the water cycle (Zheng et al. 1999). Figure 13.1 shows the possible ways through which the organic pollutants enter the water cycle.

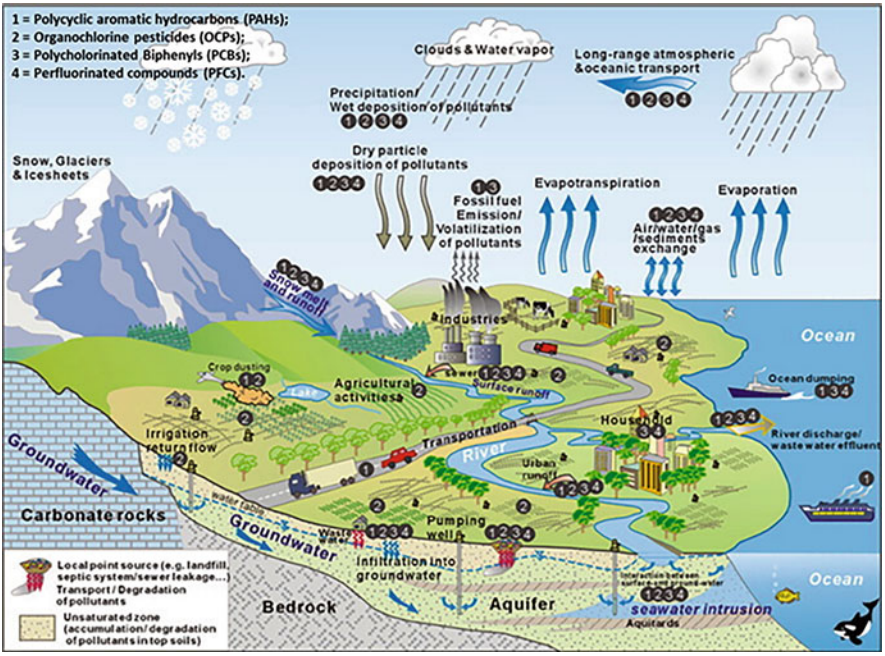


Fig. 13.1 Sources and transport processes for persistent organic pollutants and their interaction with the hydrological cycle. (Reprinted from Han and Currell (2017) with the permission of Elsevier)

The other common organic pollutants widely studied are polychlorinated biphenyls, perfluorinated compounds, brominated flame retardants, polycyclic aromatic hydrocarbons, and polychlorinated naphthalenes. Polychlorinated biphenyls have been widely used as additives to oils and industrial fluids, such as dielectric fluids in transformers. Generally, a class of 209 chlorinated aromatic compounds is being extensively used in industrial equipment and consumer products (Breivik et al. 2002; Breivik et al. 2007). Polychlorinated naphthalenes originate mainly from chlor-alkali industry and through waste incineration. These compounds deposited in the soils are being washed away by rain water to surface water.

13.3 Health Impact of Organic Pollutants on Human

The organic compounds not only enter the human body through food chain but also through water. Chemical disinfection is widely employed as a purification method to destroy pathogens in water. The disinfection byproducts are one of the main sources of organic pollutants in water. Disinfection byproducts are reported for the four major disinfectants: chlorine, ozone, chloramines, and chlorine dioxide, as well as their combinations. Table 13.1 lists the common chemical disinfectants and their byproducts.

The main health risks reported for these disinfection byproducts include bladder cancer; problems in the kidney, liver, and central nervous system; reduced ability of red blood cells to carry oxygen; early-term miscarriage (Li and Mitch 2018); and birth defects. Most of the disinfection byproducts containing nitrogen are generally more cytotoxic and genotoxic than those without nitrogen.

Swimming pool exposure of these disinfection byproducts causes asthma and other respiratory illnesses. When human inputs, such as urine, sweat, hair, and personal care products, are introduced to pools by swimmers, they react with chlorine, resulting in the formation of complex mixtures of disinfection byproducts. Epidemiologic studies have shown that such exposure to disinfection byproducts

Table 13.1 Disinfectants and associated disinfection byproducts

Disinfectant	Disinfection byproducts
Chlorine (e.g., gas, sodium hypochlorite, tablets, bleaching powder)	Trihalomethanes, haloacetic acids, chloramines, chlorinated acetic acids, halogenated acetonitriles, chloral hydrate, chlorophenols.
Chlorine dioxide	Chlorite, chlorate, and chloride.
Ozone	Bromate, formaldehyde, aldehydes, hydrogen peroxides, bromomethanes.
Chloramines	Monochloramines, dichloramines, trichloramines, haloacetonitriles, cyanogen chloride, chloral hydrate.

Acknowledgement: https://www.epa.ie/pubs/advice/drinkingwater/DrinkingWaterGuide4_v8.pdf (Open source) increases the risk of respiratory adverse effects and bladder cancer (Manasfi et al. 2017).

Even traces of pharmaceuticals were identified in ground water and surface water which are used as drinking water supply. The health risk due to pharmaceuticals is hardly reported because of their low concentration in water. The total concentration of drugs present in the contaminated water might not match the dosages prescribed by the doctors. So one cannot rule out the long-term effect of these compounds present in water, but, at the same time, it is impossible to prove that the risk of any pollutant in water is zero (Jones et al. 2005).

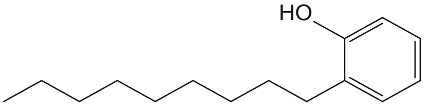
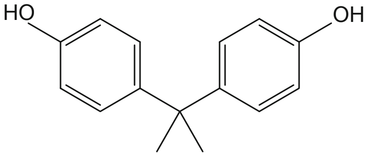
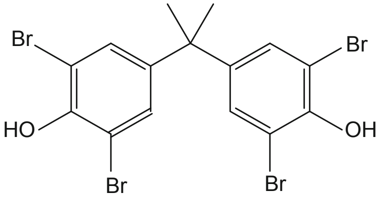
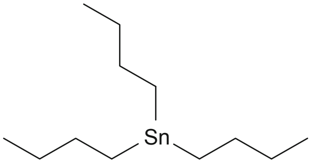
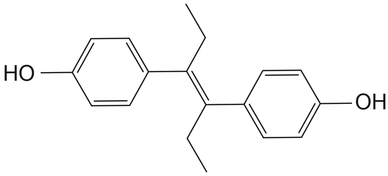
Herbicides and pesticides are the other organic contaminants which pose a threat to human health. Literature supports the link between pesticides and various types of cancer (Alavanja et al. 2004). Even fetuses are vulnerable to pesticides as they can pass through the placenta and the blood-brain barrier, and they are found in amniotic fluid (Bradman et al. 2003). It is due to the higher heart rate, food consumption pattern, and their hand-to-mouth behavior, making children more susceptible to pesticide poisoning than pregnant women (Garry 2004). Organic dyes generally impart color to water, a clear proof of water contamination. Mostly, azo dyes exhibit carcinogenic activity, and some of them causes allergic reactions too. Toxicity of dyes increases with the increase of benzene rings in their structure. A few studies have reported the DNA damage due to dyes (Uysal et al. 2017).

Some studies have shown the carcinogenic nature of organic pollutants, such as chlorinated and brominated polyaromatic compounds. Polybrominated biphenyl is reported as a probable compound that causes liver tumors (Groce and Kimbrough 1984). Generally, most of the organic pollutants on long term exert a carcinogenic effect on human health. Persistent organic chemicals contribute to large number of endocrine disrupting chemicals which mimic human hormones by blocking or binding to hormone receptors (Basile et al. 2011). Some of the common endocrine disrupting chemicals are listed in Table 13.2.

13.4 Common Methods Employed for the Treatment of Organic Pollutants

Some organic chemicals are degraded by natural events, such as bioremediation, using naturally occurring bacteria. However, most of the organic chemicals show some resistance to such degradation and require physical and chemical methods for remediation. In the last decade, numerous methods have been reported for the removal of organic contaminants from water. Among the various methods available for the removal of organic pollutants, the most common methods are adsorption, advanced oxidation, photocatalysis, electrochemical methods, and bioremediation. Different types of materials are being developed and investigated under these methods for the removal of organic pollutants. Similarly, a wide variety of

Table 13.2 Examples of endocrine disrupting chemicals

Compound	Structure	Intend use
Nonylphenol		Surfactant
Bisphenol – A		Plasticizer
Tetrabromobisphenol-A		Flame retardant
Tributyltin		Biocide
Diethylstilbestrol		Pharmaceutical waste

microorganisms are also studied for the degradation of organic pollutant using the natural pathway.

13.4.1 Adsorption

Adsorption is a process in which the adsorbate gets adsorbed on the surface of the adsorbent. Generally, the interaction between adsorbate and adsorption can be due to an electrostatic interaction which is called as physisorption. In some cases, adsorption can also occur via formation of chemical bonds, which are termed as chemisorption. Numerous adsorbents are being synthesized and tested for the removal of organic pollutants from water. Among these adsorbents, the highly investigated

Table 13.3 Different metal oxides for dye adsorption

S. no	Adsorbent	Dye	Adsorption capacity (mg/g)	Reference
1.	MgO nanoplates	Congo red	297	Hu et al. (2010))
2.	ZnO/CuO nanocomposite	Methyl orange	341	Hassanzadeh-Tabrizi et al. (2016))
3.	Hierarchical MnO_2	Methyl blue	259.2	Chen et al. (2013)
4.	Amine functionalized ZnO	Acid blue 25	1250	Mahmoodi and Najafi (2012))
5.	Fe_3O_4 hollow nanospheres	Neutral red	105	Iram et al. (2010)

material is carbon-based materials. There is a large number of reports for producing carbon-based materials from various natural sources. The most investigated source for this purpose is natural source, which includes leaf, flower, stem, seed, and fruit (Mallampati and Valiyaveettil 2012). Cereal ashes, from barley, oat, triticale, and wheat grains, have been used as adsorbents for the removal of organic pollutants, such as benzene, phenol, tetrachloroethylene, and toluene. Barley cereal ash is reported to remove benzene and toluene effectively, whereas wheat ash is found to remove tetrachloroethylene and toluene (Ghiaci et al. 2008). In some reports, synthetic organic chemicals have been also used as a source for preparing carbon-based materials. Carbon nanospheres with porous nature were synthesized by hydrothermal method and have also been tested for the removal of phenol and methylene blue as model source of organic pollutants. The triblock copolymers were used as the source for preparing the carbon nanospheres in this work. These carbon nanospheres show 98.9% adsorption for phenol and 100% adsorption for methylene blue (Kundu et al. 2018).

MgAl-LDHs nanosheets exhibit an excellent adsorption capacity of 229.82 mgL^{-1} for methyl orange (Li et al. 2016). In this work, MgAl-layered double hydroxide nanosheets with surface area of 65.94 $m^2\ g^{-1}$ were prepared by hydrothermal synthesis. Metal oxides are also being studied for the adsorptive removal of organic pollutants. Table 13.3 lists the various metal oxides which are used for the removal of organic pollutants (Nagpal and Kakkar 2019).

13.4.2 Photocatalytic Process

In recent years, photocatalysts are widely studied for the degradation of organic contaminants in the water. Photocatalysis occurs when the photocatalyst absorbs photons to create electrons and holes, which can initiate reduction and/or oxidation process in the system. In this process, free radicals, such as hydroxyl radicals, are generated to oxidize organic compounds present in the water. Peng Yue et al. developed a bismuth-based photocatalyst for the degradation of phenol and

Table 13.4 Percentage photocatalytic degradation of different dyes in water

S. no	Material studied	Pollutant	Degradation percentage	Reference
1.	Polyaniline/reduced graphene oxide	Malachite green	99.68%	Mitra et al. (2019)
		Rhodamine B	99.35%	
		Congo red	98.73%	
2.	n-Alkylamine-intercalated titanate	Methylene blue	100%	Anto Jeffrey et al. (2019)
3.	Fe4%Cr4%:BaTiO3	Methyl orange	94%	Amaechi et al. (2019))
4.	KAPs-B/Cu_2O	Methyl orange	92%	Zhao et al. (2019))
5.	SnO_2–Ta_2O_5 nanocomposite	Methylene blue	91.6%	Velaga et al. (2018))
6.	Benzoic acid/TiO_2	Tartrazine	99.08%	Zhou et al. (2019)

Rhodamine B under visible light irradiation (Yue et al. 2019). In this study, BiPO4/$BiCl_{0.9}I_{0.1}$ composite was prepared by varying the molar ratio of $BiPO_4$ and $BiOCl_{0.9}I_{0.1.}$ 300 W Xe lamp was used as light source. 3% $BiPO_4$/$BiOCl_{0.9}I_{0.1}$ showed 52.9% removal for rhodamine B. In literature, several works have been reported for the photocatalytic removal of dyes by using wide variety of photocatalytic materials. Table 13.4 shows the degradation percentage obtained for various organic pollutants using different materials.

In recent years, numerous articles were reported for the degradation of organic dyes by using a photocatalyst. Apart from dyes, various other substances are also investigated for their photocatalytic degradation. 2D-bismuth oxychloride (BiOCl)/2D-g-C_3N_4 heterojunction photocatalyst was investigated for the degradation of amine-based pharmaceutical nizatidine. The result of this study showed 96% degradation in 30 minutes (Al Marzouqi et al. 2019). $LaMnO_3$/graphitic carbon nitride (g- C_3N_4) hybrid was used as an efficient visible light photocatalyst for the degradation tetracycline. The near complete degradation of tetracycline was achieved after 270 minutes of prolonged visible light irradiation (Luo et al. 2019).

13.4.3 Advanced Oxidation Process

Advanced oxidation is a non-waste-generating process employed in water treatment. In this process, reactive oxygen species and hydroxide radical are generated by using ozone, hydrogen peroxide, and ultrasound. The efficiency of the process is normally increased by using a catalyst. Hydrogen peroxide in the presence of a catalyst, such as ferrous ion, decomposes to form hydroxide radical and hydroxide ion which is called as Fenton process. The free radical produced in this process oxidizes the organic pollutants present in the water. In a recent study, $CuFeO_2$ nanocubes and nanoplates were tested for the degradation of ofloxacin. This study proved that the oxidation efficiency of the $CuFeO_2$ material depended on the facet of oxide material (Dai et al. 2018). Fe0/CeO_2 with hydrogen peroxide act as Fenton's reagent to degrade tetracycline was studied. In this study, hydrogen peroxide alone showed less than 20% degradation of tetracycline, whereas hydrogen peroxide with Fe0/CeO_2 showed 91% degradation efficiency. The material showed recyclability up to five cycles (Zhang et al. 2019). In another study, CaO_2/Fe(II) system shows complete degradation of benzene in 10 minutes, whereas CaO_2/Fe(III) system with molar ratio of 15:15 took 80 minutes for degradation of benzene. The study also proved that molar ratio of CaO_2 and Fe influenced the degradation time of benzene (Xue et al. 2019). Fe-zeolite catalyst was studied for the removal of ibuprofen (20 mg/L) in water (Adityosulindro et al. 2018). The Fe-zeolite catalyst along with two times the stoichiometric amount of H_2O_2 showed 88% degradation of ibuprofen at natural pH. In a reaction time of 60 minute, H_2O_2 dosage of 170 mg L^{-1}, HNO3-modified coal fly ash (HFA) loading of 10.0 g L^{-1}, at pH 2.0, and mixing speed of 150 rpm showed 98% removal of p-nitro phenol (Wang et al. 2017).

13.4.4 Electrochemical Methods

Water electrooxidation is an indirect anodic oxidation process. This process is classified as an electrochemical advanced oxidation process (EAOP), as it leads to the in situ production of the hydroxyl radical (•OH). In this process boron-doped diamond electrode is used as the anode. The electrochemical reaction at the anode is

$$M + H_2O \rightarrow M(\bullet OH) + H^+ + e^- \tag{13.1}$$

where M represents the anode material and M(•OH) hydroxyl radical adsorbed on the anode. Pollutants (R) are then oxidized as follows:

$$M(\bullet OH) + R \rightarrow M + RO + H^+ + e^- \tag{13.2}$$

Lindane was oxidized by the hydroxyl radical, (•OH), formed due to the oxidation of water on the anode (M) surface (Dominguez et al. 2018). Carbon sponge and carbon felt cathodic materials showed good degradation when compared with SS cathode. The anode used was Boron-doped diamond electrode. The lindane degradation reaction at the anode surface is given in the following reaction,

$$C_6H_6Cl_6 + 12\,H_2O \rightarrow 6\,CO_2 + 6\,Cl^- + 30\,H^+ + 24\,e^- \tag{13.3}$$

The decay in lindane concentration during electrolysis was observed as a function of current density. Lindane conversion varied from 35% to 80% at current density, varying from 2.08 to 16.67 $mAcm^{-2}$, respectively, was achieved at 6 min of electrolysis. The electrooxidation process was used for the degradation of paracetamol using graphite electrode. The study shows 90% degradation of paracetamol at pH 4, having 20 mg L^{-1} paracetamol concentration at a constant current density of 5.1 mA/cm^2 with 0.1 M Na_2SO_4 as supporting electrolyte. A mechanism based on hydroxyl free radical has been proposed in the study for the degradation of paracetamol as shown in Fig. 13.2 (Periyasamy and Muthuchamy 2018).

Boron-doped diamond electrode was used for the electrooxidation of activated sludge. Organic pollutants, such as bisphenol A, triclosan, and nonylphenols, were reported to be partially oxidized. Partial degradation of selected pollutants was obtained with efficiencies of 51% for bispenol A, 69% for nonylphenols, and 62% for triclosan (Barrios et al. 2016). The current densities applied to reduce emerging pollutants in industrial sludge ranged from 20 to 40 mA cm^{-2} and a treatment time of 60 min was applied.

13.4.5 Bioremediation

Most of the synthetic organic dyes are chemically stable and cannot be degraded easily by using biological process. Most of the studies report that the microorganisms were isolated from the soil and studied under aerobic and anaerobic conditions in the laboratories for their degradation properties. *Bacillus sp*. YZU1 isolated from the soil around a textile factory was studied for of various reactive textile dyes, including azo dye. *Bacillus sp*. YZU1 shows approximately 95% decolorization of reactive black 5 in 120 hours under static condition at pH 7.0 and 40 C (Wang et al. 2013). Pajot et al. (2011) reported the degradation and also the accumulation of several textile dyes by the yeast *Trichosporon akiyoshidainum* (Pajot et al. 2011). Awasthi et al. reported the degradation of α and β isomers of endosulfan by two *Bacillus* strains. The study showed a degradation of 92.0% of α-endosulfan and 86.0% of β-endosulfan at the end of the incubation period (Awasthi et al. 2003). On the other hand, Abraham and Silambarasan reported that a defied bacterial consortium and a defied fungal consortium completely degrades the pesticide endosulfan in an aqueous phase as well as in soil amended with different nutrients, being the fungal consortium faster than the bacterial consortium (Abraham and Silambarasan 2014). *Streptomyces* M7 produced dechlorinase enzyme which degraded lindane into γ-pentachlorocyclohexene and 1,3,4,6-tetrachloro-1,4 cyclohexadiene (Cuozzo et al. 2009).

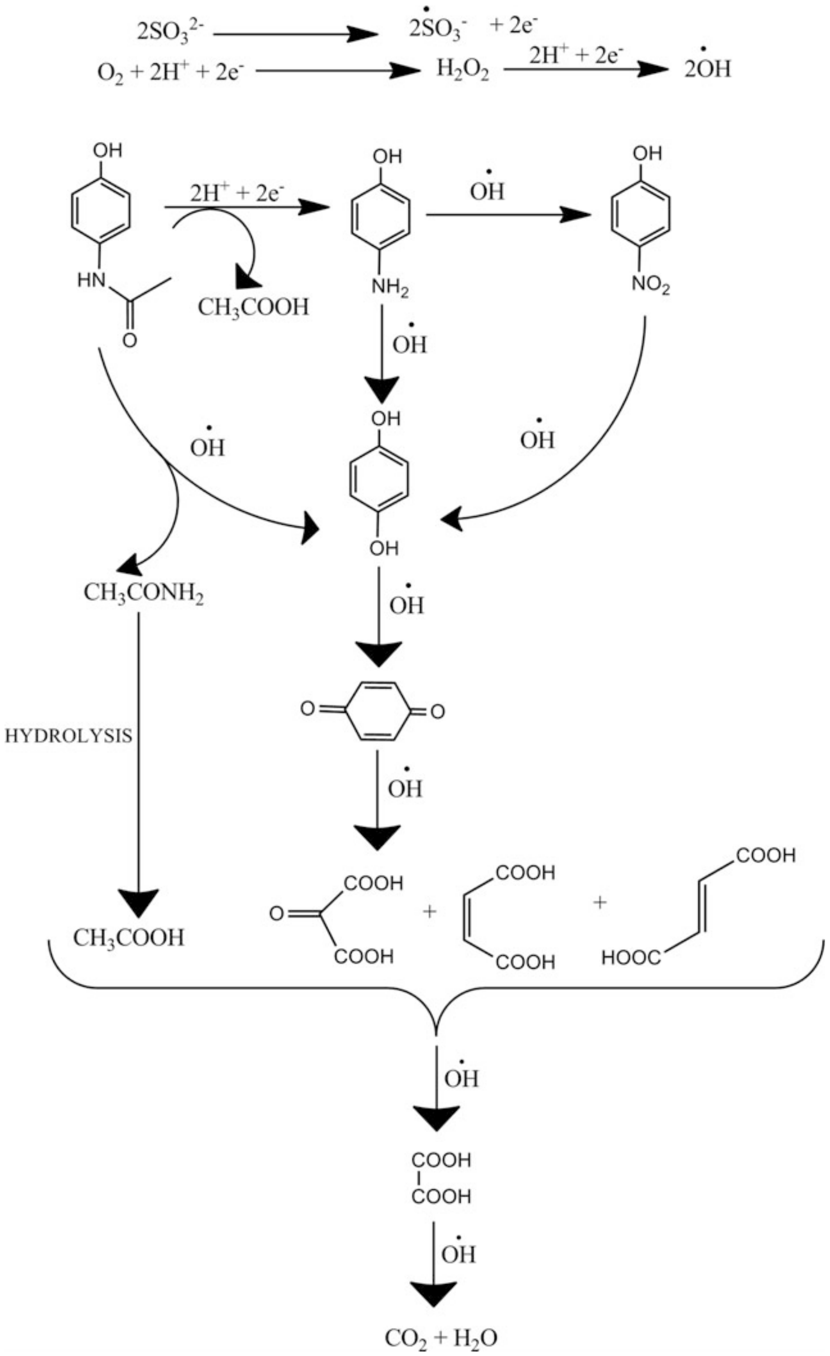


Fig. 13.2 Mechanism of paracetamol degradation by electrooxidation process. (Reprinted from Periyasamy and Muthuchamy (2018) with the permission of Elsevier)

13.5 Perspectives

Accompanied with massive industrialization, the inevitability to meet demands for various applications has led to unhindered production of a greater number of chemicals and byproducts. Consequently, these chemicals and byproducts are being let out into the environment either during the production process or as a volatile waste, though may be in smaller concentration, thanks to the compliance of rules enforced by environment protection agencies. However, there have been some anomalies in the past that have led to environmental pollution on a larger scale too, affecting both air and water quality severely. Among them, water contamination by these chemicals albeit in smaller concentration is posing a huge threat to environment. At the same time, there are clear guidelines for environmental risk assessment apart from the government enforcing ban on toxic pollutants. Wide publicity in media and awareness programs is being conducted by both state and nongovernmental agencies, emphasizing the hazards of organic pollutants and the need to sustain the good environment. Despite all these efforts, the goal to realize drastic reduction both in usage of chemicals and generation of chemical wastes and byproducts is indeed challenging. Many physical and chemical methods are being developed to remove and degrade these organic pollutants from the water bodies. All of these methods have their own advantages and disadvantages.

In case of adsorption process, the adsorbate gets adsorbed on the surface of the adsorbent. Repeated use of the adsorbent is possible only if the adsorbate is removed from the adsorbent. This again creates the disposal problem of organic pollutants. The other drawback is that complete adsorption of organic pollutants on the adsorbent is hardly reported in literature. In the photocatalytic process, the organic pollutant is normally converted into smaller products attributed to the catalytic activity of photocatalyst. Generally, carbon dioxide and water are the degradation products formed in this process. Moreover, this process generates free radicals, which degrade the organic pollutants present in the water. Advanced oxidation process uses a catalyst and oxidizing agents, such as $H_2O_{2,}$ for the degradation of organic pollutants. Complete degradation is not achieved with most of the catalysts and reagent combinations. This process leaves the oxidized products as residue in the water. In electrochemical remediation of organic pollutant, electrical energy is used to degrade the organic pollutants. This process requires higher investment and continuous maintenance for efficient degradation of pollutants. Bioremediation is a greener approach for degrading organic pollutants. Bioremediation process is highly selective with respect to microbes used in the degradation of organic pollutants. So, a wide range of organic pollutants cannot be treated effectively using this method.

Increased use of alternate and, yet, suitable greener chemicals rather than toxic organic compounds in various applications is a must for sustainable development. Government agencies must enforce stringent regulations besides ensuring such toxic organic compounds are not released into the environment even inadvertently. Simultaneously, newer methods to study and remove these toxic organic pollutants should be developed to holistically address this issue. The lessons should be drawn from developed countries where restrictions on the excessive use of toxic chemicals and sometimes even prohibitions have resolved the serious problems to a great extent.

References

Abraham J, Silambarasan S (2014) Biomineralization and formulation of endosulfan degrading bacterial and fungal consortiums. Pestic Biochem Physiol 116:24–31. https://doi.org/10.1016/j.pestbp.2014.09.006

Adityosulindro S, Julcour C, Barthe L (2018) Heterogeneous Fenton oxidation using Fe-ZSM5 catalyst for removal of ibuprofen in wastewater. J Environ Chem Eng 6(5):5920–5928. https://doi.org/10.1016/j.jece.2018.09.007

Al Marzouqi F, Al Farsi B, Kuvarega AT, Al Lawati HAJ, Al Kindy SMZ, Kim Y, Selvaraj R (2019) Controlled microwave-assisted synthesis of the 2D-BiOCl/2D-g-C 3 N 4 Heterostructure for the degradation of amine-based pharmaceuticals under solar light illumination. ACS Omega 4(3):4671–4678. https://doi.org/10.1021/acsomega.8b03665

Alavanja MCR, Hoppin JA, Kamel F (2004) Health effects of chronic pesticide exposure: Cancer and neurotoxicity. Annu Rev Public Health 25:155–197. https://doi.org/10.1146/annurev.publhealth.25.101802.123020

Amaechi IC, Hadj Youssef A, Rawach D, Claverie JP, Sun S, Ruediger A (2019) Ferroelectric Fe–Cr Codoped BaTiO3 nanoparticles for the Photocatalytic oxidation of azo dyes. ACS Appl Nano Mater 2(5):2890–2901. https://doi.org/10.1021/acsanm.9b00336

Anto Jeffrey A, Nethravathi C, Rajamathi M (2019) Nitrogen-doped Alkylamine-intercalated layered Titanates for Photocatalytic dye degradation. ACS Omega 4(1):1575–1580. https://doi.org/10.1021/acsomega.8b03207

Areerachakul N, Sakulkhaemaruethai S, Johir MAH, Kandasamy J, Vigneswaran S (2019) Photocatalytic degradation of organic pollutants from wastewater using aluminium doped titanium dioxide. J Water Process Eng 27:177–184. https://doi.org/10.1016/j.jwpe.2018.12.006

Awasthi N, Singh AK, Jain RK, Khangarot BS, Kumar A (2003) Degradation and detoxification of endosulfan isomers by a defined co-culture of two Bacillus strains. Appl Microbiol Biotechnol 62(2–3):279–283. https://doi.org/10.1007/s00253-003-1241-7

Barrios JA, Cano A, Becerril JE, Jiménez B (2016) Influence of solids on the removal of emerging pollutants in electrooxidation of municipal sludge with boron-doped diamond electrodes. J Electroanal Chem 776:148–151. https://doi.org/10.1016/j.jelechem.2016.07.018

Basile T, Petrella A, Petrella M, Boghetich G, Petruzzelli V, Colasuonno S, Petruzzelli D (2011) Review of endocrine-disrupting-compound removal technologies in water and wastewater treatment plants: an EU perspective. Ind Eng Chem Res 50(14):8389–8401. https://doi.org/10.1021/ie101919v

Bodur S, Bakırdere EG (2019) Simultaneous determination of selected herbicides in dam lake, river and well water samples by gas chromatography mass spectrometry after vortex assisted binary solvent liquid phase microextraction. Microchem J 145:168–172. https://doi.org/10.1016/j.microc.2018.10.033

Boxall ABA, Fogg LA, Blackwell PA, Kay P, Pemberton EJ, Croxford A (2004) Veterinary medicines in the environment. Rev Environ Contam Toxicol 180:1–91

Bradman A, Barr DB, Henn BGC, Drumheller T, Curry C, Eskenazi B (2003) Measurement of pesticides and other toxicants in amniotic fluid as a potential biomarker of prenatal exposure: a validation study. Environ Health Perspect 111(14):1779–1782. https://doi.org/10.1289/ehp.6259

Breivik K, Sweetman A, Pacyna JM, Jones KC (2002) Towards a global historical emission inventory for selected PCB congeners - a mass balance approach: 2. Emissions. Sci Total Environ 290(1–3):199–224. https://doi.org/10.1016/S0048-9697(01)01076-2

Breivik K, Sweetman A, Pacyna JM, Jones KC (2007) Towards a global historical emission inventory for selected PCB congeners - a mass balance approach. 3. An update. Sci Total Environ 377(2–3):296–307. https://doi.org/10.1016/j.scitotenv.2007.02.026

Chen R, Yu J, Xiao W (2013) Hierarchically porous MnO2 microspheres with enhanced adsorption performance. J Mater Chem A 1(38):11682–11690. https://doi.org/10.1039/c3ta12589k

Cuozzo SA, Rollán GG, Abate CM, Amoroso MJ (2009) Specific dechlorinase activity in lindane degradation by streptomyces sp. M7. World J Microbiol Biotechnol 25(9):1539–1546. https://doi.org/10.1007/s11274-009-0039-x

Dai C, Tian X, Nie Y, Lin HM, Yang C, Han B, Wang Y (2018) Surface facet of CuFeO2 Nanocatalyst: a key parameter for H2O2 activation in Fenton-like reaction and organic pollutant degradation. Environ Sci Technol 52(11):6518–6525. https://doi.org/10.1021/acs.est.8b01448

Daughton CG, Ternes TA (1999) Pharmaceuticals and personal care products in the environment: agents of subtle change? Environ Health Perspect 107(SUPPL. 6):907–938. https://doi.org/10.1289/ehp.99107s6907

Dominguez CM, Oturan N, Romero A, Santos A, Oturan MA (2018) Lindane degradation by electrooxidation process: effect of electrode materials on oxidation and mineralization kinetics. Water Res 135:220–230. https://doi.org/10.1016/j.watres.2018.02.037

Farré M, Ferrer I, Ginebreda A, Figueras M, Olivella L, Tirapu L, Vilanova M, Barceló D (2001) Determination of drugs in surface water and wastewater samples by liquid chromatography-mass spectrometry: methods and preliminary results including toxicity studies with Vibrio fischeri. J Chromatogr A 938(1–2):187–197. https://doi.org/10.1016/S0021-9673(01)01154-2

Garry VF (2004) Pesticides and children. Toxicol Appl Pharmacol 198(2):152–163. https://doi.org/10.1016/j.taap.2003.11.027

Ghiaci M, Arshadi M, Sedaghat ME, Kalbasi RJ, Gil A (2008) Adsorption of organic pollutants from aqueous solutions on cereal ashes. J Chem Eng Data 53(11):2707–2709. https://doi.org/10.1021/je800532p

Groce DF, Kimbrough RD (1984) Stunted growth, increased mortality, and liver tumors in offspring of polybrominated biphenyl (Pbb) dosed Sherman rats. J Toxicol Environ Health 14(5–6):695–706. https://doi.org/10.1080/15287398409530618

Hassanzadeh-Tabrizi SA, Motlagh MM, Salahshour S (2016) Synthesis of ZnO/CuO nanocomposite immobilized on γ-Al 2 O 3 and application for removal of methyl orange. Appl Surf Sci 384:237–243. https://doi.org/10.1016/j.apsusc.2016.04.165

Heberer T (2002a) Occurrence, fate, and removal of pharmaceutical residues in the aquatic environment: a review of recent research data. Toxicol Lett 131(1–2):5–17. https://doi.org/10.1016/S0378-4274(02)00041-3

Heberer T (2002b) Tracking persistent pharmaceutical residues from municipal sewage to drinking water. J Hydrol 266(3–4):175–189. https://doi.org/10.1016/S0022-1694(02)00165-8

Hu J, Song Z, Chen L, Yang H, Li J, Richards R (2010) Adsorption properties of MgO(111) nanoplates for the dye pollutants from wastewater. J Chem Eng Data 55(9):3742–3748. https://doi.org/10.1021/je100274e

Iram M, Guo C, Guan Y, Ishfaq A, Liu H (2010) Adsorption and magnetic removal of neutral red dye from aqueous solution using Fe3O4 hollow nanospheres. J Hazard Mater 181(1–3):1039–1050. https://doi.org/10.1016/j.jhazmat.2010.05.119

Jones OA, Lester JN, Voulvoulis N (2005) Pharmaceuticals: a threat to drinking water? Trends Biotechnol 23(4):163–167. https://doi.org/10.1016/j.tibtech.2005.02.001

Kolpin DW, Skopec M, Meyer MT, Furlong ET, Zaugg SD (2004) Urban contribution of pharmaceuticals and other organic wastewater contaminants to streams during differing flow conditions. Sci Total Environ 328(1–3):119–130. https://doi.org/10.1016/j.scitotenv.2004.01.015

Kundu S, Chowdhury IH, Naskar MK (2018) Hierarchical porous carbon Nanospheres for efficient removal of toxic organic water contaminants of phenol and methylene blue. J Chem Eng Data 63(3):559–573. https://doi.org/10.1021/acs.jced.7b00745

Li XF, Mitch WA (2018) Drinking water disinfection Byproducts (DBPs) and human health effects: multidisciplinary challenges and opportunities. Environ Sci Technol 52(4):1681–1689. https://doi.org/10.1021/acs.est.7b05440

Li J, Cui H, Song X, Zhang G, Wang X, Song Q, Wei N, Tian J (2016) Adsorption and intercalation of organic pollutants and heavy metal ions into MgAl-LDHs nanosheets with high capacity. RSC Adv 6(95):92402–92410. https://doi.org/10.1039/c6ra18783h

Li K, Zhou M, Liang L, Jiang L, Wang W (2019) Ultrahigh-surface-area activated carbon aerogels derived from glucose for high-performance organic pollutants adsorption. J Colloid Interface Sci 546:333–343. https://doi.org/10.1016/j.jcis.2019.03.076

Luo J, Chen J, Guo R, Qiu Y, Li W, Zhou X, Ning X, Zhan L (2019) Rational construction of direct Z-scheme LaMnO3/g-C3N4 hybrid for improved visible-light photocatalytic tetracycline degradation. Sep Purif Technol:882–894. https://doi.org/10.1016/j.seppur.2018.10.062

Mahmoodi NM, Najafi F (2012) Preparation of surface modified zinc oxide nanoparticle with high capacity dye removal ability. Mater Res Bull 47(7):1800–1809. https://doi.org/10.1016/j.materresbull.2012.03.026

Mallampati R, Valiyaveettil S (2012) Application of tomato peel as an efficient adsorbent for water purification - alternative biotechnology? RSC Adv 2(26):9914–9920. https://doi.org/10.1039/c2ra21108d

Manasfi T, Coulomb B, Boudenne JL (2017) Occurrence, origin, and toxicity of disinfection byproducts in chlorinated swimming pools: an overview. Int J Hyg Environ Health 220(3):591–603. https://doi.org/10.1016/j.ijheh.2017.01.005

Menya E, Olupot PW, Storz H, Lubwama M, Kiros Y (2018) Production and performance of activated carbon from rice husks for removal of natural organic matter from water: a review. Chem Eng Res Des 129:271–296. https://doi.org/10.1016/j.cherd.2017.11.008

Mitra M, Ahamed ST, Ghosh A, Mondal A, Kargupta K, Ganguly S, Banerjee D (2019) Polyaniline/reduced graphene oxide composite-enhanced visible-light-driven Photocatalytic activity for the degradation of organic dyes. ACS Omega 4(1):1623–1635. https://doi.org/10.1021/acsomega.8b02941

Nagpal M, Kakkar R (2019) Use of metal oxides for the adsorptive removal of toxic organic pollutants. Sep Purif Technol 211:522–539. https://doi.org/10.1016/j.seppur.2018.10.016

Pajot HF, Fariña JI, De Figueroa LIC (2011) Evidence on manganese peroxidase and tyrosinase expression during decolorization of textile industry dyes by Trichosporon akiyoshidainum. Int Biodeterior Biodegrad 65(8):1199–1207. https://doi.org/10.1016/j.ibiod.2011.05.010

Periyasamy S, Muthuchamy M (2018) Electrochemical oxidation of paracetamol in water by graphite anode: effect of pH, electrolyte concentration and current density. J Environ Chem Eng 6(6):7358–7367. https://doi.org/10.1016/j.jece.2018.08.036

Shaw LJ, Burns RG (2003) Biodegradation of organic pollutants in the rhizosphere. Adv Appl Microbiol 53:1–60. https://doi.org/10.1016/S0065-2164(03)53001-5

Steger-Hartmann T, Kümmerer K, Hartmann A (1997) Biological degradation of cyclophosphamide and its occurrence in sewage water. Ecotoxicol Environ Saf 36(2):174–179. https://doi.org/10.1006/eesa.1996.1506

Uysal H, Genic S, Ayar A (2017) Toxic effects of chronic feeding with food flazo dyes on Drosophila melanogaster Oregon R. Scientia Iranica 24(6):3081–3086. https://doi.org/10.24200/sci.2017.4523

Velaga B, Shanbogh PP, Swain D, Narayana C, Sundaram NG (2018) High surface area SnO2–Ta2O5 composite for visible light-driven Photocatalytic degradation of an organic dye. Photochem Photobiol 94(4):633–640. https://doi.org/10.1111/php.12896

Wang ZW, Liang JS, Liang Y (2013) Decolorization of reactive black 5 by a newly isolated bacterium Bacillus sp. YZU1. Int Biodeterior Biodegrad 76:41–48. https://doi.org/10.1016/j.ibiod.2012.06.023

Wang N, Zhao Q, Zhang A (2017) Catalytic oxidation of organic pollutants in wastewater: via a Fenton-like process under the catalysis of HNO3-modified coal fly ash. RSC Adv 7(44):27619–27628. https://doi.org/10.1039/c7ra04451h

Xue Y, Sui Q, Brusseau ML, Zhou W, Qiu Z, Lyu S (2019) Insight into CaO2-based Fenton and Fenton-like systems: strategy for CaO2-based oxidation of organic contaminants. Chem Eng J:919–928. https://doi.org/10.1016/j.cej.2018.12.121

Yue P, Zhang G, Cao X, Wang B, Zhang Y, Wei Y (2019) In situ synthesis of Z-scheme BiPO 4 / BiOCl 0.9 I 0.1 heterostructure with multiple vacancies and valence for efficient photocatalytic degradation of organic pollutant. Sep Purif Technol:34–44. https://doi.org/10.1016/j.seppur.2018.12.003

Zhang N, Chen J, Fang Z, Tsang EP (2019) Ceria accelerated nanoscale zerovalent iron assisted heterogenous Fenton oxidation of tetracycline. Chem Eng J:588–599. https://doi.org/10.1016/j.cej.2019.03.112

Zhao Q, Wang K, Wang J, Guo Y, Yoshida A, Abudula A, Guan G (2019) Cu2O nanoparticle hyper-cross-linked polymer composites for the visible-light Photocatalytic degradation of methyl Orange. ACS Appl Nano Mater 2(5):2706–2712. https://doi.org/10.1021/acsanm.9b00210

Zheng Z, Levin RE, Pinkham JL, Shetty K (1999) Decolorization of polymeric dyes by a novel Penicillium isolate. Process Biochem 34(1):31–37. https://doi.org/10.1016/S0032-9592(98)00061-2

Zhou Y, Qin Y, Dai W, Luo X (2019) Highly efficient degradation of Tartrazine with a benzoic acid/TiO2 system. ACS Omega 4(1):546–554. https://doi.org/10.1021/acsomega.8b03267

Chapter 14
Soil as Heterogeneous Fenton Catalyst for the Abatement of Organic Pollutants

Ansaf V. Karim, P. V. Nidheesh, and M. Suresh Kumar

Contents

Abstract Fenton oxidation process is an effectual technology for the abatement of organic compounds seen in wastewater. The homogeneous Fenton process is highly pH-dependent, sludge production, interference by the formation of complex iron ions etc. To overcome these disadvantages, environmentally friendly and cheaper heterogeneous solid catalysts which are highly reactive and stable were used as an iron source. The usage of a heterogeneous catalyst can decrease the rate of sludge production and work in an extensive range of pH. Among the different heterogeneous catalyst in Fenton oxidation, soil can be used as an efficient Fenton catalyst for the degradation of various organic pollutants. This chapter provides an inclusive review focusing on soil as a heterogeneous catalyst for Fenton processes. Three major soil classifications, such as clay, volcanic, and laterite, used for degradation of pollutants are explained. Further, the chapter also reviews the various research conducted with modified soil minerals.

A. V. Karim
Environmental Science and Engineering Department, Indian Institute of Technology, Mumbai, Maharashtra, India

P. V. Nidheesh (✉) · M. S. Kumar
CSIR-National Environmental Engineering Research Institute, Nagpur, Maharashtra, India
e-mail: pv_nidheesh@neeri.res.in

Inamuddin et al. (eds.), *Water Pollution and Remediation: Organic Pollutants*, Environmental Chemistry for a Sustainable World 54,
https://doi.org/10.1007/978-3-030-52395-4_14

Keywords Heterogeneous Fenton Process · Soil · Clay · Volcanic soil · Laterite

14.1 Introduction

Advanced oxidation processes gained much attention during the recent decades in the domain of water and wastewater treatment because of its capability to mineralize nonbiodegradable organic compounds, including those that are recalcitrant in nature. Advanced oxidation processes result in the formation of hydroxyl radicals in the water mainly by chemical methods. Hydroxyl radicals have high oxidation potential and attack pollutants nonselectively. They are the second-highest oxidant, subsequent to fluorine with a standard oxidation potential of 2.85 eV. Hydroxyl radicals attack the organic pollutant via redox reaction, dehydrogenation, and hydroxylation reactions. Complete mineralization of an organic pollutant is the most desirable feature of all advanced oxidation processes. Organic pollutants, including complex aromatic compounds, get mineralized into carbon dioxide, water, and other minerals due to their reaction with hydroxyl radicals. The intermediate compounds formed during the mineralization process are also found as more biodegradable than the parent compound, and thus combining advanced oxidation process with biological treatment was proposed to treat the wastewater to reduce the treatment time as well as treatment cost. Reduction of toxicity is another advantage of advanced oxidation processes. In most of the cases, intermediate compounds and byproducts formed after the oxidation are found less toxic than their parent compounds.

The hydrogen peroxide decomposition and successive production of hydroxyl radicals are the primary reaction in the advanced oxidation process. Decomposition of hydrogen peroxide in the presence of ferrous ion known as Fenton reaction is a recognized advanced oxidation process and got much consideration during the last few decades in water and wastewater treatment, even though the reaction was first reported by H. J. Fenton in 1984. All the transition metals having different oxidation states with a unit difference in oxidation state can decompose hydrogen peroxide as given in Eq. (14.1). Ferric ions generated via Fenton reaction can also regenerate via Eqs. (14.2) and (14.3).

$$\mathrm{Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO^\bullet} \tag{14.1}$$

$$\mathrm{Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + H^+ + HO_2^\bullet} \tag{14.2}$$

$$\mathrm{Fe^{3+} + HO_2^\bullet \longrightarrow Fe^{2+} + O_2 + H^+} \tag{14.3}$$

Based on the catalyst used, the Fenton oxidation processes can be parted into homogeneous and heterogeneous Fenton processes. The homogeneous Fenton process has certain disadvantages, such as pH dependency at the narrow range, difficulty in the separation and regeneration of end products, the generation of different ferric complexes with pH variation, etc. (Xavier et al. 2015). Researches in the direction of overcoming the drawbacks associated with homogeneous Fenton catalyst have been conducted to develop solid materials with high catalytic activity. The use of dynamic heterogeneous catalyst as a source for iron in the Fenton process can control the sludge production, effectiveness at circumneutral pH, and the option to recycle the iron promoter (Purceno et al. 2012). Immobilizing iron compounds on various solid supports, such as carbon, zeolite, clay, alumina, etc., have been comprehensively explored for the removal of organic pollutants (De Leon et al. 2013). This chapter briefly explains the use of different soil minerals as heterogeneous Fenton catalyst for toxicant degradation.

14.2 Heterogeneous Fenton Process

Classical Fenton process using ferrous ion is much efficient for the mineralization of different organic pollutants. Pollutants, such as dyes (Xavier et al. 2015), pesticides (Saini et al. 2016), phenol (Gümüş and Akbal 2016), sulfanilic acid azochromotrop (Hassan et al. 2019), and amoxicillin (Verma and Haritash 2019), were effectively decomposed via attack of hydroxyl radicals produced due to the reaction between ferrous ions and hydrogen peroxide. This process is also found effective for the treatment of real effluents generated from distillery (David et al. 2015), agro-food industry (Leifeld et al. 2018), and textile industry (Cetinkaya et al. 2018) as well as to treat turpentine processing wastewater (Huang et al. 2018), coke plant wastewater (Razaviarani et al. 2019), triethyl phosphate wastewater (Yang et al. 2019), pharmaceutical wastewater (Changotra et al. 2019), and sulfide minerals processing wastewater (Meng et al. 2019).

Generation of sludge after the treatment is one of the key limitations of the Fenton process (Nidheesh 2015; Nidheesh and Gandhimathi 2012). The main reason behind this sludge production is the rise in solution pH by Fenton reaction. Hydroxyl ion generated in Fenton reaction results in an increase in solution pH. This elevated solution pH reduces the concentration of ferrous and ferric ions in their ionic forms. Ferric ions generated via Fenton reaction undergo complexation reactions. This results in a reduction in ferrous regeneration and subsequent hydroxyl radical generation. The concentration of ferrous ions required for the maximum pollutant removal is on the scale of g/L (Nidheesh et al. 2013), and this higher concentration leads to the increased sludge generation. Thus, conventional Fenton process removes pollutants via degradation and the coagulation process.

Extended Fenton process, which utilizes external energy, is an option to reduce the sludge production and to increase the pollutant abatement rate of conventional Fenton process. The photo-Fenton process which uses energy in the form of light (Clarizia et al. 2017; Rahim Pouran et al. 2015), electro-Fenton process with electricity energy (Brillas et al. 2009; Nidheesh et al. 2018a, b), and ultrasound-based sono-Fenton process (Nidheesh et al. 2013) found effective than conventional Fenton process in terms of pollutant mineralization rate, reduced sludge production, and minimized optimal iron concentration.

Another option to minimize the sludge production in the Fenton process is to utilize insoluble iron catalysts instead of soluble ferrous ions (Nidheesh 2017, 2015). Ferrous or ferric ion in solid form reduces the complexation reactions and will help to improve the mineralization rate rather than coagulation of pollutants. Waste materials, such as fly ash (Bansal and Verma 2017; Narayani et al. 2017); iron minerals, including pyrite (Khataee et al. 2016), hematite (Changotra et al. 2018), magnetite (Nidheesh et al. 2014; Xavier et al. 2016), goethite (Wang et al. 2015), ferrite (Kurian and Nair 2015; Sharma and Singhal 2018), iron molybdophosphate (Baiju et al. 2018), and ferrihydrite (Xu et al. 2016); and zero-valent iron (Devi et al. 2016; Malik et al. 2018), are found as effective heterogeneous Fenton catalysts. These solid materials contain iron and can decompose hydrogen peroxide. Another type of heterogeneous Fenton catalysts includes the iron or iron minerals loaded over stable support. Supports, such as activated carbon (Nidheesh and Rajan 2016), alumina (di Luca et al. 2015), biosorbents (Laiju et al. 2014), biochar (Rubeena et al. 2018), zeolite (Sruthi et al. 2018), fiber (Su et al. 2018), alginate beads (Hammouda et al. 2016), silica (Jinisha et al. 2018; Kumar et al. 2016; Thirumoorthy and Satishkumar 2019), and sewage sludge, are found effective for iron and iron oxides. The performances of these catalysts are detailed in the review articles published recently (Mirzaei et al. 2017; Munoz et al. 2015; Nidheesh 2015; Nidheesh et al. 2018a, b).

Pollutant removal mechanism, as well as reusability of heterogeneous Fenton catalyst, purely depends on the iron leaching. Effective Fenton reaction rate depends on the amount of exposed iron, not on the iron content in the solid catalyst. If the iron leaching rate of solid catalyst is high, reusability of the material is less. The leached iron will undergo Fenton reactions in the water medium and follows the principles of homogeneous Fenton process. Pollutants will be removed via degradation and coagulation. At the same time, a solid catalyst with lesser iron leaching is generally highly reusable, and reactions will take place on the surface of the catalyst. Here, the pollutant removal will be mainly by degradation because of the attack of hydroxyl radicals, and adsorption of pollutants over the surface also improves the performance of heterogeneous Fenton catalyst.

14.3 Soil as Heterogeneous Fenton Catalyst

Soil can be considered as an ideal heterogeneous catalyst with higher catalytic activity and stability. They are rich in minerals and other oxide contents. Higher availability, environmental friendliness, and lower cost make them an ideal heterogeneous catalyst for pollutant degradation. The higher surface area and low leaching of iron put it into perspectives of many researchers for using it a suitable heterogeneous Fenton catalyst. Among the different soil samples, laterite, clay, and volcanic soils have been successful for heterogeneous Fenton process.

14.3.1 Laterite Soil

Laterite soil is abundant in the earth crust and is found in different parts of the world. This soil can be employed as a heterogeneous Fenton catalyst, as it is rich in iron oxides and other minerals. Typical laterite soil contains 38–43% silicon dioxide, 26–30% ferric oxide, 25–28% aluminium oxide, 3–4% titanium dioxide, 1–2% potassium oxide, 0.5% calcium oxide, and 0.2% carbon (Khataee and Pakdehi 2014). This soil is effective to decompose hydrogen peroxide in water medium and subsequently produce hydroxyl radicals by means of Fenton reactions. Such heterogeneous Fenton process is able to degrade 4-nitroaniline (Amritha and Manu 2018), 2-Aminopyridine (Karale et al. 2014), 2-nitroaniline (Amritha and Manu 2018), 3-nitroaniline (Amritha and Manu 2018), fluoroquinolone antibiotics (Kamagate et al. 2018), acid red 17 (Khataee et al. 2016), acetaminophen (Koottatep et al. 2017), sodium azide (Khataee and Pakdehi 2014), and methylene blue (Kpinsoton et al. 2018).

The dye degradation efficiency of laterite is quite higher in the presence of ultraviolet irradiation (photo-Fenton process) than in heterogeneous Fenton process (Khataee et al. 2016). After 120 min of reaction, the photo-Fenton process with 2 g/L laterite as the iron source was able to remove 94.7% of acid red 17 dye from its initial concentration of 20 mg/L. Meanwhile, the Fenton process can remove 49% of the dye with similar experimental conditions. Based on the experiments, radical generation and pollutant removal mechanisms within the sight of laterite catalyst were proposed by Khataee and Pakdehi (2014) as given below in Eqs. (14.4), (14.5), (14.6), (14.7), (14.8), (14.9).

$$\mathrm{S-Fe^{3+}+H_2O_2\rightarrow S-Fe-OOH^{2+}+H^+_{ads}} \tag{14.4}$$

$$\mathrm{S-Fe-OOH^{2+}\rightarrow S-Fe^{2+}+HO_2^*+H^+_{ads}} \tag{14.5}$$

$$\mathrm{S-Fe^{2+}+H_2O_2\rightarrow S-Fe^{3+}+HO^-+{}^*_{\cdot}OH_{ads}} \tag{14.6}$$

$$\mathrm{S-Fe^{2+}+{}^*_{\cdot}OH\rightarrow S-Fe^{3+}+HO^-_{ads}} \tag{14.7}$$

$$\mathrm{S-Fe^{3+}+H_2O^*\rightarrow S-Fe^{2+}+O_2+H^+_{ads}} \tag{14.8}$$

$$\mathrm{S-Fe^{2+}+HO_2^*\rightarrow S-Fe^{3+}+HOO^-_{ads}} \tag{14.9}$$

Laterite is indicated by S-Fe^{3+} in the above reactions.

Coupled heterogeneous Fenton process and constructed wetland are found effective for the degradation of micropollutants from real wastewater (Koottatep et al. 2017). The effectiveness of the combined process was tested by the authors for the treatment of hospital wastewater, containing 2.3 μg/L acetaminophen along with 446 mg/L of suspended solids, 506 mg/L of chemical oxygen demand, 24.5 mg/L ammoniacal nitrogen, and 13.8 mg/L phosphorus at pH 7.4. They have used laterite soil as construction wetland media. The amount of acetaminophen uptake in the plant was limited to 0.04–1.35%, while hydrogen peroxide was released with the uptake of micropollutant. This exogenous hydrogen peroxide release in the rhizosphere was found maximum at 12 days and resulted in Fenton reactions in the presence of laterite soil. The authors observed a decrease in hydrogen peroxide concentration with time and are credited to the utilization of hydrogen peroxide in Fenton reactions. Thus, about 35.34% of acetaminophen was removed with the action of hydroxyl radicals. A total of 60–64% of acetaminophen removal was occurred in the combined process, and it is also due to adsorption, microbial degradation, and byproduct transformation other than the plant uptake and Fenton reactions.

Reusability of the catalyst is a significant factor which should be considered for the real-field implementation of the heterogeneous Fenton process. Laterite is found highly reusable as reported by Khataee and Pakdehi (2014) and Kamagate et al. (2018). Fluoroquinolone antibiotics removal efficacy of the heterogeneous photo-Fenton process was 94% and 70%, respectively, at pH 3 and 6.5. A slight reduction in efficiency was observed after the first recycling. The efficacy of the photo-Fenton process to mineralize fluoroquinolone antibiotics was found 72% and 50% at pH 3 and 6.5, respectively. This efficiency remains the same after five cycles. Very low iron release from laterite was observed by Kamagate et al. (2018). This is also an important characteristic of a reusable heterogeneous catalyst.

Calcination is an option to improve the catalytic activity of every solid catalyst. Kpinsoton and co-workers (Kpinsoton et al. 2018) tested the changes in morphology and the catalytic activity of laterite with calcination. The authors did the calcination at 400, 600, and 800°C and tested its performance for the Fenton oxidation of methylene blue. Hematite and goethite are the chief iron oxides present in the laterite and are embedded in kaolinite and quartz frameworks. Calcination at 400°C resulted in the shrinkage in surface area of laterite significantly due to the transformation of goethite (which was previously associated with kaolinite) to hematite crystals. Further calcination process at 600 C resulted in the formation of "amorphous meta kaolin matrix containing mainly surface defectively crystalized hematite nanophases" (Kpinsoton et al. 2018). This calcined laterite exhibits highest Fenton catalytic activity with 99% of methylene blue removal after 100 min of reaction.

Synthesis of iron nanoparticles from laterite and its utilization in the heterogeneous Fenton process is an interesting area, recently proposed by Prof. Manu and his groups (Sangami and Manu 2019). The researchers prepared iron nanoparticles using laterite and *Tectona Grandis* extract and used it for the degradation of herbicide mixture (Sangami and Manu 2019). The mixture contains 3.5 mg/L ametryn, 94 mg/L dicamba, and 25 mg/L 2,4-D, and the authors found complete mineralization of the herbicide mixture within 135 min of heterogeneous Fenton oxidation with 430 mg/L of hydrogen peroxide and 25.29 mg/L of catalyst at pH 5. In similar way, iron nanoparticles prepared from laterite soil and eucalyptus leaves extract are able to remove ametryn completely from water medium (Sangami and Manu 2019).

14.3.2 Clay

The usage of clay minerals as heterogeneous Fenton catalyst is a highly attractive method, as it can exhibit higher catalytic property for the Fenton oxidation of organic compounds. Clay minerals are low-cost promising materials for the fabrication of reinforced catalysts with a high possibility of recovering the catalyst after the treatment. Even though clay minerals contain iron and other cations, the low concentration of iron in it can affect the heterogeneous Fenton degradation efficiency. The incorporation of iron into clays through pillaring and impregnation seems to be a potential alternative for the preparation of heterogeneous catalyst (Herney-Ramirez et al. 2010). It improved the catalytic properties of the clay mineral, and the catalyst can be reused for several degradation cycles. Also, the acid treatment of clay structures can eliminate the impurities present in its structure and increase the surface area of the clay minerals (Ayodele 2013). The stability and reusable potential of the prepared catalyst have a significant impact on the Fenton process efficiency. Among the different clay minerals, montmorillonite, bentonite, kaolinite, laponite, etc. are most commonly used as a heterogeneous Fenton catalyst.

Bentonite is a highly colloidal natural clay mineral belonging to the class of smectites and is normally formed through volcanic ash weathering in the presence of water (Gao et al. 2016; Nidheesh 2015). These clay minerals are smaller in size with higher surface area and stability (Ma et al. 2018). A study conducted by Feng et al. (2005) explored the degradation efficiency of bentonite clay-based iron nanocomposite coated on the inner wall of photo-reactor and with suspended nanocomposite catalyst for discoloration of orange II. Even though a decreased decoloration rate was observed for the film catalyst because of a decreased specific area, multiple experimental runs revealed that the coated catalyst has more stability and diminished iron leaching than the suspended nanocomposite catalyst. In another study, innovative photo-Fenton catalysts were prepared by arresting iron species on bentonite plates by two distinct techniques and utilized for the degradation of resorcinol (González-Bahamón et al. 2011). They have observed that the catalyst prepared by forced hydrolysis of ferric nitrate on the bentonite plate shown an enhanced activity due to an increased surface and high reusability potential. Iron-supported bentonite prepared by Gao et al. (2015) had shown a substantial increase in the specific surface area of the catalyst and improved the adsorption performance of the catalyst. Rhodamine B was completely removed due to the combined effects of adsorption and degradation under visible light-emitting diode lamps at natural pH 4.2, 0.25 g L^{-1} and 12 mM H_2O_2 concentration.

The synthetic clay mineral Laponite, made-up from natural inorganic mineral sources, has received significant importance as a Fenton catalyst due to its unique physical properties. As heterogeneous catalyst, laponite clay-based Fe nanocomposite was studied for the discoloration and mineralization of reactive red dye in the presence of hydrogen peroxide and ultraviolet light (Feng et al. 2003). The higher surface area and total pore volume of the catalyst resulted in complete discoloration of the compound at an optimal condition of 500 mg/L H_2O_2, 1.0 g of

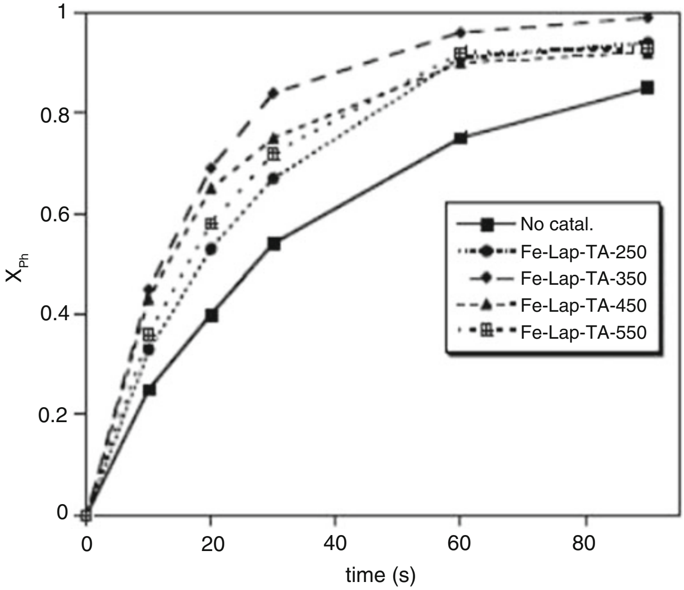


Fig. 14.1 Effect of Calcination temperature during the preparation Fe–laponite catalysts for phenol conversion. Note that the catalyst prepared by thermal treatment at a calcination temperature of 350°C given the excellent catalytic performance in the photo-Fenton removal of phenol (H_2O_2 = 50 mmol L^{-1}, pH = 3; T = 30 °C, 40 W UV-A lamp). (Adapted from (Iurascu et al. 2009) with permission. Copyright © 2008 Elsevier Ltd.)

laponite clay-based Fe nanocomposite/L, and pH 3. In a parallel study by Feng et al. (2003) with the same catalyst and operating conditions, a slower kinetic rate was observed for photo-assisted degradation of orange II. The presence of Fe ions in the clay mineral and amount of adsorbed dyes on the surface of the catalyst governs the degradation rate. Further, a detailed investigation was conducted by Sum et al. (2004) for the synthesis of laponite clay-based Fe nanocatalyst by studying the effect of thermal ageing and calcination temperature on the crystal structure and chemical compositions of the catalyst. Entire mineralization of the model pollutant acid black was observed due to higher photocatalytic property and insignificant Fe leaching of the laponite clay-based Fe nanocatalyst. In addition to that, Iurascu et al. (2009) observed that calcination temperature during the preparation catalyst has a substantial role in the catalytic activity of Fe-laponite catalysts as shown in Fig. 14.1. They have observed that the catalyst prepared by thermal treatment at a calcination temperature of 350°C given the excellent catalytic performance in the photo-Fenton removal of phenol.

Montmorillonite is a very soft phyllosilicate group of minerals with unique physicochemical properties possessing a negative charge (Nidheesh 2015; Zhang et al. 2011). An acid-modified montmorillonite clay containing a higher content of iron and higher oxidation potential in a heterogeneous Fenton system was successfully used by Deng et al. (2010) for the removal of acetaminophen. The degradation

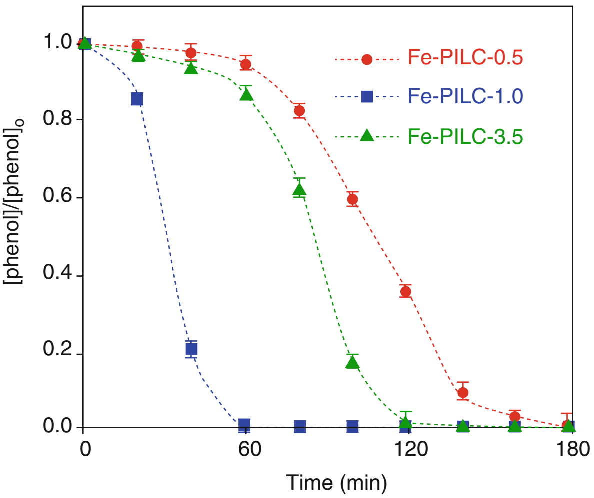


Fig. 14.2 Phenol degradation at different concentration of Fe with the trinuclear ferric–acetate complex at three different ratios of 0.5,1, and 3.5 mmol per gram of clay. (Adapted from De Leon et al. (De Leon et al. 2017) with permission. Copyright © 2017 Elsevier Ltd.)

process was primarily through the combined attack of phenoxy and superoxide radicals produced by the Fenton reaction mechanism. In a similar kind of study, aluminium-pillared montmorillonite clay blended with ferric oxalate has also shown higher stability and resistance to iron leaching during the photo-Fenton degradation of amoxicillin (Ayodele et al. 2012). Consistent performance on the catalytic activity was seen due to the increased availability of inner layer catalyst sites of the clay to reactant molecule due to aluminium pillaring. Iron-pillared montmorillonite clay of two aggregate sizes ranging below 250 μm and 250–450 μm were prepared at 400 and 600°C calcination temperature for the photo-Fenton discoloration of methylene blue aqueous solution (De Leon et al. 2013). Due to the higher surface area and pore volume, the catalyst prepared at 400°C had shown higher catalytic activity. In another study conducted by De León et al. (2017), montmorillonite was modified with the trinuclear ferric–acetate complex at three different ratios of 0.5,1, and 3.5 mmol per gram of clay, and the observed phenol degradation was shown in Fig. 14.2. The decline in degradation rate at higher iron content is due to the accumulation of maghemite nanoparticles on the surface of the catalyst which hinders the accessibility to the microporous structure of the catalyst where iron oxides are present. A hybrid heterogeneous catalyst was prepared by Barreca et al. (2014) which is rich in ferrous and was supported on montmorillonite/alginate beads for the photo-assisted Fenton degradation of 4-nitrophenol. They have concluded that even though the catalyst showed higher stability, the catalyst dosage and hydrogen peroxide concentration should be carefully selected to prevent excessive iron leaching. A highly stable visible light-responsive heterogeneous catalyst, glutamic acid-iron chelate, interpolated into montmorillonite clay was prepared by Huang et al. (2016) for the removal of reactive blue 19. Enhanced degradation of dye was observed due to the synergistic effect of chelation and the noticeable light sensitivity of glutamic acid under different pH conditions. Lanthanum–iron montmorillonite heterogeneous ion catalyst synthesized by precipitation method was also used for the removal of rhodamine B and methylene blue.

Vermiculite is an economical and commonly available clay mineral which consists of a sandwich arrangement of octahedral alumina or magnesia in the middle of two tetrahedral silicate sheets (Chen et al. 2010). Due to its layered structure and iron species being covalently bound to these clay layers, the leaching of iron species will be minimum (Barabaszová and Valášková 2013; Purceno et al. 2012). Iron-pillared vermiculite prepared by replacing the interlayer cations of the clay with iron ions in the interlayer spaces and free iron ions on its surface effectively decolorized azo dye reactive brilliant orange X-GN (Chen et al. 2010). The heterogeneous photo-Fenton catalyst enhanced the color removal by producing more hydroxyl radicals to attack the chromophoric group of pollutant and have shown longer stability resulting in more than 90% decolorization for three successive reuses studies. In another study, a heterogeneous Fenton catalyst montmorillonite K10 containing ferric oxide was used by Daud et al. (2010) for the discolorization of acid red 1, and the effects of different parameters affecting was studied. They have observed that the decolorization of dye occurs due to the catalytic reaction between the ferric ions and hydrogen peroxide and observed a maximum removal of 99% at 0.14 wt.% iron-montmorillonite K10, 5.0 g L^{-1} catalyst dosage, and 16 mM of H_2O_2 at 50 mg L^{-1} initial acid red dye concentration.

Kaolinite is a layered clay mineral consisting of one tetrahedral sheet connected through an oxygen atom with a central alumina octahedral sheet. They are rich in oxides of aluminium and silica created from the chemical weathering of rocks in the hot and wet atmosphere (Ayodele 2013). Ayodele (2013) observed that phosphoric acid treatment on kaolinite clay gave a satisfactory and suitable anchoring of iron metals because of the introduction of a monolayer of phosphate functional groups on the surface of the catalyst. In another study, Ayodele and Hameed (2013) reported that incorporating iron ions on phosphoric acid-treated kaolinite clay resulted in a larger surface area to produce sufficient hydroxyl radicals during the photo-Fenton degradation of nitrophenol. The formation of monolayer phosphate functional groups increased the negatively charged active sites on the catalysts and resulted in degradation of nitrophenol without pH adjustments. Apart from this, Guo et al. (2014) synthesized a Fe_2O_3–kaolin heterogeneous catalyst for the degradation of rhodamine B through photo-Fenton under visible light irradiation. The possible degradation mechanism occurred by the cyclic formation of ferric/ferrous ions in the system where the ferric ions get photoreduced to ferrous on the catalyst surface and to generate hydroxyl radicals while reacting with hydrogen peroxide and get oxidized into ferric ion.

Sepiolite is a microfibrous clay mineral with its basic structural units consisting of silicon–oxygen tetrahedra and magnesium–oxygen octahedra bonds (Gao et al. 2013). These clay minerals possess a high adsorbing capacity and larger surface area, due to the block and tunnel structure of the mineral, which could reduce the leaching of iron ions during the degradation reaction (Su et al. 2016). A heterogeneous catalyst poly-hydroxyl-iron/sepiolite fabricated through an impregnation method was used for the visible light irradiated photo-Fenton-like removal of

Table 14.1 Clay minerals pillared with metal ions

Clay	Pillared material	Experimental Observations	References
Montmorillonite	Mesoporous iron modified Al_2O_3 nanoparticles pillared	100% degradation of organic dyes, such as acid blue and reactive blue	Pradhan et al. (2013)
Kaolinite	Nano zero valent iron	88% degradation of direct black G at 0.6 g L^{-1} of catalyst, 33 mM H_2O_2, 100 mg L^{-1} initial dye concentration, and pH of 7.06	Liu et al. (2014)
Sepiolite	Iron and manganese	91.98% degradation of reactive brilliant blue at pH 2.5, catalyst dose 0.4 g, 0.3 mL H_2O_2 within 60 min	Su et al. (2016)
Bentonite	Iron and cerium pillared	98.13% degradation of tetracycline at initial pH 3, 0.5 gL^{-1} catalyst dose, 15 mmol L^{-1} H_2O_2 under UV irradiation for 60 min	Zhang et al. (2014)
Montmorillonite	Magnetite/Fe-Al	Complete conversion of phenol within 80 a slow induction reaction followed by an accelerated decomposition with increase in Fe in the solution	Wei et al. (2017)

organic pollutants rhodamine B and 4-nitrophenol (Gao et al. 2013). The degradation of pollutants was primarily through hydroxyl radical attack which was formed during the reaction of reduced ferrous ions on the catalyst surface of the clay and hydrogen peroxide in the solution. Apart from the abovementioned studies, few naturally available clay minerals are also used as heterogeneous catalyst. Bel Hadjltaief et al. (2014) prepared a novel heterogeneous catalyst by incorporating iron species on the surface of natural Tunisian clay. The Fe-clay plate heterogeneous catalyst showed a higher catalytic activity by attaining 100% removal of phenol in 60 mins with negligible loss in their activity at the end of five successive reaction cycles under ultraviolet irradiation. Iron-impregnated pillared saponite clay was used as a heterogeneous catalyst for Fenton by Herney-Ramirez et al. (2008) for the degradation of orange II dye. They have observed that catalyst concentration and temperature have a momentous influence on the dye oxidation process. Clay minerals pillared with few metal ions and used in the heterogeneous Fenton process are shown in Table 14.1.

14.3.3 Volcanic Soil

Volcanic soils are formed due to volcanic action and are a natural source of iron oxides. These soils are generally known as andisols and "dominated by amorphous aluminium silicates and/or Alorganic matter complexes" (van Breemen and Buurman 1998). Magnetite, maghemite, goethite, and hematite are the main iron oxides present in andisols (Pizarro et al. 2018). These oxides are found effective

Table 14.2 Chemical composition (data expressed in mass % of the corresponding element, on an oxide basis) for the whole soil and sand (including its magnetic extract) and clay fractions from the Collipulli and Metrenco soil samples. Taken from Aravena et al. (Aravena et al., 2010) with permission. Copyright © 2009, Springer Science Business Media B.V

Sample	Fraction	Fe_2O_3	Si_2O	Al_2O_3	TiO_2	MnO_2
Metrenco	Soil	12.5	42.9	10.4	1.8	nd
	Sand	16.9	51.9	19.0	2.4	nd
	Clay	11.9	56.9	10.0	1.7	nd
	Magnetic portion from sand	57.0	nd	nd	3.1	1.6
Collipulli	Soil	17.8	39.8	23.2	2.3	0.4
	Sand	14.6	43.2	23.1	2.0	0.3
	Clay	15.8	32.5	30.2	1.2	0.2
	Magnetic portion from sand	56.7	nd	nd	3.6	1.5

nd not determined

heterogeneous Fenton catalyst. For example, magnetite is found effective for the degradation of dye (Nidheesh et al. 2014), p-nitrophenol (Sun and Lemley 2011), phenol (Chun et al. 2012), bisphenol A (Cleveland et al. 2014), carbamazepine (Sun et al. 2013), and ibuprofen (Sun et al. 2013). Volcanic ultisols are found as effective heterogeneous Fenton catalysts (Aravena et al. 2010). The authors (Aravena et al. 2010) collected soil samples from Collipulli and Metrenco located in southern Chile and checked the hydrogen peroxide degradation rate. The soils are rich in iron oxides and other minerals as given in Table 14.2.

Hydrogen peroxide decomposition efficiency of sand and magnetic portions of ultisols collected from Collipulli was found the same but is more efficient than that collected from Metrenco. Collipulli sand is eight times more efficient than Metrenco sand, whereas hydrogen peroxide degradation rate in the presence of Collipulli ultisol magnetic portion is six times higher than Metrenco ultisol magnetic portions. Iron content in both ultisols is similar. The higher efficiency of ultisols collected from Collipulli may be a result of the presence and higher concentration of manganese and titanium. Manganese and titanium will undergo Fenton-like reactions and are efficient to decompose H_2O_2 (George et al. 2014; Nidheesh and Gandhimathi 2014). The same is confirmed by the authors (Aravena et al. 2010).

Effectiveness of heterogeneous Fenton catalyst is directly proportional to the iron content. This is effectively demonstrated by Matta et al. (Matta et al. 2008) for the degradation of 2,4,6-trinitrotoluene by hydrogen peroxide activated with different minerals containing iron. 2,4,6-trinitrotoluene degradation of pyrite, green rust, magnetite, and goethite has followed the first-order kinetics of $3.75\text{x}10^{-4}$ L m^{-2} min^{-1} > $2.55 \text{ x } 10^{-4}$ L m^{-2} min^{-1} > $1 \text{ x } 10^{-4}$ L m^{-2} min^{-1} > $1 \text{ x } 10^{-6}$ L m^{-2} min^{-1}, respectively (Matta et al. 2008). Lesser iron dissolution rate or lesser exposure of iron to hydrogen peroxide is one of the reasons behind the lower efficiency of these catalysts (Nidheesh 2015; Nidheesh et al. 2018a, b). Chemical treatment to the iron-bearing minerals is an option to avoid low hydrogen peroxide activation and lesser pollutant degradation rate in the heterogeneous Fenton process.

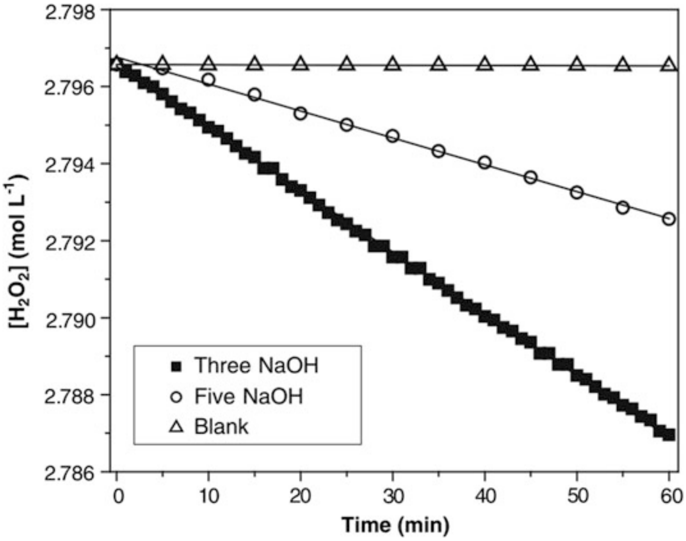


Fig. 14.3 Rate of hydrogen peroxide decomposition with alkali treatment to ultisols. Higher iron content in the soil resulted in more decomposition of hydrogen peroxide when compared to raw soil. (Taken from Manzo et al. (Manzo et al., 2011) with permission. Copyright © 2011, Springer Science Business Media B.V)

To improve the efficiency of ultisols, Manzo and co-workers (Manzo et al. 2011) treat ultisols with sodium hydroxide of 5 mol L^{-1}. Iron oxide concentration in the raw ultisols was 12.2 ± 0.3%. Alkali treatment of this soil three times increases the iron oxide content to 23.3 ± 0.7%. A similar type of treatment was carried out for the soil of size fraction <53 μm. Three and five times alkali treatment of the soil resulted in iron oxide concentration as 25.1 ± 0.2 and 23.3 ± 0.2, respectively. This improved iron content with alkali treatment resulted in higher hydrogen decomposition rate (Fig. 14.3). Raw soil was not able to decompose hydrogen peroxide. At the same time, hydrogen peroxide degradation rate constants for three and five times alkali-treated soils were found as $16.0 \pm 0.8 \times 10^{-5}$ mol L^{-1} min^{-1} and $7.1 \pm 0.7 \times 10^{-5}$ mol L^{-1} min^{-1}, respectively (Manzo et al. 2011).

14.4 Conclusions

The soil used as a heterogeneous catalyst for Fenton oxidation has gained significant attention for the treatment of organic compounds. Among different soil classifications, laterite, clay, and volcanic soils are commonly used as iron source in the Fenton process. Laterite soil is abundant in the earth crust and can be employed as a heterogeneous Fenton catalyst, as it is rich in iron oxides and other minerals. Clay minerals are highly stable and can exhibit higher photocatalytic activity for the

Fenton oxidation of organic pollutants. The incorporation of iron into clays through pillaring and impregnation improved the catalytic properties of clay. Volcanic soils formed due to volcanic action dominated by amorphous aluminium silicates and/or Al organic matters are also found effective heterogeneous Fenton catalyst. These catalysts were highly stable and exhibited less leaching and higher reuse potentials. Considering the catalytic properties and lower cost of soils, more research should be focused to improve the catalytic performance and post-recovery of catalysts. Research should also focus on increasing the surface area of the catalyst.

References

Amritha AS, Manu B (2018) Degradation of nitroaromatic compounds: a novel approach using iron from laterite soil. Appl Water Sci 8:1–4. https://doi.org/10.1007/s13201-018-0778-7

Aravena S, Pizarro C, Rubio MA, Cavalcante LCD, Garg VK, Pereira MC, Fabris JD (2010) Magnetic minerals from volcanic Ultisols as heterogeneous Fenton catalysts. Hyperfine Interact 195:35–41. https://doi.org/10.1007/s10751-009-0098-2

Ayodele OB (2013) Effect of phosphoric acid treatment on kaolinite supported ferrioxalate catalyst for the degradation of amoxicillin in batch photo-Fenton process. Appl Clay Sci 72:74–83. https://doi.org/10.1016/j.clay.2013.01.004

Ayodele OB, Hameed BH (2013) Development of kaolinite supported ferric oxalate heterogeneous catalyst for degradation of 4-nitrophenol in photo-Fenton process. Appl Clay Sci 83–84:171–181. https://doi.org/10.1016/j.clay.2013.08.019

Ayodele OB, Lim JK, Hameed BH (2012) Pillared montmorillonite supported ferric oxalate as heterogeneous photo-Fenton catalyst for degradation of amoxicillin. Appl Catal A Gen 413–414:301–309. https://doi.org/10.1016/j.apcata.2011.11.023

Baiju A, Gandhimathi R, Ramesh ST, Nidheesh PV (2018) Combined heterogeneous electro-Fenton and biological process for the treatment of stabilized landfill leachate. J Environ Manag 210:328–337. https://doi.org/10.1016/j.jenvman.2018.01.019

Bansal P, Verma A (2017) Synergistic effect of dual process (photocatalysis and photo-Fenton) for the degradation of cephalexin using TiO2 immobilized novel clay beads with waste fly ash/foundry sand. J Photochem Photobiol A Chem 342:131–142. https://doi.org/10.1016/j.jphotochem.2017.04.010

Barabaszová KČ, Valášková M (2013) Characterization of vermiculite particles after different milling techniques. Powder Technol 239:277–283. https://doi.org/10.1016/j.powtec.2013.01.053

Barreca S, Colmenares JJV, Pace A, Orecchio S, Pulgarin C (2014) Neutral solar photo-Fenton degradation of 4-nitrophenol on iron-enriched hybrid montmorillonite-alginate beads (Fe-MABs). J Photochem Photobiol A Chem 282:33–40. https://doi.org/10.1016/j.jphotochem.2014.02.008

Bel Hadjltaief H, Da Costa P, Beaunier P, Gálvez ME, Ben Zina M (2014) Fe-clay-plate as a heterogeneous catalyst in photo-Fenton oxidation of phenol as probe molecule for water treatment. Appl Clay Sci 91–92:46–54. https://doi.org/10.1016/j.clay.2014.01.020

Brillas E, Sirés I, Oturan MA (2009) Electro-Fenton process and related electrochemical technologies based on Fenton's reaction chemistry. Chem Rev 109:6570–6631. https://doi.org/10.1021/cr900136g

Cetinkaya S, Morcali H, Akarsu S, Ziba C, Dolaz M (2018) Comparison of classic Fenton with ultrasound Fenton processes on industrial textile wastewater. Sustain Environ Res J 28:165–170. https://doi.org/10.1016/j.serj.2018.02.001

Changotra R, Varshney L, Paul Guin J, Dhir A (2018) Performance of hematite particles as an Iron source for the degradation of ornidazole in photo-Fenton process. J Sol-Gel Sci Technol 85:203–212. https://doi.org/10.1007/s10971-017-4499-4

Changotra R, Rajput H, Dhir A (2019) Treatment of real pharmaceutical wastewater using combined approach of Fenton applications and aerobic biological treatment. J Photochem Photobiol A Chem 376:175–184. https://doi.org/10.1016/j.jphotochem.2019.02.029

Chen Q, Wu P, Dang Z, Zhu N, Li P, Wu J, Wang X (2010) Iron pillared vermiculite as a heterogeneous photo-Fenton catalyst for photocatalytic degradation of azo dye reactive brilliant orange X-GN. Sep Purif Technol 71:315–323. https://doi.org/10.1016/j.seppur.2009.12.017

Chun, J., Lee, H., Lee, S.-H., Hong, S.-W., Lee, Jaesang, Lee, C., Lee, Jinwoo, 2012. Magnetite/mesocellular carbon foam as a magnetically recoverable Fenton catalyst for removal of phenol and arsenic. Chemosphere 89, 1230–1237. doi:https://doi.org/10.1016/j.chemosphere.2012.07.046

Clarizia L, Russo D, Di Somma I, Marotta R, Andreozzi R (2017) Homogeneous photo-Fenton processes at near neutral pH: a review. Appl Catal B Environ 209:358–371. https://doi.org/10.1016/j.apcatb.2017.03.011

Cleveland V, Bingham J-P, Kan E (2014) Heterogeneous Fenton degradation of bisphenol a by carbon nanotube-supported Fe3O4. Sep Purif Technol 133:388–395. https://doi.org/10.1016/j.seppur.2014.06.061

Daud NK, Ahmad MA, Hameed BH (2010) Decolorization of acid red 1 dye solution by Fenton-like process using Fe-Montmorillonite K10 catalyst. Chem Eng J 165:111–116. https://doi.org/10.1016/j.cej.2010.08.072

David C, Arivazhagan M, Tuvakara F (2015) Decolorization of distillery spent wash effluent by electro oxidation (EC and EF) and Fenton processes: a comparative study. Ecotoxicol Environ Saf 121:142–148. https://doi.org/10.1016/j.ecoenv.2015.04.038

De Leon MA, Sergio M, Bussi J (2013) Iron-pillared clays as catalysts for dye removal by the heterogeneous photo-Fenton technique. React Kinet Mech Catal 110:101–117. https://doi.org/10.1007/s11144-013-0593-y

De León MA, Rodríguez M, Marchetti SG, Sapag K, Faccio R, Sergio M, Bussi J (2017) Raw montmorillonite modified with iron for photo-Fenton processes: influence of iron content on textural, structural and catalytic properties. J Environ Chem Eng 5:4742–4750. https://doi.org/10.1016/j.jece.2017.09.014

Deng C, Ren C, Wu F, Deng N, Glebov EM, Pozdnyakov IP, Plyusnin VF (2010) Montmorillonite KSF as catalyst for degradation of acetaminophen with heterogeneous Fenton reactions. React Kinet Mech Catal 100:277–288. https://doi.org/10.1007/s11144-010-0178-y

Devi LG, Srinivas M, ArunaKumari ML (2016) Heterogeneous advanced photo- Fenton process using peroxymonosulfate and peroxydisulfate in presence of zero valent metallic iron: a comparative study with hydrogen peroxide photo-Fenton process. J Water Process Eng 13:117–126. https://doi.org/10.1016/j.jwpe.2016.08.004

di Luca C, Ivorra F, Massa P, Fenoglio R (2015) Iron–alumina synergy in the heterogeneous Fenton-type peroxidation of phenol solutions. Chem Eng J 268:280–289. https://doi.org/10.1016/j.cej.2015.01.074

Feng J, Hu X, Yue PL, Zhu HY, Lu GQ (2003) Discoloration and mineralization of reactive red HE-3B by heterogeneous photo-Fenton reaction. Water Res 37:3776–3784. https://doi.org/10.1016/S0043-1354(03)00268-9

Feng J, Hu X, Yue PL (2005) Discoloration and mineralization of Orange II by using a bentonite clay-based Fe nanocomposite film as a heterogeneous photo-Fenton catalyst. Water Res 39:89–96. https://doi.org/10.1016/j.watres.2004.08.037

Gao Y, Gan H, Zhang G, Guo Y (2013) Visible light assisted Fenton-like degradation of rhodamine B and 4-nitrophenol solutions with a stable poly-hydroxyl-iron/sepiolite catalyst. Chem Eng J 217:221–230. https://doi.org/10.1016/j.cej.2012.11.115

Gao Y, Wang Y, Zhang H (2015) Removal of Rhodamine B with Fe-supported bentonite as heterogeneous photo-Fenton catalyst under visible irradiation. Appl Catal B Environ 178:29–36. https://doi.org/10.1016/j.apcatb.2014.11.005

Gao Y, Guo Y, Zhang H (2016) Iron modified bentonite: enhanced adsorption performance for organic pollutant and its regeneration by heterogeneous visible light photo-Fenton process at circumneutral pH. J Hazard Mater 302:105–113. https://doi.org/10.1016/j.jhazmat.2015.09.036

George SJ, Gandhimathi R, Nidheesh PV, Ramesh ST (2014) Electro-Fenton oxidation of salicylic acid from aqueous solution: batch studies and degradation pathway. Clean (Weinh) 42:1701–1711. https://doi.org/10.1002/clen.201300453

González-Bahamón LF, Hoyos DF, Benítez N, Pulgarín C (2011) New Fe-immobilized natural bentonite plate used as photo-Fenton catalyst for organic pollutant degradation. Chemosphere 82:1185–1189. https://doi.org/10.1016/j.chemosphere.2010.11.071

Gümüş D, Akbal F (2016) Comparison of Fenton and electro-Fenton processes for oxidation of phenol. Process Saf Environ Prot 103:252–258. https://doi.org/10.1016/j.psep.2016.07.008

Guo S, Zhang G, Wang J (2014) Photo-Fenton degradation of rhodamine B using Fe2O3-kaolin as heterogeneous catalyst: characterization, process optimization and mechanism. J Colloid Interface Sci 433:1–8. https://doi.org/10.1016/j.jcis.2014.07.017

Hammouda SB, Fourcade F, Assadi A, Soutrel I, Adhoum N, Amrane A, Monser L (2016) Effective heterogeneous electro-Fenton process for the degradation of a malodorous compound, indole, using iron loaded alginate beads as a reusable catalyst. Appl Catal B Environ 182:47–58. https://doi.org/10.1016/j.apcatb.2015.09.007

Hassan AK, Rahman MM, Chattopadhay G, Naidu R (2019) Kinetic of the degradation of sulfanilic acid azochromotrop (SPADNS) by Fenton process coupled with ultrasonic irradiation or L-cysteine acceleration. Environ Technol Innov 15:100380. https://doi.org/10.1016/j.eti.2019.100380

Herney-Ramirez J, Lampinen M, Vicente MA, Costa CA, Madeira LM (2008) Experimental design to optimize the oxidation of orange II dye solution using a clay-based Fenton-like catalyst. Ind Eng Chem Res 47:284–294. https://doi.org/10.1021/ie070990y

Herney-Ramirez J, Vicente MA, Madeira LM (2010) Heterogeneous photo-Fenton oxidation with pillared clay-based catalysts for wastewater treatment: a review. Appl Catal B Environ 98:10–26. https://doi.org/10.1016/j.apcatb.2010.05.004

Huang Z, Wu P, Gong B, Yang S, Li H, Zhu Z, Cui L (2016) Preservation of glutamic acid-iron chelate into montmorillonite to efficiently degrade reactive blue 19 in a Fenton system under sunlight irradiation at neutral pH. Appl Surf Sci 370:209–217. https://doi.org/10.1016/j.apsusc.2016.02.126

Huang C, Peng F, Guo H-J, Wang C, Luo M-T, Zhao C, Xiong L, Chen X-F, Chen X-D (2018) Efficient COD degradation of turpentine processing wastewater by combination of Fe-C micro-electrolysis and Fenton treatment: Long-term study and scale up. Chem Eng J 351:697–707. https://doi.org/10.1016/j.cej.2018.06.139

Iurascu B, Siminiceanu I, Vione D, Vicente MA, Gil A (2009) Phenol degradation in water through a heterogeneous photo-Fenton process catalyzed by Fe-treated laponite. Water Res 43:1313–1322. https://doi.org/10.1016/j.watres.2008.12.032

Jinisha R, Gandhimathi R, Ramesh ST, Nidheesh PV, Velmathi S (2018) Removal of rhodamine B dye from aqueous solution by electro-Fenton process using iron-doped mesoporous silica as a heterogeneous catalyst. Chemosphere 200. https://doi.org/10.1016/j.chemosphere.2018.02.117

Kamagate M, Assadi AA, Kone T et al (2018) Use of laterite as a sustainable catalyst for removal of fluoroquinolone antibiotics from contaminated water. Chemosphere 195:847–853. https://doi.org/10.1016/j.chemosphere.2017.12.165

Karale RS, Manu B, Shrihari S (2014) Fenton and Photo-fenton Oxidation Processes for Degradation of 3-Aminopyridine from Water. APCBEE Procedia 9:25–29. https://doi.org/10.1016/j.apcbee.2014.01.005

Khataee AR, Pakdehi SG (2014) Removal of sodium azide from aqueous solution by Fenton-like process using natural laterite as a heterogeneous catalyst: Kinetic modeling based on nonlinear regression analysis. J Taiwan Inst Chem Eng 45:2664–2672. https://doi.org/10.1016/j.jtice.2014.08.007

Khataee A, Gholami P, Vahid B (2016) Heterogeneous sono-Fenton-like process using nanostructured pyrite prepared by Ar glow discharge plasma for treatment of a textile dye. Ultrason Sonochem 29:213–225. https://doi.org/10.1016/j.ultsonch.2015.09.012

Koottatep T, Phong VHN, Chapagain SK et al (2017) Potential of Laterite Soil Coupling Fenton Reaction in Acetaminophen (ACT) Removal in Constructed Wetlands. Water Air Soil Pollut 228. https://doi.org/10.1007/s11270-017-3454-x

Kpinsoton GMR, Karoui H, Richardson Y et al (2018) New insight into the microstructure of natural calcined laterites and their performance as heterogeneous Fenton catalyst for methylene blue degradation. React Kinet Mech Catal 124:931–956. https://doi.org/10.1007/s11144-018-1406-0

Kumar A, Priyadarshinee R, Singha S, Dasgupta D, Mandal T (2016) Rice husk ash-based silica-supported iron catalyst coupled with Fenton-like process for the abatement of rice mill wastewater. Clean Techn Environ Policy 18:2565–2577. https://doi.org/10.1007/s10098-016-1165-4

Kurian M, Nair DS (2015) Heterogeneous Fenton behavior of nano nickel zinc ferrite catalysts in the degradation of 4-chlorophenol from water under neutral conditions. J Water Process Eng 8: e37–e49. https://doi.org/10.1016/j.jwpe.2014.10.011

Laiju AR, Sivasankar T, Nidheesh PV (2014) Iron-loaded mangosteen as a heterogeneous Fenton catalyst for the treatment of landfill leachate. Environ Sci Pollut Res 21:10900–10907. https://doi.org/10.1007/s11356-014-2883-y

Leifeld V, dos Santos TPM, Zelinski DW, Igarashi-Mafra L (2018) Ferrous ions reused as catalysts in Fenton-like reactions for remediation of agro-food industrial wastewater. J Environ Manag 222:284–292. https://doi.org/10.1016/j.jenvman.2018.05.087

Liu X, Wang F, Chen Z, Megharaj M, Naidu R (2014) Heterogeneous Fenton oxidation of direct black G in dye effluent using functional kaolin-supported nanoscale zero iron. Environ Sci Pollut Res 21:1936–1943. https://doi.org/10.1007/s11356-013-2099-6

Ma C, He Z, Jia S, Zhang X, Hou S (2018) Treatment of stabilized landfill leachate by Fenton-like process using Fe 3 O 4 particles decorated Zr-pillared bentonite. Ecotoxicol Environ Saf 161:489–496. https://doi.org/10.1016/j.ecoenv.2018.06.031

Malik SN, Ghosh PC, Vaidya AN, Mudliar SN (2018) Catalytic ozone pretreatment of complex textile effluent using Fe2+ and zero valent iron nanoparticles. J Hazard Mater 357:363–375. https://doi.org/10.1016/j.jhazmat.2018.05.070

Manzo V, Pizarro C, Rubio MA, Cavalcante LCD, Garg VK, Fabris JD (2011) Preparative treatment with NaOH to selectively concentrate iron oxides of a Chilean volcanic soil material to produce effective heterogeneous Fenton catalyst. Hyperfine Interact 203:59–66. https://doi.org/10.1007/s10751-011-0368-7

Matta R, Hanna K, Kone T, Chiron S (2008) Oxidation of 2,4,6-trinitrotoluene in the presence of different iron-bearing minerals at neutral pH. Chem Eng J 144:453–458. https://doi.org/10.1016/j.cej.2008.07.013

Meng X, Khoso SA, Wu J, Tian M, Kang J, Liu H, Zhang Q, Sun W, Hu Y (2019) Efficient COD reduction from sulfide minerals processing wastewater using Fenton process. Miner Eng 132:110–112. https://doi.org/10.1016/j.mineng.2018.11.054

Mirzaei A, Chen Z, Haghighat F, Yerushalmi L (2017) Removal of pharmaceuticals from water by homo/heterogonous Fenton-type processes – a review. Chemosphere 174:665–688. https://doi.org/10.1016/j.chemosphere.2017.02.019

Munoz M, de Pedro ZM, Casas JA, Rodriguez JJ (2015) Preparation of magnetite-based catalysts and their application in heterogeneous Fenton oxidation - a review. Appl Catal B Environ. https://doi.org/10.1016/j.apcatb.2015.04.003

Narayani H, Augustine R, Sumi S, Jose M, Deepa Nair K, Samsuddin M, Prakash H, Shukla S (2017) Removal of basic and industrial azo reactive dyes from aqueous solutions via Fenton-like reactions using catalytic non-magnetic Pd-flyash and magnetic Pd-Fe3O4-flyash composite particles. Sep Purif Technol 172:338–349. https://doi.org/10.1016/j.seppur.2016.08.027

Nidheesh PV (2015) Heterogeneous Fenton catalysts for the abatement of organic pollutants from aqueous solution: a review. RSC Adv 5:40552–40577. https://doi.org/10.1039/C5RA02023A

Nidheesh PV (2017) Graphene-based materials supported advanced oxidation processes for water and wastewater treatment: a review. Environ Sci Pollut Res 24:27047–27069. https://doi.org/10.1007/s11356-017-0481-5

Nidheesh PV, Gandhimathi R (2012) Trends in electro-Fenton process for water and wastewater treatment: an overview. Desalination 299:1–15. https://doi.org/10.1016/j.desal.2012.05.011

Nidheesh PV, Gandhimathi R (2014) Comparative removal of Rhodamine B from aqueous solution by electro-Fenton and electro-Fenton-like processes. Clean (Weinh) 42:779–784. https://doi.org/10.1002/clen.201300093

Nidheesh PV, Rajan R (2016) Removal of rhodamine B from a water medium using hydroxyl and sulphate radicals generated by iron loaded activated carbon. RSC Adv 6:5330–5340. https://doi.org/10.1039/C5RA19987E

Nidheesh PV, Gandhimathi R, Ramesh ST (2013) Degradation of dyes from aqueous solution by Fenton processes: a review. Environ Sci Pollut Res. https://doi.org/10.1007/s11356-012-1385-z

Nidheesh PV, Gandhimathi R, Velmathi S, Sanjini NS (2014) Magnetite as a heterogeneous electro Fenton catalyst for the removal of Rhodamine B from aqueous solution. RSC Adv 4:5698–5708. https://doi.org/10.1039/c3ra46969g

Nidheesh PV, Olvera-Vargas H, Oturan N, Oturan MA (2018a) In: Zhou M, Oturan MA, Sirés I (eds) Heterogeneous electro-Fenton process: principles and applications. Springer, Singapore, pp 85–110. https://doi.org/10.1007/698_2017_72Electro-Fenton Process: New Trends and Scale-Up

Nidheesh PV, Zhou M, Oturan MA (2018b) An overview on the removal of synthetic dyes from water by electrochemical advanced oxidation processes. Chemosphere 197:210–227. https://doi.org/10.1016/j.chemosphere.2017.12.195

Pizarro C, Escudey M, Gacitúa M, Fabris JD (2018) Iron-bearing minerals from soils developing on volcanic materials from southern Chile: application in heterogeneous catalysis. J Soil Sci Plant Nutr 18:0–0. https://doi.org/10.4067/s0718-95162018005002001

Pradhan AC, Varadwaj GBB, Parida KM (2013) Facile fabrication of mesoporous iron modified Al2O3 nanoparticles pillared montmorillonite nanocomposite: a smart photo-Fenton catalyst for quick removal of organic dyes. Dalton Trans 42:15139–15149. https://doi.org/10.1039/c3dt51952j

Purceno AD, Teixeira APC, Souza AB, Ardisson JD, de Mesquita JP, Lago RM (2012) Ground vermiculite as catalyst for the Fenton reaction. Appl Clay Sci 69:87–92. https://doi.org/10.1016/j.clay.2012.08.010

Rahim Pouran S, Abdul Aziz AR, Wan Daud WMA (2015) Review on the main advances in photo-Fenton oxidation system for recalcitrant wastewaters. J Ind Eng Chem 21:53–69. https://doi.org/10.1016/j.jiec.2014.05.005

Razaviarani V, Zazo JA, Casas JA, Jaffé PR (2019) Coupled Fenton-denitrification process for the removal of organic matter and total nitrogen from coke plant wastewater. Chemosphere 224:653–657. https://doi.org/10.1016/j.chemosphere.2019.02.178

Rubeena KK, Hari Prasad Reddy P, Laiju AR, Nidheesh PV (2018) Iron impregnated biochars as heterogeneous Fenton catalyst for the degradation of acid red 1 dye. J Environ Manag 226:320–328. https://doi.org/10.1016/j.jenvman.2018.08.055

Saini R, Raghunath CV, Pandey P, Kumar P (2016) Optimization of Fenton oxidation for the removal of methyl parathion in aqueous solution. Perspect Sci 8:670–672. https://doi.org/10.1016/j.pisc.2016.06.054

Sangami S, Manu B (2019) Catalytic efficiency of laterite-based FeNPs for the mineralization of mixture of herbicides in water. Environ Technol (United Kingdom) 40:2671–2683. https://doi.org/10.1080/09593330.2018.1449899

Sharma R, Singhal S (2018) Spinel ferrite mediated photo-Fenton degradation of phenolic analogues: a detailed study employing two distinct inorganic oxidants. Clean (Weinh) 46:1700605. https://doi.org/10.1002/clen.201700605

Sruthi T, Gandhimathi R, Ramesh ST, Nidheesh PV (2018) Stabilized landfill leachate treatment using heterogeneous Fenton and electro-Fenton processes. Chemosphere 210:38–43. https://doi.org/10.1016/j.chemosphere.2018.06.172

Su C, Li W, Liu X, Huang X, Yu X (2016) Fe-Mn-sepiolite as an effective heterogeneous Fenton-like catalyst for the decolorization of reactive brilliant blue. Front Environ Sci Eng 10:37–45. https://doi.org/10.1007/s11783-014-0729-y

Su C, Cao G, Lou S, Wang R, Yuan F, Yang L, Wang Q (2018) Treatment of cutting fluid waste using activated carbon Fiber supported Nanometer Iron as a heterogeneous Fenton catalyst. Sci Rep 8:10650. https://doi.org/10.1038/s41598-018-29014-4

Sum OSN, Feng J, Hu X, Yue PL (2004) Pillared laponite clay-based Fe nanocomposites as heterogeneous catalysts for photo-Fenton degradation of acid black. Chem Eng Sci 59:5269–5275. https://doi.org/10.1016/j.ces.2004.09.032

Sun S-P, Lemley AT (2011) P-Nitrophenol degradation by a heterogeneous Fenton-like reaction on nano-magnetite: process optimization, kinetics, and degradation pathways. J Mol Catal A Chem 349:71–79. https://doi.org/10.1016/j.molcata.2011.08.022

Sun S-P, Zeng X, Lemley AT (2013) Nano-magnetite catalyzed heterogeneous Fenton-like degradation of emerging contaminants carbamazepine and ibuprofen in aqueous suspensions and montmorillonite clay slurries at neutral pH. J Mol Catal A Chem 371:94–103. https://doi.org/10.1016/j.molcata.2013.01.027

Thirumoorthy K, Satishkumar G (2019) Enhanced stability of abundant amorphous Iron (III) oxide grafted AlSBA-15 as highly efficient heterogeneous Fenton catalyst for the destruction of phenol. ChemistrySelect 4:7388–7395. https://doi.org/10.1002/slct.201901510

van Breemen N, Buurman P (1998) Formation of Andisols. In: van Breemen N, Buurman P (eds) Soil formation. Springer, Dordrecht, pp 271–289. https://doi.org/10.1007/978-0-585-31788-5_12

Verma M, Haritash AK (2019) Degradation of amoxicillin by Fenton and Fenton-integrated hybrid oxidation processes. J Environ Chem Eng 7:102886. https://doi.org/10.1016/j.jece.2019.102886

Wang Y, Gao Y, Chen L, Zhang H (2015) Goethite as an efficient heterogeneous Fenton catalyst for the degradation of methyl orange. Catal Today 252:107–112. https://doi.org/10.1016/j.cattod.2015.01.012

Wei X, Wu H, Sun F (2017) Magnetite/Fe-Al-montmorillonite as a Fenton catalyst with efficient degradation of phenol. J Colloid Interface Sci 504:611–619. https://doi.org/10.1016/j.jcis.2017.05.110

Xavier S, Gandhimathi R, Nidheesh PV, Ramesh ST (2015) Comparison of homogeneous and heterogeneous Fenton processes for the removal of reactive dye Magenta MB from aqueous solution. Desalin Water Treat 53:109–118. https://doi.org/10.1080/19443994.2013.844083

Xavier S, Gandhimathi R, Nidheesh PV, Ramesh ST (2016) Comparative removal of Magenta MB from aqueous solution by homogeneous and heterogeneous photo-Fenton processes. Desalin Water Treat 57:12832–12841. https://doi.org/10.1080/19443994.2015.1054887

Xu D, Zhang Y, Cheng F, Dai P (2016) Efficient removal of dye from an aqueous phase using activated carbon supported ferrihydrite as heterogeneous Fenton-like catalyst under assistance of microwave irradiation. J Taiwan Inst Chem Eng 60:376–382. https://doi.org/10.1016/j.jtice.2015.10.036

Yang L, Sheng M, Zhao H, Qian M, Chen X, Zhuo Y, Cao G (2019) Treatment of triethyl phosphate wastewater by Fenton oxidation and aerobic biodegradation. Sci Total Environ 678:821–829. https://doi.org/10.1016/j.scitotenv.2019.05.020

Zhang S, Liang S, Wang X, Long J, Li Z, Wu L (2011) Trinuclear iron cluster intercalated montmorillonite catalyst: microstructure and photo-Fenton performance. Catal Today 175:362–369. https://doi.org/10.1016/j.cattod.2011.02.054

Zhang YP, Jia CG, Peng R, Ma F, Ou GN (2014) Heterogeneous photo-assisted Fenton catalytic removal of tetracycline using Fe-Ce pillared bentonite. J Cent South Univ 21:310–316. https://doi.org/10.1007/s11771-014-1942-3

Chapter 15
Analytical Methods for Phthalates in Water Samples

Chengjun Sun, Rui Sun, Xin Wu, Shuo Yin, Yongxin Li, and Danni Yang

Contents

Abstract Phthalates or phthalate esters, formed from phthalic acids and the alcohols with 1–14 carbon atoms, are extensively used as additives in the production of plastics and related products, such as packaging materials, toys, medical blood bags, hoses, floors, wallpapers, detergents, lubricants, and personal care products. Without

---

C. Sun (✉) · Y. Li
West China School of Public Health and West China Fourth Hospital, Sichuan University, Chengdu, China

Provincial Key Lab for Food Safety Monitoring and Risk Assessment of Sichuan, Chengdu, China
e-mail: sunchj@scu.edu.cn

R. Sun · S. Yin · D. Yang
West China School of Public Health and West China Fourth Hospital, Sichuan University, Chengdu, China

X. Wu
Jiangxi Institute for Food Control, Nanchang, China

Inamuddin et al. (eds.), *Water Pollution and Remediation: Organic Pollutants*, Environmental Chemistry for a Sustainable World 54,
https://doi.org/10.1007/978-3-030-52395-4_15

stable chemical bonds to polymer, they can migrate easily from these products into the environment and pollute food, water, and air. Through drinking, digestion, and inhalation, the phthalates in the environment can easily enter into the human body and bioaccumulate in the adipose tissue. The rivers, lakes, seas, even drinking water, and rainwater around the world have been detected with phthalates. The epidemiological and laboratory evidence has shown their adverse effects on human health which leads to widespread concern all over the world. There have been numerous reports on their analytical methods in water samples in the past decade, which is beneficial to the accurate evaluation of their potential risk to human health, and their pollution trend predication and remediation effect assessment. The sample treatment methods of phthalates in water samples mainly include liquid-liquid extraction, liquid-liquid microextraction, solid-phase extraction, solid-phase microextraction, and their derivative techniques. The separation and detection methods are mainly gas chromatography with flame ionization detection or mass spectrometric detection, high-performance liquid chromatography with ultraviolet detection or mass spectrometric detection. Owing to the ubiquity of phthalates in the environment, strict prevention measures should be taken during the analysis of phthalates.

In the future, except for the development of novel adsorption materials for extraction of trace phthalates in water, the application of carbon nanotubes, magnetic carbon nanotubes, graphene oxide, electrospun nanofibers will be further exploited. In addition to the highly sensitive gas and liquid chromatography coupled with a high-resolution mass spectrometer, it is also necessary to develop new analytical techniques that are capable of on-line or on-site detection, such as miscellaneous biosensors, micro-total analysis system, surface-enhanced Raman scattering system, and surface plasmon resonance system.

Keywords Phthalates · Water · Sample treatment · Analytical method

15.1 Introduction

Phthalates, also known as phthalate esters, generally refers to the esters formed from phthalic acids and the alcohols with 1 to 14 carbon atoms. Since the 1920s, they have been produced and added in plastics such as polyvinyl chloride, polyethylene terephthalate, polyvinyl acetates and polyethylene to enhance the suppleness, flexibility and longevity of the plastics. Approximately 8.4 million tonnes of phthalates were produced globally each year, and China was the single-largest plasticizer market in the world, accounting for nearly 42% of world consumption in 2017. (https://ihsmarkit.com/products/plasticizers-chemical-economics-handbook.html). Except for the production of plastics and the related products such as food packaging materials, medical blood bags, toys, hoses, floors, wallpapers, phthalates are also used for production of detergents, lubricants and personal care products such as nail polish, hair spray, soap and shampoo. Phthalates can be subdivided as high and low molecular weight phthalates, depending on their molecular weight. High molecular weight phthalates include those with 7 or more carbon atoms in their chemical backbone, giving them increased permanency and durability. The most common high molecular weight phthalates are di(2-ethylhexyl) phthalate and dioctyl phthalate. Low molecular weight phthalates include those with less than 7 carbon atoms in their chemical backbone. The most common low molecular weight phthalates include dimethyl phthalate and diethyl phthalate.

15.1.1 The Toxicity and the Physicochemical Properties of Phthalates

Without stable chemical bonds to polymer, the phthalates in flexible plastics can be released easily and migrate into the environment. Through drinking water, digestion of food and inhalation of air, the phthalates in the environment can easily enter into the human body and then bioaccumulate in fat tissues, because they are lipophilic chemicals.

Many epidemiological and laboratory evidences have shown that phthalates are toxic, especially to the reproductive and endocrine systems, which can lead to fetal malformations and abnormal growth, as well as the maldevelopment of children (Li et al. 2019; Rashad et al. 2018; Gao et al. 2017; Keresztes et al. 2013).

Herreros et al. (2013) found that di(2-ethylhexyl) phthalate interfered with the estrogen level. The blood estrogen level of the sheep exposed to di(2-ethylhexyl) phthalate was significantly higher than that of the control group, and the blood progesterone concentration was also significantly increased from the second day of the luteal cycle. Swan et al. (2005) found that fetal phthalate exposure could reduce the anogenital distance in male infants and affect their development of the reproductive system. These findings supported the hypothesis that exposure to phthalates at fetal environmental levels could adversely affect male reproductive development. Studies by Parks et al. (2000) have indicated that di(2-ethylhexyl) phthalate has an antiandrogen effect, and it could reduce the testosterone level of male fetal mice in the critical period of reproductive system differentiation to the female level. Ferguson et al. (2014) found that spontaneous abortion was strongly correlated with the concentration of phthalate metabolites in the urine of pregnant women in the third trimester of pregnancy. In addition, the carcinogenicity of phthalates was studied by the National Toxicology Agency (National Toxicology Program, NTP) in 1982 (Chen and Ni 2010). The results showed that long-term absorption of phthalates for rats and mice could lead to their liver cancer. The mutagenicity and neurotoxicity of phthalates and their association with obesity in adults (Stahlhut et al. 2007), asthma, and allergic symptoms in children (Bornehag et al. 2004) have also been reported. Yang et al. (2008) confirmed the adjuvant effect of di(2-ethylhexyl) phthalate in mice immunized with ovalbumin. The dose of di(2-ethylhexyl)

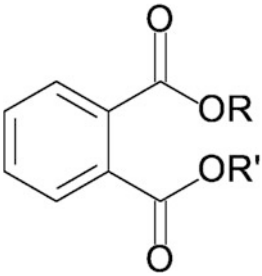


Fig. 15.1 The general chemical structure of phthalates. R and R’ in the structure is an alkyl or an aryl group

phthalate exposure was positively correlated with airway hyperresponsiveness, airway remodeling, and eosinophil infiltration in mice, suggesting that phthalates may be related to asthma. Wang (2002) studied the mutagenicity of di(2-ethylhexyl) phthalate by Ames test, micronucleus test of mouse bone marrow polychromatic erythrocytes, and chromosome aberration test in mouse bone marrow cells. The results showed that di(2-ethylhexyl) phthalate had micronucleus and chromosome effects. Zhu et al. (2006) found that dibutyl phthalate exposure had a significant inhibitory effect on the proliferation of nerve cell line PC12 cells and had a toxic effect mainly on apoptosis under the condition of low dose chronic exposure.

At room temperature, the majority of phthalates are colorless oily liquids with distinctive odors. Their boiling points vary greatly within the range of 190–530 °C with the melting points below 10 °C. But some of them have higher melting points, like dibenzyl phthalate (+40–42 °C), dicyclohexyl phthalate (+63–67 °C), dimethyl terephthalate (+141 °C), and diphenyl phthalate (+73 °C), so they exist in solid form at room temperature (Yang et al. 2015). Most of the phthalates display stable chemical properties in the natural environment. Low molecular weight phthalates are slightly soluble in water, whereas high molecular weight phthalates are insoluble in water, but easily soluble in most organic solvents (Yu et al. 2015). For low molecular weight phthalates, the water solubility decreases with the increase of the number of carbon atoms in the alkyl chain. The relationship between the water solubility of high molecular weight phthalates and their number of carbon atoms is not conclusive. Phthalates can be hydrolyzed in alkaline medium to form phthalic acids and alcohols, but almost do not hydrolyze in water. Figure 15.1 is the general chemical structure of phthalates. Table 15.1 is the physicochemical properties of the common phthalates.

15.1.2 The Contamination Level of Phthalates in Water

Since phthalates are not covalently bonded to the polymeric matrix, such as soft polyvinyl chloride plastic, and exist in a leachable form, they can migrate into the environment easily upon disposal through the plastic aging and decomposition (Gao et al. 2018) and lead to their ubiquitous occurrence in environmental matrices. These chemicals have been detected in drinking water and many environmental water samples, including wastewater, surface water, seawater, rainwater, tap water, and

Table 15.1 The physicochemical properties of the common phthalates[a]

No.	Phthalate	Abbreviation	CAS No.	Molecular weight (g/mol)	Formula	Melting point (°C)	Boiling point (°C)	Vapor pressure (mmHg)	Density (g/mL)	Log $K_{o/w}$
1	Benzyl butyl phthalate	BBP	85-68-7	312.4	$C_{19}H_{20}O_4$	<−35	370	8.25×10^{-6}	1.12	4.9
2	Benzyl 2-ethylhexyl phthalate	BEHP	18750-05-5	368.5	$C_{23}H_{28}O_4$	–	485	–	1.08	6.8
3	Bis(2-butoxyethyl) phthalate	BBEP	117-83-9	366.5	$C_{20}H_{30}O_6$	−55	270	2.17×10^{-3}	1.07	4.4
4	Bis(2-ethoxyethyl) phthalate	BEEP	605-54-9	310.3	$C_{16}H_{22}O_6$	–	345	–	1.12	2.2
5	Bis(2-methoxyethyl) phthalate	BMEP	117-82-8	282.3	$C_{14}H_{18}O_6$	−45	340	2.28×10^{-4}	1.16	1.4
6	Butyl cyclohexyl phthalate	BCP	84-64-0	304.4	$C_{18}H_{24}O_4$	−25	386	4.77×10^{-6}	1.10	5.41
7	Butyl decyl phthalate	BDP	89-19-0	362.5	$C_{22}H_{34}O_4$	–	397	–	1.00	8.0
8	Butyl octyl phthalate	BOP	84-78-6	334.5	$C_{20}H_{30}O_4$	–	377	–	1.01	6.9
9	Di(2-ethylhexyl) hexahydrophthalate	DHHP	84-71-9	396.6	$C_{24}H_{44}O_4$	–	464	–	0.96	7.8
10	Diallyl phthalate	DAP	131-17-9	246.3	$C_{14}H_{14}O_4$	−70	290	1.16×10^{-3}	1.12	3.2
11	Diamyl phthalate	DAMP	131-18-0	306.4	$C_{18}H_{26}O_4$	−55	342	–	1.03	5.8
12	Dibenzyl phthalate	DBZP	523-31-9	346.4	$C_{22}H_{18}O_4$	40–42	494	–	1.21	5.2
13	Dicyclohexyl phthalate	DCHP	84-61-7	330.4	$C_{20}H_{26}O_4$	63–67	218	8.69×10^{-7}	1.15	5.2
14	Diethyl phthalate	DEP	84-66-2	222.2	$C_{12}H_{14}O_4$	−40.5	302	2.1×10^{-3}	1.12	2.5
15	Di(2-ethylhexyl) adipate	DEHA	103-23-1	370.6	$C_{22}H_{42}O_4$	−67	417	8.35×10^{-6}	0.928	6.8
16	Dimethyl phthalate	DMP	131-11-3	194.2	$C_{10}H_{10}O_4$	5.5	283.7	3.08×10^{-3}	1.19	1.6

(continued)

Table 15.1 (continued)

No.	Phthalate	Abbreviation	CAS No.	Molecular weight (g/mol)	Formula	Melting point (°C)	Boiling point (°C)	Vapor pressure (mmHg)	Density (g/mL)	Log $K_{o/w}$
17	Dimethyl terephthalate	DMTP	120-61-6	194.2	$C_{10}H_{10}O_4$	141	288	1.06×10^{-2}	1.29	2.3
18	Diisoamyl phthalate	DIAMP	605-50-5	306.4	$C_{18}H_{26}O_4$	–	225 (5.33 kPa)	–	1.03	5.6
19	Diisobutyl phthalate	DIBP	84-69-5	278.4	$C_{16}H_{22}O_4$	−64	320	–	1.00	4.1
20	Diisodecyl phthalate	DIDP	26761-40-0	446.7	$C_{28}H_{46}O_4$	−50	250 (0.5 kPa)	5.28×10^{-7}	0.97	10.6
21	Diisononyl phthalate	DINP	28553-12-0	418.6	$C_{26}H_{42}O_4$	48	244–252 (0.7 kPa)	5.4×10^{-7}	0.97	9.8
22	Diisopropyl phthalate	DIPP	605-45-8	250.3	$C_{14}H_{18}O_4$	–	302	–	1.06	2.8
23	Diheptyl phthalate	DHP	3648-21-3	362.5	$C_{22}H_{34}O_4$	–	360	2.07×10^{-6}	1.00	7.0
24	Dihexyl phthalate	DIHP	84-75-3	334.5	$C_{20}H_{30}O_4$	58	210 (5 mmHg)	1.4×10^{-5}	1.01	6.9
25	Dinbutyl phthalate	DnBP	84-74-2	278.3	$C_{16}H_{22}O_4$	−35	340	2.01×10^{-5}	1.04	4.7
26	Dindecyl phthalate	DNDP	84-77-5	446.7	$C_{28}H_{46}O_4$	2.5	261 (5 mmHg)	7.89×10^{-9}	0.97	11.2
27	Dinonyl phthalate	DNP	84-76-4	418.6	$C_{26}H_{42}O_4$	–	413	5.14×10^{-7}	0.97	10.1
28	Dioctyl phthalate	DOP	117–84-0	390.6	$C_{24}H_{38}O_4$	25	220	1.0×10^{-7}	0.99	9.1
29	Dipentyl phthalate	DPEP	131-18-0	306.4	$C_{18}H_{26}O_4$	<−55	342	–	1.03	5.9
30	Dipropyl phthalate	DPP	131-16-8	250.3	$C_{14}H_{18}O_4$	–	304	3.89×10^{-4}	1.08	3.4

31	Di(2-ethylhexyl) phthalate	DEHP	117-81-7	390.6	$C_{24}H_{38}O_4$	−55	384	1.42×10^{-7}	0.98	7.4
32	Diphenyl phthalate	DPHP	84-62-8	318.3	$C_{20}H_{14}O_4$	74–76	400–405		1.28	4.5
33	Ditridecyl phthalate	DTDP	119-06-2	530.8	$C_{34}H_{58}O_4$	−36.9	530	2.51×10^{-11}	0.96	12.1
34	Diundecyl phthalate	DUP	3648-20-2	474.7	$C_{30}H_{50}O_4$	35.5	472.6	1.22×10^{-9}	0.96	12.3
35	Hexyl 2-ethylhexyl phthalate	HEHP	75673-16-4	362.5	$C_{22}H_{34}O_4$	–	379.9	–	1.00	6.7

[a] Guidechem Database (http://china.guidechem.com) and https://pubchem.ncbi.nlm.nih.go

bottled water, even purified water. For example, the total concentration of the six phthalates, including dimethyl phthalate, diethyl phthalate, benzyl butyl phthalate, dioctyl phthalate, di(2-ethylhexyl) phthalate, and dinbutyl phthalate, in lake water of Taihu, China was found to be 0.740–13.0 μg/L (Gao et al. 2019). In more than 300 brands of bottled water samples collected from 21 countries, the detected frequencies of the five phthalates were 67.6% for dinbutyl phthalate, 61.7% for di (2-ethylhexyl) phthalate, 47.1% for diethyl phthalate, 36.9% for benzyl butyl phthalate, and 30.1% for dimethyl phthalate. The phthalate concentrations from the top five countries were 61.1, 8.8, 6.3, 6.2, and 6.1 μg/L (Luo et al. 2018). The total concentrations of 14 phthalates in the seawater of seamount area in the tropical western Pacific Ocean were found to be from 12.13 ng/ L to 60.69 ng/ L with an average concentration of 28.86 ng/ L, dominated by dinbutyl phthalate, di (2-ethylhexyl) phthalate, and diisobutyl phthalate (Zhang et al. 2019). Dinbutyl phthalate and di(2-ethylhexyl) phthalate were detected in greywater from French households with the concentrations of 9.64 μg/L and 6.21 μg/L, respectively (Deshayes et al. 2017). Phthalates have also been detected in rainwater in China, with di(2-ethylhexyl) phthalate and dinbutyl phthalate both at levels of over 1 μg/L (Zhu et al. 2004). Dimethyl phthalate, dinbutyl phthalate, dioctyl phthalate, and di (2-ethylhexyl) phthalate were detected in river water and lake water in Anshan, China with the concentrations of 0.0446–18.186 mg/L (Yao et al. 2011), which were much higher than other reports. Dargnat et al. (2009) detected six phthalates, including dimethyl phthalate, diethyl phthalate, dinbutyl phthalate, benzyl butyl phthalate, di(2-ethylhexyl) phthalate, and dioctyl phthalate in the densely populated estuary of the Seine in France. The detection rates of dimethyl phthalate, diethyl phthalate, dinbutyl phthalate, and di(2-ethylhexyl) phthalate were 100%, and the highest concentration range of di(2-ethylhexyl) phthalate was 160–314 ng/L. Yuan et al. (2002) detected eight phthalates in surface water and river sediment in Taiwan, China, and the contents of di(2-ethylhexyl) phthalate and dinbutyl phthalate were the highest in all samples. The distribution of 14 phthalates in the water and sediment of Eshan lake in South Korea has been studied. The total concentration of phthalates in the water body was less than 2.29 μg/L, with the highest concentration of di (2-ethylhexyl) phthalate, followed by dinbutyl phthalate (Lee et al. 2019).

Phthalates were extensively detected globally, and their potential risk to human health has aroused widespread concern all over the world. The United States Environmental Protection Agency has identified six congeners, including dimethyl phthalate, diethyl phthalate, dinbutyl phthalate, di(2-ethylhexyl) phthalate, dioctyl phthalate, and benzyl butyl phthalate, as priority pollutants (Gao et al. 2018) and has set an enforceable regulation for di(2-ethylhexyl) phthalate in drinking water, a maximum contaminant level at 6 μg/L. (https://www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-regulations). China has listed diethyl phthalate, dioctyl phthalate, and dimethyl phthalate as priority control pollutants and set the limit of di(2-ethylhexyl) phthalate in drinking water at 8 μg/ L (Ministry of Health2006). The limits of di(2-ethylhexyl) phthalate in drinking water set by Australia, Japan, and New Zealand are 9, 100, and 10 μg/L, respectively. The European Union proposed a guideline of 1.3 μg/L for di(2-ethylhexyl) phthalate in fresh and marine waters (Net et al. 2015).

The rivers, lakes, and the seas around the world have been contaminated by phthalates, owing to their mass production and application in the world. Due to concerns about the impact on human health, there have been numerous reports on the detection methods of phthalates in water in the last decade. In this chapter, we will summarize the analytical methods of phthalates in different water matrices, with emphasis on the sample treatment techniques, the separation, and detection methods.

15.2 The Sample Treatment Methods

Phthalates are present at very low concentrations in water samples except for some wastewater samples, so the development of sample treatment methods with high enrichment factor is indispensable. Sample treatment procedure includes extraction, cleanup, and concentration steps. Liquid–liquid extraction is a classical and commonly used extraction and preconcentration technique for organic analytes, because it has reliable accuracy and satisfactory precision. But it is time-consuming, tedious, and expensive, and the evaporation and redissolution procedures are usually required to concentrate the analytes and enhance the sensitivity of the method. So liquid–liquid extraction has been gradually replaced by other superior treatment methods, such as solid-phase extraction, solid-phase microextraction, liquid-phase microextraction, and their derivative techniques, such as dispersive liquid-phase microextraction, solidified floating organic drop microextraction, hollow fiber liquid-liquid microextraction, and magnetic solid phase extraction.

15.2.1 Liquid–Liquid Extraction

Liquid–liquid extraction is a traditional sample pretreatment method in which the analytes are transferred from one solvent to another based on the different partition coefficients of the analytes in two insoluble or partially soluble solvents. Liquid–liquid extraction has been extensively applied to the extraction of analytes from aqueous samples for its satisfactory reproducibility and accuracy, but it is time-consuming, tedious, and needs a large amount of samples and organic solvents. Some researchers used n-hexane or dichloromethane to extract phthalates from water samples. For example, Qi et al. (2006) used dichloromethane as extractant to extract eight phthalates in environmental water samples; after blown to dryness under nitrogen flow, the residue was redissolved with organic solvent and finally analyzed using gas chromatography. The method had the recovery rates of 73.5–114.6% and the relative standard deviations of 0.47–1.83%.

15.2.2 Liquid–Liquid Microextraction

Liquid–liquid extraction uses a large volume of organic solvents and samples, i.e. dozens of milliliters to hundred milliliters, which is not friendly to the environment. Liquid–liquid microextraction, proposed by Liu (Liu and Dasgupta 1996) and Jeannot et al. (Jeannot and Cantwell 1996, 1997) in the mid-1990s, provides a miniaturized liquid–liquid extraction mode in which the organic solvent used is in the range of tens to hundreds of microliters, and the amount of sample is in the range of several to tens of milliliters. This greatly reduces the cost of analysis, and very small volume of organic solvents can bring very high enrichment factor, so no subsequent concentration steps are needed. Liquid–liquid microextraction integrates sampling, separation, purification, and concentration into one step. It is especially suitable for the analysis of trace phthalates in water samples. In addition, fewer operational steps and less solvent consumption could reduce the risk of phthalates contamination. The technique has been utilized for the extraction of analytes in complex matrices, including water, food, and biological materials. But its extraction efficiency and precision need further improvement.

Liquid–liquid microextraction can be classified into single drop microextraction, dispersive liquid–liquid microextraction, solidified floating organic drop microextraction, and hollow fiber liquid–liquid microextraction (Yamini et al. 2019). Except single drop microextraction, hollow fiber liquid–liquid microextraction, dispersive liquid–liquid microextraction, and solidified floating organic drop microextraction have been extensively applied in the extraction of phthalates in water samples.

Hollow Fiber Liquid–Liquid Microextraction

Hollow fiber liquid–liquid microextraction is membrane-based liquid–liquid microextraction which has become popular for their advantages over the other microextraction methods, such as more effective sample cleanup, more stable extraction procedures, greater enrichment factor, and negligible consumption of organic solvents. It has a three-phase mode and two-phase mode. The three-phase mode is an aqueous–organic–aqueous system in which the immobilized organic solvent or supported liquid membrane is exposed to two aqueous phases of the sample solution and the aqueous acceptor phase located inside the hollow fiber. In contrast, in the two-phase mode, the acceptor phase solution is also the same as an organic solvent of supported liquid membrane, and both are immiscible in water (Esrafili et al. 2018). In hollow fiber liquid–liquid microextraction, assisted by magnetic stirring, the extraction time is commonly more than tens of minutes (Sarafraz-Yazdi and Amiri 2010). The method needs a special extraction device, and the operational requirements are relatively high. Toluene and ionic liquid [BMIm]PF6 have been utilized as extractants by many researchers to extract phthalates in water samples. For example, Psillakis et al. (Psillakis and Kalogerakis

2003) applied hollow fiber membrane liquid–liquid microextraction for the extraction of six phthalates, including dimethyl phthalate, diethyl phthalate, dinbutyl phthalate, benzyl butyl phthalate, di(2-ethylhexyl) phthalate, and dioctyl phthalate, in water samples. They used toluene as the extraction solvent, because it can provide high solubility for the target phthalates and compatible with the gas chromatographic system. Furthermore, it has a low solubility in water to prevent solvent dissolution during extraction, and it has a polarity matching that of the hollow fiber material, so it could impregnate and become immobilized within the pores of the hollow fiber. The method had linear ranges of 0.02–10 μg/L for most target phthalates with the limits of detection of 0.005–0.1 μg/L. The relative standard deviations of the method varied between 4% and 11%. Vortex solvent bar microextraction, an improved hollow fiber solvent bar microextraction method, has been proposed for the extraction of nine phthalates in bottled mineral water samples. It used 2 cm length Q3/2 hollow fibers immobilized with xylene (extraction solvent) as the solvent bar, which was then thrown into the stirring water sample and stirred around the bottom of the vortex during extraction. After extraction, the fibers were vortex eluted with microamount of acetone, and the eluent was applied to gas chromatography–mass spectrometric analysis. The vortex solvent bar microextraction gave enrichment factors over 1500, with the relative standard deviations of less than 7.1% (Huang et al. 2012). Yang et al. (2018a) extracted four phthalates in water using hollow fiber liquid-phase microextraction and determined the phthalates by high performance liquid chromatography. An ionic liquid, i.e. [BMIm]PF6, was used as extractant, and dodecanol was used as the supporting membrane. The detection limits of the method were 1.67–7.38 μg/L with the relative standard deviations of 2.1% −5.7%.

Dispersive Liquid–Liquid Microextraction

Dispersive liquid–liquid microextraction, developed by Rezaee and coworkers in 2006 (Rezaee et al. 2006), is that the water-insoluble extractant is dispersed into the aqueous phase to form a cloud-like solution, and the contact area between the aqueous phase and the extraction phase increases tremendously, so that the analytes can be quickly transferred from the aqueous phase into the extraction phase. The extraction solvent is reaggregated by centrifugation, and then it is withdrawn for subsequent analysis.

Dispersive liquid–liquid microextraction is much time-saving, and a very small amount of organic solvents is needed compared with other extraction methods. Furthermore, it does not need a special device and is easy to operate (Viñas et al. 2015). Based on the density of the extraction solvent, this technique can be divided into a high-density solvent dispersive liquid–liquid microextraction and a low density solvent dispersive liquid–liquid microextraction.

Dispersive liquid–liquid microextraction requires an organic dispersant which has to be fully soluble with the aqueous phase. For this purpose, acetone, acetonitrile, and methanol are usually used. The extraction solvent should have satisfactory extraction efficiency for the analytes. Also, the extraction solvent has to be soluble in the dispersant, but it is insoluble in the aqueous phase. Furthermore, the density of the extraction solvent has to be different greatly from that of the aqueous phase to facilitate the phase separation (Zgoła-Grześkowiak and Grześkowiak 2011). It is worth to note that the dispersant may change the polarity of the aqueous phase and affect the partition coefficient of the analytes, in turn, to affect the extraction efficiency of the analytes. There are many modes, such as ultrasonic-assisted dispersive liquid–liquid microextraction, vortex-assisted dispersive liquid–liquid microextraction, and air-assisted dispersive liquid–liquid microextraction. Ultrasonic- and vortex-assisted dispersive liquid–liquid microextraction can achieve dispersion without any dispersant, but it would take much longer time to achieve full dispersion. For high-density solvent dispersive liquid–liquid microextraction, after extraction and centrifugation, the extractant deposits under the aqueous phase, and then it can be withdrawn using a syringe for analysis. For example, carbon tetrachloride (Liang et al. 2008), 1,1,2,2-tetrachloroethane (Farajzadeh and Mogaddam 2012), and the mixture of chloroform, dichloromethane, and carbon tetrachloride (Farajzadeh and Khoshmaram 2015) have been reported for extraction of phthalates in water samples. But high-density solvents are usually halogen-containing solvents which are highly toxic to human health. The low toxic ionic liquid (Zhang et al. 2011) and other low-density organic solvents, such as n-hexane (Xu et al. 2007), toluene (Psillakis and Kalogerakis 2003; Zhang and Lee 2013), and xylene (Huang et al. 2012), have been used for extraction of phthalates in water samples. For low-density dispersive liquid–liquid microextraction, after centrifugation, the extractant phase will float on the surface of the aqueous phase. Figure 15.2 is the schematic diagrams of high-density solvent dispersive liquid–liquid microextraction.

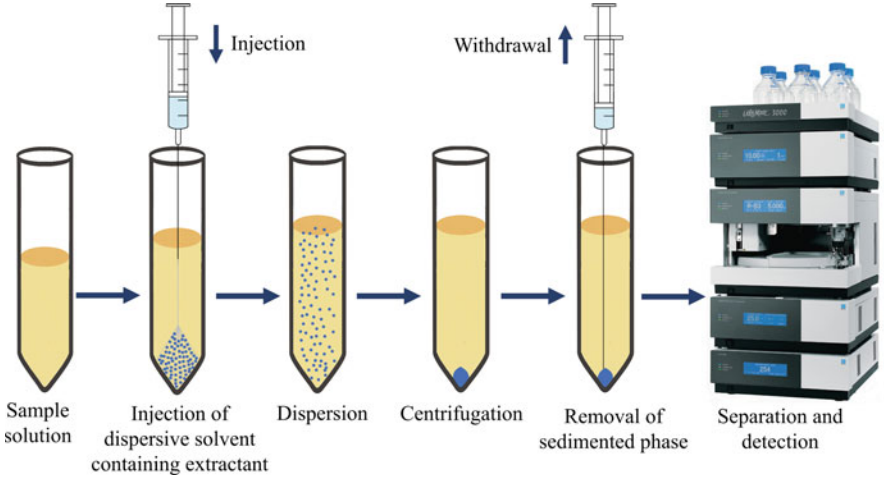


Fig. 15.2 The high-density solvent dispersive liquid–liquid microextraction procedure. Into the water sample, a dispersive solvent containing high-density extractant is injected. The extractant is dispersed into the water sample quickly, and a cloud-like solution is formed. The analytes are transferred from the water to the extractant. After centrifugation, the sedimented phase, i.e. the extractant is withdrawn with a syringe and injected into a chromatograph for analysis

Solidified Floating Organic Drop Microextraction

Solidified floating organic drop microextraction uses a low-density extraction solvent with a melting point range of 10–30 °C. After extraction and centrifugation, the extractant floating on the surface of the aqueous phase can be quickly solidified at a lower temperature, and then the solidified extractant is taken out by using a metal spoon and placed in a glass vial. After melting at room temperature, the melted solution is used for analysis. In the recent years, the low-density solvents, such as dodecane (Ranjbari and Hadjmohammadi 2012), 1-dodecanol (Farahani et al. 2008; Yang et al. 2018b), and n-hexadecane (Pérez-Outeiral et al. 2016), have been used often in the extraction of phthalates in water samples. Farahani et al. (2008) used suspended 1-dodecanol microdrop to extract seven phthalates, including dimethyl phthalate, diethyl phthalate, diallyl phthalate, dinbutyl phthalate, benzyl butyl phthalate, dicyclohexyl phthalate, and di(2-ethylhexyl) phthalate from 10 ml of tap, mineral, and river water samples by magnetic agitation in a sealed vial. After extraction, the vial was placed in an ice beaker, and 1-dodecanol was quickly solidified. The solidified 1-dodecanol was transferred into a conical vial and melted immediately at room temperature. The melted solution was used for analysis. The detection limits of the method were in the range of 0.02–0.05 μg/L, whereas the relative standard deviations for the analysis of 5.0 μg/L of the analytes were below 7.7%. The method exhibited enrichment factors ranging from 307 to 412. Figure 15.3 is the schematic diagrams of solidified floating organic drop microextraction procedure.

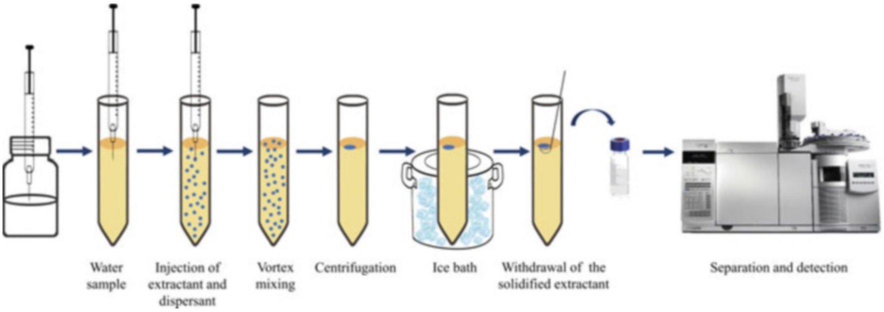


Fig. 15.3 The solidified floating organic drop microextraction procedure. Milliliters of water sample is taken into a test tube and then into the water sample; a low-density extractant (melting point 10–30 °C) and a dispersant are injected. After vortex mixing and centrifugation, the extractant floating on the surface of water phase can be quickly solidified in an ice bath, and, finally, the solidified extractant is taken out by using a metal spoon and placed in a glass vial. After melting at room temperature, the melted solution is used for analysis

15.2.3 Solid-Phase Extraction

Solid-phase extraction is based on the principle of liquid–solid chromatography. The solid adsorbent is used to adsorb the target compounds or impurities in the liquid sample. After elution of the impurities with an adequate solvent, the target compounds are then eluted with a specific solvent from the solid adsorbent, and the eluted solvent is used for analysis. This technique can be divided into online solid-phase extraction and offline solid-phase extraction. The former connects the extraction cartridge with the chromatographic system to achieve simultaneous extraction and analysis. Compared with the liquid–liquid extraction, solid-phase extraction has the advantages of simple operation and solvent-saving and is conducive to the realization of automation. However, most of the commercialized solid-phase extraction cartridges use plastic columns, which are easy to bring high phthalate background. The reproducibility of lab-made glass cartridges is poor, and also, they are rather expensive.

According to the physicochemical characteristics of the packing material, solid-phase extraction can roughly be divided into three modes, i.e. normal phase, reverse phase, and ion exchange. The mode used in the extraction of phthalates in water is usually reverse phase.

The packing materials of the reverse phase cartridges used for phthalates extraction are generally non-polar or weak polar materials, such as octadecylsilane (Salazar-Beltrán et al. 2017), magnetic graphene (Ye et al. 2014), ionic liquid-mixed hemimicelles (Li et al. 2008), poly(2,6-diphenyl-1,4-phenylene ether) (Liu et al. 2008), and molecularly imprinted polymers (Yang et al. 2016; Guo et al. 2019a). Chao et al. (2016) used octadecylsilane glass as solid-phase extraction cartridge to extract 16 phthalates in water samples. They used dichloromethane as eluent, and the eluent was separated and detected by gas chromatography–mass spectrometry. The average recovery rates of the method were 72.0–112%. Ma et al. (2009) compared the extraction efficiencies of different cartridges, i.e. Supelclean LC-18, Supelclean ENVI-Carb, and Cleanert ODS-SPE, for phthalates in water samples. Supelclean LC-18 was considered superior, so it was applied to the extraction of dimethyl phthalate, di(2-ethylhexyl) phthalate, and dioctyl phthalate in tap water samples and then eluted with methanol, and finally, the phthalates were analyzed by high-performance liquid chromatography. The recoveries of the method were between 83.6% and 110.2%. Cai et al. (2003) used multi-walled carbon nanotubes packed cartridges to extract four phthalates in tap, river, and sea water samples using acetonitrile as eluent. The eluent was separated and detected by high-performance liquid chromatography, and the recoveries of 80.3–104.5% were obtained.

Solid-Phase Microextraction

Solid-phase microextraction, developed by Pawliszyn and coworkers (Piri-Moghadam et al. 2016) in 1989, uses adsorbent-coated fibers (extraction head) to concentrate the analytes from the water samples. After the extraction procedure, the fibers are inserted into the injection port of the gas chromatograph; the analytes are thermo-desorbed from the fibers and then directly carried to the gas chromatographic system by carrier gas for analysis. There are two main modes for solid-phase microextraction, i.e. direct immersion and head-space solid-phase microextractions. The former is mainly used for the extraction of the analytes with higher boiling points and low volatility. The latter is mainly used for the extraction of the analytes with higher volatility. Solid-phase microextraction has numerous advantages, including (1) minimum or no solvent consumption, (2) small sample amount requirement, (3) short sample preparation time, (4) simplified automation leading to high-throughput analysis, (5) extraction and preconcentration of analytes from solid, liquid, and gaseous sample matrices (Risticevic et al. 2009). In recent years, solid-phase microextraction in combination with gas chromatography or gas chromatography–mass spectrometry has been widely applied to the analysis of numerous compounds, including phthalates. It was also introduced for direct coupling with high-performance liquid chromatography and ultra-performance liquid chromatography coupled with tandem mass spectrometry in order to analyze involatile or thermally labile compounds which are not amenable to gas chromatography or gas chromatography–mass spectrometry (Risticevic et al. 2009).

The main commercially available solid-phase microextraction heads include non-polar polydimethylsiloxane, polar divinylbenzene/polyacrylate, and bipolar diethylbenzene/carbon molecular sieve/polydimethylsiloxane. For the extraction of phthalates in water samples, the most commonly used solid-phase microextraction heads are polydimethylsiloxane/divinylbenzene (Cao 2008). Some new coating materials have been reported for phthalates extraction in water, such as carbon nanotubes (Luo et al. 2012; Song et al. 2016), polyaniline fiber (Li et al. 2006), nano-TiO_2 fiber (Banitaba et al. 2013), polypyrrole-coated Fe_3O_4 magnetic microsphere (Meng et al. 2011), Carbowax–divinylbenzene fiber (Luks-Betlej et al. 2001), and mag-graphene@PDA (Wang et al. 2015a).

Luks-Betlej et al. (Luks-Betlej et al. 2001) compared the solid-phase microextraction performances of six different non-polar and polar fibers for the extraction of seven phthalates from drinking water. They concluded that 70 μm Carbowax–divinylbenzene fiber was especially suitable for the extraction of the selected phthalates.

Zhang et al. (2017) applied a probe of CNWBOND Si SPME to the extraction of 16 phthalates in sea water. The probe was immersed in 10 ml sample solution with stirring at 500 rpm for 40 min at 35 °C. After the extraction, the probe was thermally desorbed for gas chromatography–mass spectrometric analysis. The limits of detection of the method were 0.005–0.32 μg/L, and the relative standard deviations were 0.24–8.8%. Liu et al. (2009) extracted 13 phthalates in lake water with 100 μ m polydimethylsiloxane fibers and determined the phthalates by gas chromatography. The limits of detection of the method were 0.02–0.83 μg/L, and the recovery rates were 75.3–111.0%. Zhao et al. (2013) used bamboo charcoal as a fiber-coating material for the extraction of 11 phthalates in environmental water samples and determined by gas chromatography–mass spectrometry. The limits of detection were

0.004–0.023 μg/L, and the recoveries were 67.9–87.1%. Amanzadeh et al. (2016) used graphene/polyvinyl chloride-coated fibers for head-space solid-phase microextraction of four phthalates in drinking water, and the separation and detection were performed on a gas chromatograph. The limits of detection of the method were 0.06–0.08 μg/L with the recoveries of 87–112%, and the relative standard derivations were less than 8.3%.

Magnetic Solid-Phase Extraction

Magnetic solid-phase extraction is a kind of dispersive solid-phase extraction, in which magnetic adsorbent materials are dispersed in an aqueous sample to adsorb the target compounds, and then the magnetic adsorbent materials are aggregated on one side of the glass tube by the external magnetic field to realize the separation of the adsorbent from the aqueous sample. The target compounds on the adsorbent can be eluted by using a proper eluent, and the eluent can be injected into the chromatographic system for analysis. Magnetic solid-phase extraction is simple and time-saving and has high extraction efficiency and low organic solvent consumption. So far, there are few commercial magnetic adsorbents available.

In recent years, magnetic nanomaterials have been extensively used as adsorbents for the concentration of the analytes from aqueous samples in solid-phase extraction. There are numerous magnetic materials reported for adsorption of phthalates from water samples, such as mag-graphene@PDA (Wang et al. 2015a), Fe_3O_4@SiO_2-G (Wang et al. 2013), magnetic multi-walled carbon nanotubes (Luo et al. 2012), Py-rGOx-Fe_3O_4(Pinsrithong and Bunkoed, 2018), Fe_3O_4@PPy magnetic nanoparticles (Zhao et al. 2016), polypyrrole-coated Fe_3O_4 magnetic microsphere (Meng et al. 2011), Fe_3O_4@r-GO magnetic nanoparticles (Santana-Mayor et al. 2018), Fe_3O_4@void@C–molecularly imprinted polymers (Yang et al. 2016), and 3D N-Co@C/HCF (Wang et al. 2019c). These magnetic nanomaterials have a large specific surface area and macroporous structure and exhibit high adsorption capacity and selectivity to the analytes.

Figure 15.4 is the schematic diagram of magnetic solid-phase extraction procedure.

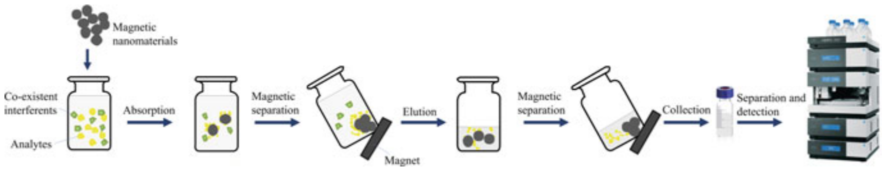


Fig. 15.4 The magnetic solid-phase extraction procedure. The magnetic nanomaterials are dispersed in an aqueous sample to adsorb the analytes, and then the magnetic nanomaterials are aggregated on one side of the glass vial by the external magnetic field to realize the separation. The magnetic adsorbent is collected, and the target compounds on the adsorbent are eluted using a proper solvent, and finally, the eluted solvent is used for chromatographic analysis

Ye et al. (2014) extracted seven phthalates from water samples by using magnetic graphene solid-phase extraction. They used ethyl acetate to desorb ultrasonically the analytes. The eluted solution was applied to gas chromatography–mass spectrometric analysis. The method had recovery rates of 88–110%, and the limits of detection were 0.01–0.056 μg/L, with the relative standard deviations less than 8.5%. Zhao et al. (2016) prepared Fe_3O_4@PPy magnetic nanoparticles as sorbents for the preconcentration of 16 phthalates in tap and lake water. They analyzed the phthalates by gas chromatography coupled with tandem mass spectrometry and obtained recovery rates of 80.4–108.2%, with the limits of detection of 0.006–0.021 μg/L, and the relative standard deviations were less than 12.8%. Luo et al. (2012) prepared magnetic carbon nanotubes and used it for the extraction of 16 phthalates from tap water samples. A small amount, i.e. 0.10 mL, of magnetic carbon nanotubes suspension was added into 10 mL sample solution and vortex agitated for 3 min. Then an external magnet was applied to gather magnetic adsorbent, and the phthalates were eluted with 1.00 mL acetone which was collected and evaporated to dryness at 35 °C under nitrogen flow followed by redissolving in 0.10 mL acetone for the subsequent gas chromatography–mass spectrometric analysis. The limits of detection of the method were 0.0049–0.038 μg/L, and the recovery rates were 64.6–125.6%, with the relative standard deviations less than 11.7% (intra-day) and 14.6% (inter-day). Wang et al. (2015a) used magnetic graphite carbon nitride nanocomposites for the determination of four phthalates in water samples by high-performance liquid chromatography. The detection limits of the method were 0.05 ± 0.1 μg/L, and the recoveries were in the range of 79.4–99.4%. Wu et al. (2012) used graphene-based magnetic nanoparticles as adsorbents for the analysis of five phthalates in water and beverage by high-performance liquid chromatography. The detection limits of the method were 0.01–0.04 μg/L, and the enrichment factors were 1574–2880. Liu et al. (2015a) used magnetic nanoporous carbon to adsorb phthalates in lake water and juice samples, and the detection limits of three phthalates in water samples were 0.10 μg/L, with the relative standard deviations of 4.2–7.0%. The magnetic zeolite imidazolate framework-8 has been applied to the extraction of five phthalates in environmental water and separation and detection by high-performance liquid chromatography. The detection limits were 0.08–0.24 μg/L, and the relative standard deviations were less than 5.5%, with the recoveries of 85.6–103.6% (Liu et al. 2015b). The magnetic molecularly imprinted polymer nanoparticles combined with gas chromatography–tandem mass spectrometry has been reported to detect di(2-ethylhexyl) phthalate in water samples. The method has a detection limit of 0.02 μg/L. The recoveries were 93.3–103.2%, and the relative standard deviations were 1.2–3.2% (Li et al. 2016).

15.3 The Separation and Detection Methods for Phthalates in Water

The commonly used separation and detection methods for phthalates in water samples are gas chromatography with flame ionization detection or mass spectrometric detection and high-performance liquid chromatography with ultraviolet detection or mass spectrometric detection. The mass spectrometric detection is most favorable, because it not only has strong qualitative ability but also has very high sensitivity, but for accurate quantification, isotope or deuterated internal standards are needed.

15.3.1 Gas Chromatography

Gas chromatography has the characteristics of high resolution, high selectivity, and rapidity, and there is almost no plastic parts used in the instrument, so its background contamination can be ignored. Most phthalates are weak polar chemicals; with the boiling point below 400 °C, it is suitable for analyzing them without derivatization. Flame ionization detector and mass spectrometer especially tandem mass spectrometer have been often used for detection of phthalates. The different brands and specifications of capillary columns with weak or non-polarity, such as HP-5 (30 m × 0.32 mm, 0.25 μm)(Li et al. 2006), DB-17 (30 m × 0.25 mm, 0.25 μm) (He et al. 2010), HP-1 (30 m × 0.32 mm, 1 μm) (Mousa et al. 2013), and SPB-1 (30 m × 0.25 mm, 0.25 μm) (Farajzadeh and Khoshmaram 2015), have been used for separation of phthalates in water samples.

A head-space solid-phase microextraction has been applied to the extraction of six phthalates from water samples, and then the target phthalates were separated on an HP-5 capillary column (50 m × 0.32 mm, 0.52 μm) and detected by a flame ionization detector. The method had the linear ranges of 1–100 μg/L, and the limits of detection were 0.032–0.451 μg/L with the relative standard deviations less than 9.73% (Guo et al. 2019b). Liu et al. (2010) used an HP-5 column to separate 13 phthalates from water samples and detected by a flame ionization detector. OV-1701 column (Jia et al. 2005) and SE-54 column (Li and Liao, 2016) have been reported too as the separation column for the phthalates in water samples.

Compared with flame ionization detector, mass spectrometric detector not only has high sensitivity, but also can provide rich chemical structure information of the target analytes, so it can identify partially separated or even unseparated analytes, based on the library of National Institute of Standards and Technology of the United States or other databases.

Zhang et al. (2017) applied solid-phase microextraction to absorb 16 phthalates in sea water and determined the phthalates by gas chromatography–tandem mass spectrometry. They used DB-1MS column (30 m × 0.25 mm, 0.25 μm) as separation column. The recovery rates of the method were 55.4–114%. The limits of detection were 0.005–0.32 μg/L, and the relative standard deviations were 0.24–8.8%. Ye et al. (2014) used gas chromatography–tandem mass spectrometry to determine seven phthalates in environmental water samples. The phthalates were separated by HP-5MS column, and selective ion monitoring was applied for quantification. The recoveries were in the range of 88–110% with the relative standard deviations less than 8.5%.

The electron capture detector was reported for detection of phthalates in mineral water, river water, and bottled water (Eskandarpour and Sereshti 2018) with similar sensitivities to a flame ionization detector.

15.3.2 High-Performance Liquid Chromatography

High-performance liquid chromatography is selective, sensitive, accurate, and reproducible, and it is particularly suitable for the analysis of difficult-to-volatile analytes, so it has a very wide application in analysis of the organic compounds. The high molecular weight phthalates have a boiling point higher than 300 °C, and it is difficult to be effectively volatile under the normal inlet port temperature of a gas chromatograph. So it is preferable to analyze them by high-performance liquid chromatography. Even low molecular weight phthalates have satisfactory sensitivities. The benzene ring and double bond in the chemical structure of phthalates make them be easily detected by an ultraviolet detector or a diode array detector. Of course, a mass spectrometer is the best choice for phthalates detection. The most often used separation columns are octadecylsilane chemically bonded silica column (Yang et al. 2018a, b; Santana-Mayor et al. 2018) and octylsilane chemically bonded silica column (Liang et al. 2008). The mobile phase is generally composed of methanol–acetonitrile and water–formic acid solution.

Yang et al. (2018b) determined 15 phthalates in tap water, bottled water, and river water by high-performance liquid chromatography after solidified floating organic drop microextraction. The separation was performed on an octadecylsilane column (250 × 4.6 mm, 5 μm) and detected by an ultraviolet detector. The method's linear ranges were 0.1–100 μg/L, and the limits of detection were 0.013–0.158 μg/L. The recovery rates of the method were 86.8–119% with the relative standard deviations of 3.0–13.7%. Luo et al. (2014) established a high-performance liquid chromatography with diode array detection for the analysis of five phthalates in tap water and bottled water. ZORBAX SB-octadecylsilane column was used for separation with methanol–water as mobile phase. The detection wavelength was 226 nm, and the recoveries were 87.7–100.9%. Octylsilane column was used as separation column, and acetonitrile–water was used as mobile phase has been reported for analysis of phthalates in water samples too (Liu et al. 2015b).

The sensitivity and qualitative ability of ultra-performance liquid chromatography coupled with tandem mass spectrometry are much higher than those of ultraviolet detection-based conventional liquid chromatography and are suitable for trace analysis of phthalates. However, the instrument is quite expensive, and the maintenance cost is high as well. Santana-Mayor et al. (2018) concentrated and cleaned-up 14 phthalates from mineral water, pond water, and wastewater samples by using magnetic-micro-dispersive solid-phase extraction technique; then the separation was performed on an octadecylsilane column (50 mm × 2.1 mm, 1.7 μm), and finally detected by tandem mass spectrometer; dinbutyl phthalate-d4 was used as an internal standard. The method had recoveries varying from 70% to 120%, and the limits of quantification were 0.006–0.178 μg/L, with the relative standard deviations less than 20%. Fifteen phthalates in drinking water were separated on a phenyl column. The mobile phase was methanol–water, and electrospray ionization in multiple reaction monitoring mode was applied. The detection limits of the method were 0.7–632 ng/L, and the recoveries were between 81.3% and 109% (Zhang et al. 2014). López-Jiménez et al. (2005) used ultra-performance liquid chromatography coupled with tandem mass spectrometry to detect di(2-ethylhexyl) phthalate, benzyl butyl phthalate, and dinbutyl phthalate in waste water. The detection limits were 0.07–0.1 μg/L, with the relative standard deviations of 2–5%.

15.3.3 Other Methods

Based on the principle of chromatographic separation, capillary micellar electrokinetic chromatography can achieve efficient and rapid analysis with less solvent consumption. Sun et al. (2014) used capillary micellar electrokinetic chromatography to detect three phthalates in environmental water samples with the limits of detection of 2.07–4.06 ng/mL.

Enzyme-linked immunosorbent assay has the characteristics of no sample pretreatment, simplicity, rapidity, and high specificity. Zhou et al. (2017b) synthesized the hapten 4-amino-dibutyl phthalate of dinbutyl phthalate and prepared the polyclonal antibody against dinbutyl phthalate by immunizing New Zealand white rabbits with the corresponding immunogen. The hapten 4-amino phthalate diethyl ester of diethyl phthalate was synthesized, and the monoclonal antibody of diethyl phthalate was achieved after immunizing Balb/C mice with the corresponding immunogen. The indirect competitive enzyme-linked immunosorbent assay for dinbutyl phthalate and diethyl phthalate was established and applied to the analysis of dinbutyl phthalate and diethyl phthalate in water and sediment samples.

In addition, sensor detection holds the characteristics of rapid, high sensitivity, and high selectivity, and it has also been used in phthalate analysis. Zhou et al. (2017a) synthesized a fluorescent molecularly imprinted sensor for the determination of dinbutyl phthalate in tap water. The recovery rate was 97.8%, and the limits of detection were 0.04 μmol/L. Table 15.2 presents the analytical methods for phthalates in water samples.

15.4 The Pollution Preventive Measures

Owing to the presence of phthalates in many laboratory chemicals and glassware, high background may occur for the analysis of phthalates in real samples. To avoid any carryover of phthalates, all laboratory glassware was washed with concentrated hydrochloric acid and then rinsed with deionized water and acetone, finally dried in the laboratory oven at 100 °C for 1 h (Ye et al. 2014). Some researchers used acetone

Table 15.2 The analytical methods for phthalates in water samples

Number of phthalates detected	Sample treatment method	Sample matrix	Separation and detection method	Method performance	References
6	Head-space solid-phase microextraction	Water	Gas chromatography with flame ionization detection; Column: HP-5 (50 m × 0.32 mm, 0.52 μm)	LODs:0.032–0.451μg/L; RSDs:<9.73%	Guo et al. (2019b)
7	Solid-phase extraction	Water	Gas chromatography–mass spectrometry; Column:HP-5MS (30 m × 0.25 mm, 0.25μm).	Recovery:88–110%; LODs:0.01–0.056μg/L; RSDs <8.5%	Ye et al. (2014)
5	Solid-phase extraction	Water	High-performance liquid chromatography-ultraviolet detection Column: Diamonsil-C18 (250 mm × 4.6 mm, 4μm)	Recovery:76–85%; LODs:0.12–0.17μg/L; RSDs:4.1–5.9%	Li et al. (2008)
5	Solid-phase extraction	Ultrapure water	Gas chromatography–mass spectrometry; Column: DB-5MS (30 m × 0.25 mm, 0.25μm)	Recovery:15–101%; LODs:36-95 ng/L: RSDs: 5.9–10.1%	Liu et al. (2008)
3	Electro-enhanced solid-phase microextraction	Seawater	Gas chromatography–mass spectrometry; Column: HP-1 (30 m × 320 mm, 1μm)	Recovery:73.9–93.4%; LODs:0.004–0.15 μg/L; RSDs:2.7–6.2%	Mousa et al. (2013)
3	Surfactant-containing extraction phase solvent bar microextraction	Mineral, river, and seawater	High-performance liquid chromatography-ultraviolet detection;	Recovery:88.2–103.8%; LODs:0.012–0.03 μg/L; RSDs:2.1–2.6%	Bandforuzi and Hadjmohammadi (2018)

(continued)

Table 15.2 (continued)

Number of phthalates detected	Sample treatment method	Sample matrix	Separation and detection method	Method performance	References
			Column: C18 (15 cm × 4.6 mm, 5μm)		
3	Solid-phase extraction	River, lake, and ground water	Gas chromatography–mass spectrometry; Column: HP-5MS (30 m × 0.25 mm, 0.25 μm).	Recovery:89.5–112.3%; LOD:0.5-1 ng/L; RSD;4.8–7.5%	Wang et al. (2019b)
5	Solid-phase microextraction	Tap water, pond water, and barreled drinking water	Gas chromatography–mass spectrometry; Column: HP-5 MS (30 m × 0.25 mm, 0.5μm)	Recovery:73.4–103.8%; LODs:0.0012–0.018μg/L; RSDs:5.8–9.21%	Song et al. (2016)
7	Stir bar sorptive extraction with liquid desorption	Tap and bottled mineral water	Gas chromatography–mass spectrometry; Column:TRB-5MS (30 m × 0.25 mm, 0.25 μm)	Recovery:5.1–98.5%; LODs:3–40μg/L; RSDs:<14.8%	Serodio and Nogueira (2006)
4	Head-space solid-phase microextraction	Drinking water	Gas chromatography-flame ionization detection; Column: CP-Sil 8 CB (30 m × 0.32 mm, 0.25 μm).	Recovery:91–105%; LODs:0.06–0.08μg/L RSDs:6.1–7.8%	Amanzadeh et al. (2016)
5	Magnetic solid-phase extraction	River water, tap water, and bottled mineral water	High-performance liquid chromatography-diode array detection; Column: C8 (150mm × 4.6 mm, 5μm)	Recovery:85.6–103.6%; LOD:0.09–0.24μg/L; RSD:2.1–5.5%	Liu et al. (2015b)

9	Head-space solid-phase microextraction	Bottled water	Gas chromatography–mass spectrometry; Column: DB-5MS (30 m × 0.25 mm, 0.25 μm,	LODs:0.003–0.085μg/L; RSDs:0.78–21.7%	Cao (2008)
3	Online solid-phase extraction	Bottled water	High-performance liquid chromatography-ultraviolet detection; Column: C18 (250 mm × 4.6 mm, 5 μm)	Recovery:80–115%; LOD:0.7–2.4μg/L; RSD:0.9–4.0%	Salazar-Beltrán et al. (2017)
5	Solid-phase microextraction	Water	Gas chromatography-flame ionization detection; Column: HP-5 (30 m × 0.32 mm, 0.25μm)	LOD:0.003–10 μg/L; RSD:2.16–19%	Li et al. (2006)
16	Solid-phase microextraction	Seawater	Gas chromatography–mass spectrometry; Column: DB-1MS (30 m × 0.25 mm, 0.25 μm)	Recovery:55.4–114%; LODs:0.005–0.32μg/L; RSDs:0.24–8.8%	Zhang et al. (2017)
9	Hollow fiber-based liquid–liquid microextraction	Mineral, pond, tap, and wastewater	Gas chromatography–tandem mass spectrometry; Column: SPB-5 (30 m × 0.25 mm, 0.25 μm)	Recovery: 74–120%; RSDs:<20%	González-Sálamo et al. (2018)
5	Magnetic solid-phase extraction	River water	High-performance liquid chromatography-ultraviolet detection, Column: ZORBAX SB-C18 (150 mm × 4.6 mm, 5μm)	Recovery:92.4–104.7%; LODs:0.025–0.089μg/L; RSDs:<6%	Wang et al. (2019a, b, c)

(continued)

Table 15.2 (continued)

Number of phthalates detected	Sample treatment method	Sample matrix	Separation and detection method	Method performance	References
6	Magnetic solid-phase extraction	Pond water	Gas chromatography–mass spectrometry Column:HP-5MS (30 m × 0.25 mm, 0.25μm)	Recovery:43–96.5%; LODs:0.05–5 μg/L; RSDs:3.8–8.31%	Wang et al. (2015a)
1	Dispersive solid-phase microextraction	River water	High-performance liquid chromatography-ultraviolet detection; Column: C18 (150 mm × 3.9 mm, 5μm)	Recovery:82–92%; LODs:0.92μg/L; RSDs:<6.7%	Cheng et al. (2017)
5	Head-space solid-phase microextraction	Mineral, river, and bottled water	Gas chromatography-μ-electron capture detection; Column:HP-5 MS (30 m × 0.32 mm, 0.25μm)	Recovery:;90.3–107%; LODs:0.0400–0.193μg/L; RSDs:1.86–10.9%	Eskandarpour and Sereshti, (2018)
5	Magnetic solid-phase extraction	Reservoir and river water	High-performance liquid chromatography-ultraviolet detection; Column:C18-BDS (200 mm × 4.6 mm, 5μm)	Recovery:87.2–109%; LODs:0.07–0.1μg/L; RSDs:2.7–6.1%	Wang et al. (2013)
16	Magnetic solid-phase extraction	Tap water	Gas chromatography–mass spectrometry; Column:Rxi® − 5MS (30 m × 0.25 mm, 0.25μm)	Recovery:64.6–125.6%; LODs:0.0049–0.038 μg/L; RSDs:<11.7%(intra-day); <14.6% (inter-day)	Luo et al. (2012)

5	Solid-phase extraction	Tap and bottled water	High-performance liquid chromatography-ultraviolet detection; Column: C18 (150 mm × 4.6 mm,5 μm)	Recovery:84.3–105.5%; LODs:0.09–0.33μg/L; RSDs:0.3–7.6%	Luo et al. (2014)
15	Dispersive solid-phase microextraction	Ultrapure water, river, and seawater	Gas chromatography–mass spectrometry; Column:HP-5MS (30 m × 0.25 mm., 0.25μm)	Recovery 71–117%;: LODs:2–7μg/L; RSDs:1–10%	Wu et al. (2013)
6	Magnetic solid-phase extraction	Bottled water	Gas chromatography–tandem mass spectrometry; Column:DB-5MS (60 m × 0.32 mm, 1μm)	Recovery:87.5–99.1%; LOD:0.005–0.01μg/L; RSD:0.6–7.7%	Pinsrithong and Bunkoed (2018)
7	Magnetic solid-phase extraction	Water	High-performance liquid chromatography-ultraviolet detection; Column: C18 (250 mm × 4.6 mm, 5 μm)	Recovery: 77–120%; LODs:0.02–0.05μg/L; RSDs:1.0–4.9% (intra-day)	Wang et al. (2019a)
5	Molecularly imprinted polymer-solid-phase microextraction	Reservoir water, tap water, and bottled water	Gas chromatography–tandem mass spectrometry; Column: DB-17 (30 m × 0.25 mm,0.25 μm)	Recovery:94.54–105.34%; LODs:0.02–0.34μg/L; RSDs:1.5–8.04%	He et al. (2010)
8	Molecularly imprinted polymer-solid-phase extraction	River, lake, pond, and wellwater	Gas chromatography–tandem mass spectrometry; Column: HP-5MS (30 m × 250 mm,0.25 mm)	Recovery:>92.9%; LODs:0.01–0.05μg/L; RSDs:<3.8%	Guo et al. (2019)

(continued)

Table 15.2 (continued)

Number of phthalates detected	Sample treatment method	Sample matrix	Separation and detection method	Method performance	References
16	Solid-phase microextraction	Tap water and lake water	Gas chromatography–tandem mass spectrometry; Column: TG-5MS (30 m × 0.25 mm, 0.25μ m)	Recovery:80.4% - 108.2%; LODs:0.006–0.021μg/L; RSDs:<12.8%	Zhao et al. (2016)
7	Solid-phase microextraction	Tap water	Gas chromatography–tandem mass spectrometry; Column: HP-5MS (30 m × 250 mm,0.25 mm)	Recovery:91.1–113.4%; LODs:0.006–0.068μg/L; RSDs:3.4–11.7%	Meng et al. (2011)
14	Magnetic-micro dispersive solid-phase extraction	Mineral, pond, and wastewater	Ultrahigh-performance liquid chromatography-tandem mass spectrometry; Column: C18 (50 mm × 2.1 mm, 1.7μm)	Recovery:70–120%; LODs:0.002–0.06μg/L; RSDs:<20%	Santana-Mayor et al. (2018)
6	Magnetic molecularly imprinted polymer solid-phase extraction	Lake, river, and tap water	Gas chromatography–tandem mass spectrometry; Column:HP-5MS (30 m × 250 mm, 0.25 mm)	Recovery:86.1–103.1%; LODs:0.0016–0.0052 μg/L; RSDs:<6.7%	Yang et al. (2016)
4	Solid-phase microextraction	Bottled mineral water	Gas chromatography-flame ionization detection; Column: CP-SIL 8CB (25 m × 0.32 mm, 0.25 μm)	Recovery:86–107%; LOD:0.05–0.12 μg/L; RSD:6.6–11.1%	Banitaba et al. (2013)

8	Solid-phase microextraction	Drinking water	Ultrahigh-performance liquid chromatography-ultraviolet detection; Column:C18 (350 mm × 100 mm, 3.0 μm)	Recovery:75.5–99.7%; LODs:0.18–2.95 μg/L; RSDs:<6.2%	Lirio et al. (2016)
7	Solid-phase microextraction	Drinking water	Gas chromatography–tandem mass spectrometry; Column: HP-5MS (30 m × 0.20 mm, 0.25 μm)	LODs:0.005–0.04 μg/L; RSDs:4.4–28.3%	Luks-Betlej et al. (2001)
11 + 9 mono-phthalates	Solid-phase extraction	Seawater and fresh water	Ultrahigh-performance liquid chromatography-Orbitrap-mass spectrometry; Column:Hypersil gold (100 mm × 1.9 mm, 2.1 μm)	Recovery:98.5–105.8% LODs:5-25 ng/L; RSDs:<10%	Huysman et al. (2019)
9	Dispersive solid-phase extraction	Tap water, pond water, and wastewater	Ultrahigh-performance liquid chromatography-tandem mass spectrometry; Column: C18 (100 mm × 4.6 mm, 3.5 μm)	Recovery:70–118%; LODs:0.024–0.069 μg/L; RSDs:<20%	González-Sálamo et al. (2019)
5	Air-assisted liquid–liquid microextraction	Bottled and mineral water	Gas chromatography-flame ionization detection; Column:HP-5 MS (30 m × 0.25 mm.,0.25μm)	Recovery:91–104%; LODs:0.12–1.15 μg/L; RSDs:2–3%	Farajzadeh and Mogaddam (2012)
3	Dispersive liquid–liquid microextraction	Lake, tap, and bottled water	High-performance liquid chromatography-ultraviolet detection; Column:C8 (150mm × 4.6 mm,5μm)	Recovery:84–113%; LODs:0.64–1.8ug/L; RSDs:3.1–6.8%	Liang et al. (2008)

(continued)

Table 15.2 (continued)

Number of phthalates detected	Sample treatment method	Sample matrix	Separation and detection method	Method performance	References
3	Surfactant-containing extraction phase solvent bar microextraction	Mineral, sea, and river water	High-performance liquid chromatography-ultraviolet detection; Column:C18(15cm×4.6mm, 5um)	Recovery:88.2–107.8%; LODs:0.012 to 0.03 ug/L; RSDs:1.8–2.6%	Bandforuzi and Hadjmohammadi (2018)
3	Ionic liquid cold-induced aggregation dispersive liquid–liquid microextraction	Tap, bottled mineral, and river water	High-performance liquid chromatography-ultraviolet detection; Column:C18 (250 mm × 4.6 mm, 5μm)	Recovery:90.1–99.2%; LODs:0.68–1.36 μg/L; RSDs:2.2–3.7%	Zhang et al. (2011)
5	Ultrasound-assisted dispersive liquid–liquid microextraction followed by solidification of floating organic drop	Mineral water	Gas chromatography-flame ionization detection; Cloumn: HP-5 (30 m × 0.250 mm, 0.25 μm)	Recovery: 95–109%; LODs:0.64–2.82 μg/L; RSDs:2.7–9.3%	Pérez-Outeiral et al. (2016)
6	Dispersive liquid–liquid microextraction	Mineral water,	Gas chromatography-flame ionization detection; Column:SPB-1 (30 m × 0.25 mm, 0.25μm)	Recovery: 2–90%; LODs: 0.03–0.15 μg/L; RSDs:4–8%	Farajzadeh and Khoshmaram (2015)
3	Dynamic liquid–liquid microextraction	Lake, tap, and bottled water	Gas chromatography-flame ionization detection; Column:DB-5MS (30 m × 0.25 mm, 0.25μm)	Recovery:84–102%; LODs:0.43–4.3 μg/L; RSDs:5.2–6.4%	Xu et al. (2007)

6	Low-density solvent-based vortex-assisted surfactant-enhanced-emulsification liquid–liquid microextraction	Bottled water	Gas chromatography–tandem mass spectrometry; Column:DB-5MS (30 m × 0.25 mm,0.25μm)	Recovery:73.5–106.6%; LODs:8–25 ng/L; RSDs:0.80–11.9%	Zhang and Lee (2013)
4	Magnetic stirring-assisted dispersive liquid–liquid microextraction	Tap water seawater, and river water	High-performance liquid chromatography-ultraviolet detection; Column:C18 (250 × 4.6 mm, 10 μm)	Recovery:80.4–104.7%; LODs:0.13 to 0.38 μg/ml; RSDs:1.5–3.35%	Ranjbari and Hadjmohammadi (2012)
7	Liquid–liquid microextraction	Tap, mineral, and river water	Gas chromatography–mass spectrometry; Column:DB-5MS (30 m × 0.25 mm, 0.25μm)	Recovery:84–115%; LODs:0.02–0.05 μg/L; RSDs:<7.7%	Farahani et al. (2008)
9	Vortex solvent bar microextraction	Bottled mineral water	Gas chromatography–mass spectrometry; Column:DB-5MS (30 m × 0.25 mm, 0.25μm)	LODs:0.4–76 ng/L; RSDs:3.0–7.1%	Huang et al. (2012)
6	Vortex-assisted micro-solid-phase extraction combined with low-density solvent based dispersive liquid–liquid microextraction	River water	Gas chromatography–mass spectrometry; Column:DB-5 MS (30 m × 0.25 mm,0.25 μm)	Recovery:85.8–104.1%; LODs:0.006–0.02 μg/L; RSDs:4.7–9.6%	Guo and Lee (2013)
15	Dispersive liquid–liquid microextraction-solidification of floating organic drop	Tap, bottled, and river water	High-performance liquid chromatography-ultraviolet detection; Column: C18 (250 mm × 4.6 mm, 5 μm)	Recovery:86.8–119%; LODs:0.013–0.158 μg/;L RSDs:3.0–13.7%	Yang et al. (2018b)

LODs limits of detection, *RSDs* relative standard deviations to soak all laboratory glassware used in the experiment for at least 30 min and then rinsed with n-hexane, and finally dried at 120 °C for at least 4 h before use. The organic solvents used have to be treated with aluminum oxide before use (Luo et al. 2012). Furthermore, phthalates free gloves and pipette tips were employed during the experiment (Santana-Mayor et al. 2018).

15.5 Conclusion and Perspectives

In recent years, many novel analytical methods for phthalates in water sample have continuously emerged. In order to concentrate trace level of phthalates in water samples, pretreatment methods, such as liquid–liquid microextraction and solid-phase extraction and their derivative techniques, including dispersive liquid–liquid microextraction, hollow fiber liquid-phase microextraction, solidified floating organic drop microextraction, and magnetic solid-phase extraction, are mostly used. The commonly used separation and detection methods are gas chromatography with flame ionization detection, gas chromatography–tandem mass spectrometry, high-performance liquid chromatography-ultraviolet or diode array detection, and ultra-performance liquid chromatography–tandem mass spectrometry. Researchers have developed numerous new adsorption materials for the concentration of trace phthalates in water samples. Some of these adsorption materials have good specificity and higher enrichment factors. Besides, other new adsorption materials, such as carbon nanotubes/magnetic carbon nanotubes, graphene oxide, and electrospun nanofibers, have been increasingly obtained attention, because they are environmentally friendly, non-toxic, cheap, and easily available. However, the current analytical methods seldom cover all the possible phthalates that occur in the different water matrices. In the future, in addition to the highly sensitive gas and liquid chromatography coupled with high-resolution mass spectrometers, it is also necessary to develop new analytical techniques that are rapid, sensitive, accurate, or capable of on-line or on-site detection, such as various biosensors, micro-total analysis system, surface-enhanced Raman scattering device, and surface plasmon resonance system. These techniques have potential applications in phthalates analysis in water, especially in real-time or on-site analysis.

References

Amanzadeh H, Yamini Y, Moradi M, Asl Y (2016) Determination of phthalate esters in drinking water and edible vegetable oil samples by headspace solid phase microextraction using graphene/polyvinylchloride nanocomposite coated fiber coupled to gas chromatography-flame ionization detector. J Chromatogr A 1465:38–46. https://doi.org/10.1016/j.chroma.2016.08.068

Bandforuzi S, Hadjmohammadi M (2018) Application of non-ionic surfactant as a developed method for the enhancement of two-phase solvent bar microextraction for the simultaneous determination of three phthalate esters from water samples. J Chromatogr A 1561:39–47. https://doi.org/10.106/j.chroma.2018.05.039

Banitaba M, Davarani S, Pourahadi A (2013) Solid-phase microextraction of phthalate esters from aqueous media by electrophoretically deposited TiO_2 nanoparticles on a stainless steel fiber. J Chromatogr A 1283:1–8. https://doi.org/10.1016/j.chroma.2013.01.092

Bornehag C, Sundell J, Weschler C, Sigsgaard T, Lundgren B, Hasselgren M, Hagerhed-Engman L (2004) The association between asthma and allergic symptoms in children and phthalates in house dust: a nested case-control study. Environ Health Perspect 112(14):1393–1397. https://doi.org/10.1289/ehp.7187

Cai Y, Jiang G, Liu J, Zhou Q (2003) Multi-walled carbon nanotubes packed cartridge for the solid-phase extraction of several phthalate esters from water samples and their determination by high performance liquid chromatography. Anal Chim Acta 494(1–2):149–156. https://doi.org/10.1016/j.aca.2003.08.006

Cao X (2008) Determination of phthalates and adipate in bottled water by headspace solid-phase microextraction and gas chromatography/mass spectrometry. J Chromatogr A 1178 (1–2):231–238. https://doi.org/10.1016/j.chroma.2007.11.095

Chao Z, Zhao W, Gao Y, Hua Z, Xie T (2016) Determination of 16 kinds of phthalates in drinking water by solid phase extraction - gas chromatography mass spectrometry. Chin J Health Lab Technol 18:2607–2610 (in Chinese)

Chen B, Ni J (2010) Toxicological effects of phthalic acid esters on human health. Technol Dev Chem Ind 39(11):46–49 (in Chinese)

Cheng L, Pan S, Ding C, He J, Wang C (2017) Dispersive solid-phase microextraction with graphene oxide based molecularly imprinted polymers for determining bis(2-ethylhexyl) phthalate in environmental water. J Chromatogr A 1511:85–91. https://doi.org/10.1016/j.chroma.2017.07.012

Dargnat C, Blanchard M, Chevreuil M, Teil M (2009) Occurrence of phthalate esters in the Seine River estuary (France). Hydrol Process 23(8):1192–1201. https://doi.org/10.1002/hyp.7245

Deshayes S, Eudes V, Bigourie M, Droguet C, Moilleron R (2017) Alkylphenol and phthalate contamination of all sources of greywater from French households. Sci Total Environ 599-600:883–890. https://doi.org/10.1016/j.scitotenv.2017.05.038

Eskandarpour N, Sereshti H (2018) Electrospun polycaprolactam-manganese oxide fiber for headspace-solid phase microextraction of phthalate esters in water samples. Chemosphere 191:36–43. https://doi.org/10.1016/j.chemosphere.2017.10.029

Esrafili A, Baharfar M, Tajik M, Yamini Y, Ghambarian M (2018) Two-phase hollow fiber liquid-phase microextraction. TrAC Trend Anal Chem 108:314–322. https://doi.org/10.1016/j.trac.2018.09.015

Farahani H, Ganjali M, Dinarvand R, Norouzi P (2008) Screening method for phthalate esters in water using liquid-phase microextraction based on the solidification of a floating organic microdrop combined with gas chromatography–mass spectrometry. Talanta 76(4):718–723. https://doi.org/10.1016/j.talanta.2008.03.002

Farajzadeh M, Khoshmaram L (2015) Development of dispersive liquid-liquid microextraction technique using ternary solvents mixture followed by heating for the rapid and sensitive analysis of phthalate esters and di(2-ethylhexyl) adipate. J Chromatogr A 1379:24–33. https://doi.org/10.1016/j.chroma.2014.12.049

Farajzadeh M, Mogaddam M (2012) Air-assisted liquid–liquid microextraction method as a novel microextraction technique; application in extraction and preconcentration of phthalate esters in aqueous sample followed by gas chromatography–flame ionization detection. Anal Chim Acta 728:31–38. https://doi.org/10.1016/j.aca.2012.03.031

Ferguson K, McElrath T, Ko Y, Mukherjee B, Meeker J (2014) Variability in urinary phthalate metabolite levels across pregnancy and sensitive windows of exposure for the risk of preterm birth. Environ Int 70:118–124. https://doi.org/10.1016/j.envint.2014.05.016

Gao H, Xu R, Cao W, Qian L, Wang M, Lu L, Xu Q, Yu S (2017) Effects of six priority controlled phthalate esters with long-term low-dose integrated exposure on male reproductive toxicity in rats. Food Chem Toxicol 101:94–104. https://doi.org/10.1016/j.fct.2017.01.011

Gao D, Li Z, Wang H, Liang H (2018) An overview of phthalate acid ester pollution in China over the last decade: environmental occurrence and human exposure. Sci Total Environ 645:1400–1409. https://doi.org/10.1016/j.scitotenv.2018.07.093

Gao X, Li J, Wang X, Zhou J, Fan B, Li W, Liu Z (2019) Exposure and ecological risk of phthalate esters in the Taihu Lake basin, China. Ecotox Environ Safe 171:564–570. https://doi.org/10.1016/j.ecoenv.2019.01.001

González-Sálamo J, González-Curbelo M, Socas-Rodríguez M, Hernández-Borges J, Rodríguez-Delgado M (2018) Determination of phthalic acid esters in water samples by hollow fiber liquid-phase microextraction prior to gas chromatography tandem mass spectrometry. Chemosphere 201:254–261. https://doi.org/10.1016/j.chemosphere.2018.02.180

González-Sálamo J, González-Curbelo M, Hernández-Borges J, Rodríguez-Delgado M (2019) Use of Basolite® F300 metal-organic framework for the dispersive solid-phase extraction of phthalic acid esters from water samples prior to LC-MS determination. Talanta 195:236–244. https://doi.org/10.1016/j.talanta.2018.11.049

Guo L, Lee H (2013) Vortex-assisted micro-solid-phase extraction followed by low-density solvent based dispersive liquid–liquid microextraction for the fast and efficient determination of phthalate esters in river water samples. J Chromatogr A 1300:24–30. https://doi.org/10.1016/j.chroma.2013.01.030

Guo L, Ma X, Xie X, Huang R, Zhang M, Li J, Zeng G, Fan Y (2019a) Preparation of dual-dummy-template molecularly imprinted polymers coated magnetic graphene oxide for separation and enrichment of phthalate esters in water. Chem Eng J 361:245–255. https://doi.org/10.1016/j.cej.2018.12.076

Guo H, Song N, Wang D, Ma J, Jia Q (2019b) A modulation approach for covalent organic frameworks: application to solid phase microextraction of phthalate esters. Talanta 198:277–283. https://doi.org/10.1016/j.talanta.2019.02.025

He J, Lv R, Zhan H, Wang H, Cheng J, Lu K, Wang F (2010) Preparation and evaluation of molecularly imprinted solid-phase micro-extraction fibers for selective extraction of phthalates in an aqueous sample. Anal Chim Acta 674(1):53–58. https://doi.org/10.1016/j.aca.2010.06.018

Herreros M, Encinas T, Torres-Rovira L, Garcia-Fernandez R, Flores J, Ros J, Gonzalez-Bulnes A (2013) Exposure to the endocrine disruptor di(2-ethylhexyl)phthalate affects female reproductive features by altering pulsatile LH secretion. Environ Toxicol Pharmacol 36(3):1141–1149. https://doi.org/10.1016/j.etap.2013.09.020

Huang G, Li H, Zhang B, Ma Y, Lin J (2012) Vortex solvent bar microextraction for phthalate esters from aqueous matrices. Talanta 100:64–70. https://doi.org/10.1016/j.talanta.2012.08.009

Huysman S, Van Meulebroek L, Janssens O, Vanryckeghem F, Van Langenhove H, Demeestere K, Vanhaecke L (2019) Targeted quantification and untargeted screening of alkylphenols, bisphenol A and phthalates in aquatic matrices using ultra-high-performance liquid chromatography coupled to hybrid Q-Orbitrap mass spectrometry. Anal Chim Acta 1049:141–151. https://doi.org/10.1016/j.aca.2018.10.045

Jeannot M, Cantwell F (1996) Solvent microextraction into a single drop. Anal Chem 68(13):2236–2240. https://doi.org/10.1021/ac960042z

Jeannot M, Cantwell F (1997) Solvent microextraction as a speciation tool: determination of free progesterone in a protein solution. Anal Chem 69(15):2935–2940. https://doi.org/10.1021/ac970207j

Jia N, Xu H, Hu Y, Lin X, Chen M, Zhang S, Wang G, Ren R (2005) Determination of the phthalates in water samples in Beijing city by solid-phase extraction and gas chromatography. Chin J Anal Lab 11:23–26(in Chinese). https://doi.org/10.13595/j.cnki.issn1000-0720.2005.0253

Keresztes S, Tatár E, Czégény Z, Záray G, Mihucz V (2013) Study on the leaching of phthalates from polyethylene terephthalate bottles into mineral water. Sci Total Environ 458-460 (451–458). https://doi.org/10.1016/j.scitotenv.2013.04.056

Lee Y, Lee J, Choe W, Kim T, Lee J, Kho Y, Choi K, Zoh K (2019) Distribution of phthalate esters in air, water, sediments, and fish in the Asan Lake of Korea. Environ Int 126:635–643. https://doi.org/10.1016/j.envint.2019.02.059

Li J, Liao L (2016) Determination of phthalic acid esters in water using cloud point extraction-gas chromatography. Strait Pharm J (1):45–48.(in Chinese)

Li X, Zhong M, Xu S, Sun C (2006) Determination of phthalates in water samples using polyaniline-based solid-phase microextraction coupled with gas chromatography. J Chromatogr A 1135(1):101–108. https://doi.org/10.1016/j.chroma.2006.09.051

Li J, Cai Y, Shi Y, Mou S, Jiang G (2008) Analysis of phthalates via HPLC-UV in environmental water samples after concentration by solid-phase extraction using ionic liquid mixed hemimicelles. Talanta 74(4):498–504. https://doi.org/10.1016/j.talanta.2007.06.008

Li C, Ma X, Zhang X, Wang R, Chen Y, Li Z (2016) Magnetic molecularly imprinted polymer nanoparticles-based solid-phase extraction coupled with gas chromatography–mass spectrometry for selective determination of trace di-(2-ethylhexyl) phthalate in water samples. Anal Bioanal Chem 408(27):7857–7864. https://doi.org/10.1007/s00216-016-9889-x

Li X, Mo J, Zhu Q, Ni C, Wang Y, Li H, Lin Z, Ge R (2019) The structure–activity relationship (SAR) for phthalate-mediated developmental and reproductive toxicity in males. Chemosphere 223:504–513. https://doi.org/10.1016/j.chemosphere.2019.02.090

Liang P, Xu J, Li Q (2008) Application of dispersive liquid–liquid microextraction and high-performance liquid chromatography for the determination of three phthalate esters in water samples. Anal Chem Acta 609(1):53–58. https://doi.org/10.1016/j.aca.2007.12.025

Lirio S, Fu C, Lin J, Hsu M, Huang H (2016) Solid-phase microextraction of phthalate esters in water sample using different activated carbon-polymer monoliths as adsorbents. Anal Chim Acta 927:55–63. https://doi.org/10.1016/j.aca.2016.05.006

Liu H, Dasgupta P (1996) Analytical chemistry in a drop. Solvent extraction in a microdrop. Anal Chem 68(11):1817–1821. https://doi.org/10.1021/ac960145h

Liu H, Den W, Chan S, Kin K (2008) Analysis of trace contamination of phthalate esters in ultrapure water using a modified solid-phase extraction procedure and automated thermal desorption–gas chromatography/mass spectrometry. J Chromatogr A 1188(2):286–294. https://doi.org/10.1016/j.chroma.2008.02.078

Liu F, Chen X, Li R (2009) Determination of phthalates in Baiyang Lake by dispersive liquid-liquid microextraction and gas chromatography. Administr Tech Environ Monit (2):26–28 (in Chinese)

Liu F, Gao L, Shen J, Liu W, Cai L (2010) Determination of phthalate esters in Baiyangdian lake by solid phase microextraction and gas chromatography. Chin J Chromatogr 28(5):517–520 (in Chinese). https://doi.org/10.374/SP.J.113.010.00517

Liu L, Hao Y, Ren Y, Wang C, Wu Q, Wang Z (2015a) Magnetic nanoporous carbon as an adsorbent for the extraction of phthalate esters in environmental water and aloe juice samples. J Sep Sci 38(8):1411–1418. https://doi.org/10.1002/jssc.201401457

Liu X, Sun Z, Chen G, Zhang W, Cai Y, Kong R, Wang X, Suo Y, You J (2015b) Determination of phthalate esters in environmental water by magnetic Zeolitic Imidazolate Framework-8 solid-phase extraction coupled with high-performance liquid chromatography. J Chromatogr A 1409:46–52. https://doi.org/10.1016/j.chroma.2015.07.068

López-Jiménez F, Rubio S, Pérez-Bendito D (2005) Determination of phthalate esters in sewage by hemimicelles-based solid-phase extraction and liquid chromatography–mass spectrometry. Anal Chim Acta 551(1–2)(142):–149. https://doi.org/10.1016/j.aca.2005.07.032

Luks-Betlej K, Popp P, Janoszka B, Paschke H (2001) Solid-phase microextraction of phthalates from water. J Chromatogr A 938(1):93–101. https://doi.org/10.1016/S0021-9673(01)01363-2

Luo Y, Yu Q, Yuan B, Feng Y (2012) Fast microextraction of phthalate acid esters from beverage, environmental water and perfume samples by magnetic multi-walled carbon nanotubes. Talanta 90:123–131. https://doi.org/10.1016/j.talanta.2012.01.015.104

Luo X, Zhang F, Ji S, Yang B, Liang X (2014) Graphene nanoplatelets as a highly efficient solid-phase extraction sorbent for determination of phthalate esters in aqueous solution. Talanta 120:71–75. https://doi.org/10.1016/j.talanta.2013.11.079

Luo Q, Liu Z, Yin H, Dang Z, Wu P, Zhu P, Lin Z, Liu Y (2018) Migration and potential risk of trace phthalates in bottled water: a global situation. Water Res 147:362–372. https://doi.org/10.1016/j.watres.2018.10.002

Ma J, Li M, Zhao X, Li S, Xiao R (2009) Determination of phthalate esters in water by SPE-RPHPLC. Chin J Anal Lab (3):6–9. https://doi.org/10.13595/j.cnki.issn1000-0720.2009.0066

Meng J, Bu J, Deng C, Zhang X (2011) Preparation of polypyrrole-coated magnetic particles for micro solid-phase extraction of phthalates in water by gas chromatography-mass spectrometry analysis. J Chromatogr A 1218(12):1585–1591. https://doi.org/10.1016/j.chroma.2011.01.057

Ministry of Health, the People's Republic of China (2006) Standards for drinking water quality (GB 5749–2006). China Standard Press, Beijing

Mousa A, Basheer C, Rahman Al-Arfaj A (2013) Application of electro-enhanced solid-phase microextraction for determination of phthalate esters and bisphenol A in blood and seawater samples. Talanta 115:308–313. https://doi.org/10.1016/j.talanta.2013.05.011

Net S, Delmont A, Sempéré R, Paluselli A, Ouddane B (2015) Reliable quantification of phthalates in environmental matrices (air, water, sludge, sediment and soil): a review. Sci Total Environ 515–516:162–180. https://doi.org/10.1016/j.scitotenv.2015.02.013

Parks L, Ostby J, Lambright C, Abbott B, Klinefelter G, Barlow N, Gray L (2000) The plasticizer diethylhexyl phthalate induces malformations by decreasing fetal testosterone synthesis during sexual differentiation in the male rat. Toxicol Sci 58(2):339–349. https://doi.org/10.1093/toxsci/58.2.339

Pérez-Outeiral J, Millán E, Garcia-Arrona R (2016) Determination of phthalates in food simulants and liquid samples using ultrasound-assisted dispersive liquid–liquid microextraction followed by solidification of floating organic drop. Food Control 62:171–177. https://doi.org/10.1016/j.foodcont.2015.10.016

Pinsrithong S, Bunkoed O (2018) Hierarchical porous nanostructured polypyrrole-coated hydrogel beads containing reduced graphene oxide and magnetite nanoparticles for extraction of phthalates in bottled drinks. J Chromatogr A 1570:19–27. https://doi.org/10.1016/j.chroma.2018.07.074

Piri-Moghadam H, Ahmadi F, Pawliszyn J (2016) A critical review of solid phase microextraction for analysis of water samples. TrAC-Trend Anal Chem 85:133–143. https://doi.org/10.1016/j.trac.2016.05.029

Psillakis E, Kalogerakis N (2003) Hollow-fibre liquid-phase microextraction of phthalate esters from water. J Chromatogr A 999(1–2):145–153. https://doi.org/10.1016/S0021-9673(03)00390-X

Qi W, Zhu P, Wu W(2006) Determination of phthalate esters in water by using liquid-liquid extraction gas chromatography. Arid Environ Monit 4:196–199 (in Chinese)

Ranjbari E, Hadjmohammadi M (2012) Magnetic stirring-assisted dispersive liquid–liquid microextraction followed by high performance liquid chromatography for determination of phthalate esters in drinking and environmental water samples. Talanta 100:447–453. https://doi.org/10.1016/j.talanta.2012.08.019

Rashad M, Galal M, Abou-El-Sherbini K, EL-Behairy A, Gouda E, Moussa S (2018) Nano-sized selenium attenuates the developmental testicular toxicity induced by di-n-butyl phthalate in pre-pubertal male rats. Biomed Pharmacother 107:1754–1762. https://doi.org/10.1016/j.biopha.2018.09.006

Rezaee M, Assadi Y, Milani Hosseini M, Aghaee E, Ahmadi F, Berijani S (2006) Determination of organic compounds in water using dispersive liquid–liquid microextraction. J Chromatogr A 1116(1):1–9. https://doi.org/10.1016/j.chroma.2006.03.007

Risticevic S, Niri V, Vuckovic D, Pawliszyn J (2009) Recent developments in solid-phase microextraction. Anal Bioanal Chem 393(3):781–795. https://doi.org/10.1007/s00216-008-2375-3

Salazar-Beltrán D, Hinojosa-Reyes L, Ruiz-Ruiz E, Hernández-Ramírez A, Luis Guzmán-Mar J (2017) Determination of phthalates in bottled water by automated on-line solid phase extraction coupled to liquid chromatography with UV detection. Talanta 168:291–297. https://doi.org/10.1016/j.talanta.2017.03.060

Santana-Mayor Á, Socas-Rodríguez B, Afonso M, Palenzuela-López J, Rodríguez-Delgado M (2018) Reduced graphene oxide-coated magnetic-nanoparticles as sorbent for the determination of phthalates in environmental samples by micro-dispersive solid-phase extraction followed by ultra-high-performance liquid chromatography tandem mass spectrometry. J Chromatogr A 1565:36–47. https://doi.org/10.1016/j.chroma.2018.06.031

Sarafraz-Yazdi A, Amiri A (2010) Liquid-phase microextraction. TrAC - Trend Anal Chem 29 (1):1–14. https://doi.org/10.1016/j.trac.2009.10.003

Serodio P, Nogueira J (2006) Considerations on ultra-trace analysis of phthalates in drinking water. Water Res 40(13):2572–2582. https://doi.org/10.1016/j.watres.2006.05.002

Song X, Chen Y, Yuan J, Qin Y, Zhao R, Wang X (2016) Carbon nanotube composite microspheres as a highly efficient solid-phase microextraction coating for sensitive determination of phthalate acid esters in water samples. J Chromatogr A 1468:17–22. https://doi.org/10.1016/j.chroma.2016.09.030

Stahlhut R, van Wijngaarden E, Dye T, Cook S, Swan S (2007) Concentrations of urinary phthalate metabolites are associated with increased waist circumference and insulin resistance in adult U.S. males. Environ Health Perspect 115(6):876–882. https://doi.org/10.1289/ehp.9882

Sun H, Jiang F, Chen L, Zheng J, Wu Y, Liu M (2014) Determination of three phthalate esters in environmental samples by coal cinder extraction and cyclodextrin modified micellar electrokinetic chromatography. J Chromatogr Sci 52(6):547–552. https://doi.org/10.1093/chromsci/bmt078

Swan S, Main K, Liu F, Stewart S, Kruse R, Calafat A, Mao C, Redmon J, Ternand C, Sullivan S, Teague J (2005) Decrease in anogenital distance among male infants with prenatal phthalate exposure. Environ Health Perspect 113(8):1056–1061. https://doi.org/10.1289/ehp.8100

Viñas P, Campillo N, Andruch V (2015) Recent achievements in solidified floating organic drop microextraction. TrAC - Trend Anal Chem 68:48–77. https://doi.org/10.1016/j.trac.2015.02.005

Wang M (2002) Mutagenicity test of (2-ethylhexyl) phthalate. Occupation and Health 11:35–36 (in Chinese)

Wang W, Ma R, Wu Q, Wang C, Wang Z (2013) Fabrication of magnetic microsphere-confined graphene for the preconcentration of some phthalate esters from environmental water and soybean milk samples followed by their determination by HPLC. Talanta 109:133–140. https://doi.org/10.1016/j.talanta.2013.02.008

Wang X, Song G, Deng C (2015a) Development of magnetic graphene @hydrophilic polydopamine for the enrichment and analysis of phthalates in environmental water samples. Talanta 132:753–759. https://doi.org/10.1016/j.talanta.2014.10.014

Wang M, Yang X, Bi W (2015b) Application of magnetic graphitic carbon nitride nanocomposites for the solid-phase extraction of phthalate esters in water samples. J Sep Sci 38(3):445–452. https://doi.org/10.1002/jssc.201400991

Wang X, Feng J, Tian Y, Li C, Ji X, Luo C, Sun M (2019a) Melamine-formaldehyde aerogel functionalized with polydopamine as in-tube solid-phase microextraction coating for the determination of phthalate esters. Talanta 199:317–323. https://doi.org/10.1016/j.talanta.2019.02.081

Wang R, Ma X, Zhang X, Li X, Li D, Dang Y (2019b) C8-modified magnetic graphene oxide based solid-phase extraction coupled with dispersive liquid-liquid microextraction for detection of trace phthalate acid esters in water samples. Ecotox Environ Safe 170:789–795. https://doi.org/10.1016/j.ecoenv.2018.12.051

Wang Y, Tong Y, Xu X, Zhang L (2019c) Developed magnetic multiporous 3D N-Co@C/HCF as efficient sorbent for the extraction of five trace phthalate esters. Anal Chim Acta 1054:176–183. https://doi.org/10.1016/j.aca.2018.12.046

Wu Q, Liu M, Ma X, Wang W, Wang C, Zang X, Wang Z (2012) Extraction of phthalate esters from water and beverages using a graphene-based magnetic nanocomposite prior to their determination by HPLC. Microchim Acta 177(1–2):23–30. https://doi.org/10.1007/s00604-011-0752-7

Wu X, Hong H, Liu X, Guan W, Meng L, Ye Y, Ma Y (2013) Graphene-dispersive solid-phase extraction of phthalate acid esters from environmental water. Sci Total Environ 444:224–230. https://doi.org/10.1016/j.scitotenv.2012.11.060

Xu J, Liang P, Zhang T (2007) Dynamic liquid-phase microextraction of three phthalate esters from water samples and determination by gas chromatography. Anal Chim Acta 597(1):1–5. https://doi.org/10.1016/j.aca.2007.06.047

Yamini Y, Rezazadeh M, Seidi S (2019) Liquid-phase microextraction – the different principles and configurations. TrAC-Trend Anal Chem 112:264–272. https://doi.org/10.1016/j.trac.2018.06.010

Yang G, Qiao Y, Li B, Yang J, Liu D, Yao H, Xu D, Yang X (2008) Adjuvant effect of di-(2-ethylhexyl) phthalate on asthma-like pathological changes in ovalbumin-immunised rats. Food Agric Immunol 19(4):351–362. https://doi.org/10.1080/09540100802545869

Yang J, Li Y, Wang Y, Ruan J, Zhang J, Sun C (2015) Recent advances in analysis of phthalate esters in foods. TrAC-Trend Anal Chem 72:10–26. https://doi.org/10.1016/j.trac.2015.03.018

Yang R, Liu Y, Yan X, Liu S (2016) Simultaneous extraction and determination of phthalate esters in aqueous solution by yolk-shell magnetic mesoporous carbon-molecularly imprinted composites based on solid-phase extraction coupled with gas chromatography-mass spectrometry. Talanta 161:114–121. https://doi.org/10.1016/j.talanta.2016.08.037

Yang J, Shi L, Zhu Y, Zhao C, Yang Y (2018a) Determination of 4 kinds of phthalate esters in water samples by hollow fibre liquid-phase micro-extraction and highly efficient liquid chromatography. Ind Water Treat 38(5):94–97 (in Chinese)

Yang D, Yang Y, Li Y, Yin S, Chen Y, Wang J, Xiao J, Sun C (2018b) Dispersive liquid-liquid microextraction based on solidification of floating organic drop combined with high performance liquid chromatography for analysis of 15 phthalates in water. J AOAC Int 102(6):1–12. https://doi.org/10.5740/jaoacint.18-0160

Yao H, Li Q, Zheng H, Wu Y, Zhang W (2011) Determination and analysis of the five phthalates in environmental water samples in Anshan city. Science paper Online 9:692–695 (in Chinese)

Ye Q, Liu L, Chen Z, Hong L (2014) Analysis of phthalate acid esters in environmental water by magnetic graphene solid phase extraction coupled with gas chromatography–mass spectrometry. J Chromatogr A 1329:24–29. https://doi.org/10.1016/j.chroma.2013.12.086

Yu X, Yue D, Ren Y (2015) Possible mechanisms involved in degradation of phthalic acid esters in the environment. Ecol Sci (4):180–187 (in Chinese). https://doi.org/10.14108/j.cnki.1008-8873.2015.04.029

Yuan S, Liu C, Liao C, Chang B (2002) Occurrence and microbial degradation of phthalate esters in Taiwan river sediments. Chemosphere 49(10):1295–1299. https://doi.org/10.1016/S0045-6535(02)00495-2

Zgoła-Grześkowiak A, Grześkowiak T (2011) Dispersive liquid-liquid microextraction. TrAC-Trend Anal Chem 30(9):1382–1399. https://doi.org/10.1016/j.trac.2011.04.014

Zhang Y, Lee H (2013) Low-density solvent-based vortex-assisted surfactant-enhanced-emulsification liquid–liquid microextraction combined with gas chromatography–mass spectrometry for the fast determination of phthalate esters in bottled water. J Chromatogr A 1274:28–35. https://doi.org/10.1016/j.chroma.2012.12.017

Zhang H, Chen X, Jiang X (2011) Determination of phthalate esters in water samples by ionic liquid cold-induced aggregation dispersive liquid–liquid microextraction coupled with high-performance liquid chromatography. Anal Chim Acta 689(1):137–142. https://doi.org/10.1016/j.aca.2011.01.024

Zhang H, Hu X, Lin S (2014) Determination of 15 phthalate esters in drinking water by solid phase extraction-ultra performance liquid chromatography-tandem mass spectrometry. Chin J Anal Chem 42:1281–1287(in Chinese)

Zhang Z, Zhang H, Li J, Yang G (2017) Determination of phthalic acid esters in seawater and sediment by solid-phase microextraction and gas chromatography-mass spectrometry. Chin J Anal Chem 45(3):348–356. https://doi.org/10.1016/S1872-2040(17)60999-X

Zhang Q, Song J, Li X, Peng Q, Yuan H, Li N, Duan L, Ma J (2019) Concentrations and distribution of phthalate esters in the seamount area of the Tropical Western Pacific Ocean. Mar Pollut Bull 140:107–115. https://doi.org/10.1016/j.marpolbul.2019.01.015

Zhao R, Liu Y, Zhou J, Chen X, Wang X (2013) Bamboo charcoal as a novel solid-phase microextraction coating material for enrichment and determination of eleven phthalate esters in environmental water samples. Anal Bioanal Chem 405(14):4993–4996. https://doi.org/10.1007/s00216-013-6865-6

Zhao H, Huang M, Wu J, Wang L, He H (2016) Preparation of Fe_3O_4@PPy magnetic nanoparticles as solid-phase extraction sorbents for preconcentration and separation of phthalic acid esters in water by gas chromatography–mass spectrometry. J Chromatogr B 1011:33–44. https://doi.org/10.1016/j.jchromb.2015.12.041

Zhou Z, Li T, Xu W, Huang W, Wang N, Yang W (2017a) Synthesis and characterization of fluorescence molecularly imprinted polymers as sensor for highly sensitive detection of dibutyl phthalate from tap water samples. Sensor Actuat B-Chem 240:1114–1122. https://doi.org/10.1016/j.snb.2016.09.092

Zhou J, Zhu R, Shao Q, Huang M, Zhang Z, Wu X (2017b) Establishment of enzyme linked immunosorbent assay for dibutylphthalate and investigation of water pollution in Zhenjiang. Jiangsu Agr Sci 45(05):289–292(in Chinese). https://doi.org/10.15889/j.issn.1002-1302.2017.05.075

Zhu K, Zhang L, Hart W, Liu M, Chen H (2004) Quality issues in harvested rainwater in arid and semi-arid Loess Plateau of northern China. J Arid Environ 57(4):487–505. https://doi.org/10.1016/S0140-1963(03)00118-6

Zhu C, Xiong H, Li Y, Zhang Y, Li L, Lin H, Han J, Xu B, Wang X, Wu B, Ma X, Han J, Shu W, Cao J (2006) Low dose dibutylphathalate and its toxic effect on nervous system. Chin J Clin Rehabilitation 8:76–78 (in Chinese)

Chapter 16
Environmental Impact and Treatment of Tannery Waste

Naveen Patel, Shraddha Shahane, Deepak Chauhan, Dhananjai Rai, Md. Zafar Ali Khan, Biswanath Bhunia, and Vinod Kumar Chaudhary

Contents

N. Patel (✉) · S. Shahane
Department of Civil Engineering, NIT, Agartala, Tripura, India

D. Chauhan · D. Rai
Department of Civil Engineering, BIET, Jhansi, Uttar Pradesh, India

M. Z. A. Khan
Department of Civil Engineering, Government Polytechnic College, Gonda, Uttar Pradesh, India

B. Bhunia
Department of Bio Engineering, National Institute of Technology Agartala, Agartala, Tripura, India

V. K. Chaudhary
Department of Environmental Sciences, Dr Ram Manohar Lohia Avadh University, Ayodhya, Uttar Pradesh, India
e-mail: vinodkrchaudhary@rmlau.ac.in

Inamuddin et al. (eds.), *Water Pollution and Remediation: Organic Pollutants*, Environmental Chemistry for a Sustainable World 54,
https://doi.org/10.1007/978-3-030-52395-4_16

Abstract Tannery industry is considered to be one of the most important industry because of their economic, employment, and export potential. At the same time, because of the discharge of untreated effluents, these are treated as primary source of pollutants which has immense potential to pollute the soil and water. More than 200 chemicals are being used in this process, and further a mixture of complex toxic substances, such as polychlorinated biphenyl, chromium, sulphides, nitrates, etc., gets discharged as waste. Chromium is considered as the most toxic to humans and biota along with other environments. Various environmental agencies have enforced regulations related to the discharge of these toxic chemicals in to the water bodies. Thus, removal of toxic, such as hexavalent chromium, from the water becomes utmost important. Less work has been reported for the removal of chromium, sulphides, and toxic substances from tannery wastewater.

In this chapter, we have discussed (1) tanning process, which involves various processes through which leather is produced in the tannery industry; (2) characteristics of tannery waste, i.e. liquid waste, solid waste, and gaseous waste; (3) effect of waste on the environment that includes its effect on the soil, water, plant growth, and plant and animal health; (4) treatment technologies, that involve various treatment techniques through which these wastes can be treated or neutralized; and further (5) tannery waste management.

Keywords Tannery · Effluents · Environments · Untreated · Hexavalent chromium · Toxic substances · Waste management · Wastewater

16.1 Introduction

The basic need of one's life is water. Every organism, including human beings, plants, and animals, needs this essential resource for their survival. Apart from domestic purposes, such as drinking, cooking, washing, etc., water has many other essential usages, such as in agricultural purposes, industrial purposes, hydropower generation, and maintenance of healthy ecosystem (Bibi et al. 2016). While due to the continuous increase in the population, demand of water is rising at a rapid rate in order to satisfy their needs. Water is one of the main threats that the whole world is facing today in terms of quality and quantity. This problem further deteriorates in the case of developing countries, as most of them are not able to provide clean potable water to the majority of the population, resulting in severe health ailments or even death; approximately, 3.1% of the deaths are related to consumption of contaminated water (Pawari and Gawande 2015). Some health impacts are immediate, whereas some are noticed over time; these include illnesses related to the stomach and intestines, such as vomiting, diarrhea, cramps, and many other harmful effects (Montgomery and Elimelech 2007). The World Health Organization indicates that nearly 80% of diseases are somewhere and somehow related to water contamination, and a notable number of countries are not able to fulfil the standards laid by them for drinking water (Khan et al. 2013). There are a number of reasons associated with this issue; out of which, the most common is the enormous increase in the number of industries in the last few decades because of their contribution in economic growth. Rapid industrialization is associated with increase in level of environmental pollution in context of not only water but also to noise, air, and soil.

We all know that for any industrial process, water acts as a key raw material; in any form either volume or weight, it exceeds all other liquid or solid inputs used in manufacturing process. It also plays a key role in deciding the location of any industrial setup (Kollar and MacAuley 1980). As observed, most of them are located near banks of water bodies so that water is readily available. Apart from huge water requirement for different industrial purposes, the problem further rises, as only a small fraction of the water is converted in their required product, and only a small amount is lost by evaporation, and the rest makes its way into water bodies in form of waste. The waste generated from industrial units joins the municipalities which results in pollution of natural water bodies. These industrial wastes join water bodies either directly or emptied into municipal sewers carrying waste, which affect normal functioning of the water body. Now, a general perception of people has changed towards industries that only chemical industries cause pollution; apart from them, a number of industries are there which are degrading the natural environmental balance, and the extent of pollution varies from industry to industry. In general, no industry is pollution free in present scenario. Some of the industries related to cement, steel, petroleum, textile, pesticides, chemicals, transport vehicles, and leather are hugely polluting the nature. Waste originating from different industries can be divided into three main categories: biodegradable, nonbiodegradable, and radioactive or poisonous waste.

Tannery industry is one of the industries that is polluting the environment and its resources particularly water bodies (Leta et al. 2003). This ancient craft was initially practiced for over years at the village level of developed countries, and with the passage of time, this industry has shown a notable growth in developing countries as well due to strict norms of the former. Now, it has acquired status of a mature industry which plays an important role in the economy of producing country and lead to its development, as leather is an important foreign exchange earner due to its application in making a number of useful products (Joseph and Nithya 2009).

Tannery industry is basically associated with the manufacturing of leather and related products; more specifically, it is the place where a process termed as tanning takes place. Tanning is a process in which skin and hides of animals are processed through many stages to make leather (Dargo and Ayalew 2014). This process uses variety of chemicals, such as sodium sulfide, lime, ammonium sulfate, vegetable tannins, sodium chloride, chrome salts, and bactericides, and further high quantity of water is used for its processing (Cooman et al. 2003). Conventional tanning technology is adversely affecting the environment due to large amount of chemical and organic pollutant generation. These generated pollutants mostly present in effluent discharge and emerge as a serious threat to the environment.

16.2 Tannery Process

Manufacturing of leather during tanning process is a complex method which is performed into two parts: beam house operations and tanning process. Figure 16.1 shows various processes that are involved in the manufacturing of leather. In first step, i.e. beam house operations, blood and dirt from hides of animals are removed by washing which is followed by softening and salt removal from hides by soaking in water (Cassano et al. 2001). Fatty acids are also removed by fleshing. In order to provide better penetration of tanning agents and hair removal, swelling of hides is required which is done by liming. We use alkaline medium of sulphide and lime for chemical dissolution of the hair and epidermis. To facilitate de-hairing, sodium sulphide is added (O'Flaherty et al. 1965). In the process of liming, a high concentration of sodium sulphide, organic matter, and lime is produced which joins the effluent. To remove hair remnants and to degrade proteins, hides are neutralized by ammonium salts followed by treatment with enzymes. This leads to generation of high ammonium waste in the effluent.

After these stages, hides are prepared for tanning by a process known as pickling. Acids, mainly sulphuric acid, are added in order to adjust the pH value of hides (Cassano et al. 2001). In order to prevent hides from swelling, salts are added. In tanning process, reaction of collagen fibers present in hides takes place with chromium, tannins, alum, or other chemical agents. There are a number of compounds which are used as tanning agents; some of them are alum, formaldehyde, syntans, heavy oils, and glutaraldehyde. Nearly 300 kg of chemicals are used per ton of hides during the tanning process. Table 16.1 shows list of chemicals that are consumed for leather processing.

On the basis of tanning agent, tanning operations are further divided in chrome tanning and vegetable tanning. In vegetable tanning, natural organic substances are used which are derived from plants, and it is done in series of vats (Zywicki et al. 2002). In the case of chrome tanning, chromium salts are used, and it is performed at higher pH. Out of the total leather produced nearly 90% uses chromium salt for tanning (Stein and Schwedt 1994). When tanning is completed, tanned leather is piled down, wrung, and graded for required thickness and quality. Retaining, fat liquoring, and dyeing are the additional steps which are used in chrome tanning unlike vegetable tanning. During fat liquoring, oil gets introduced into the skin

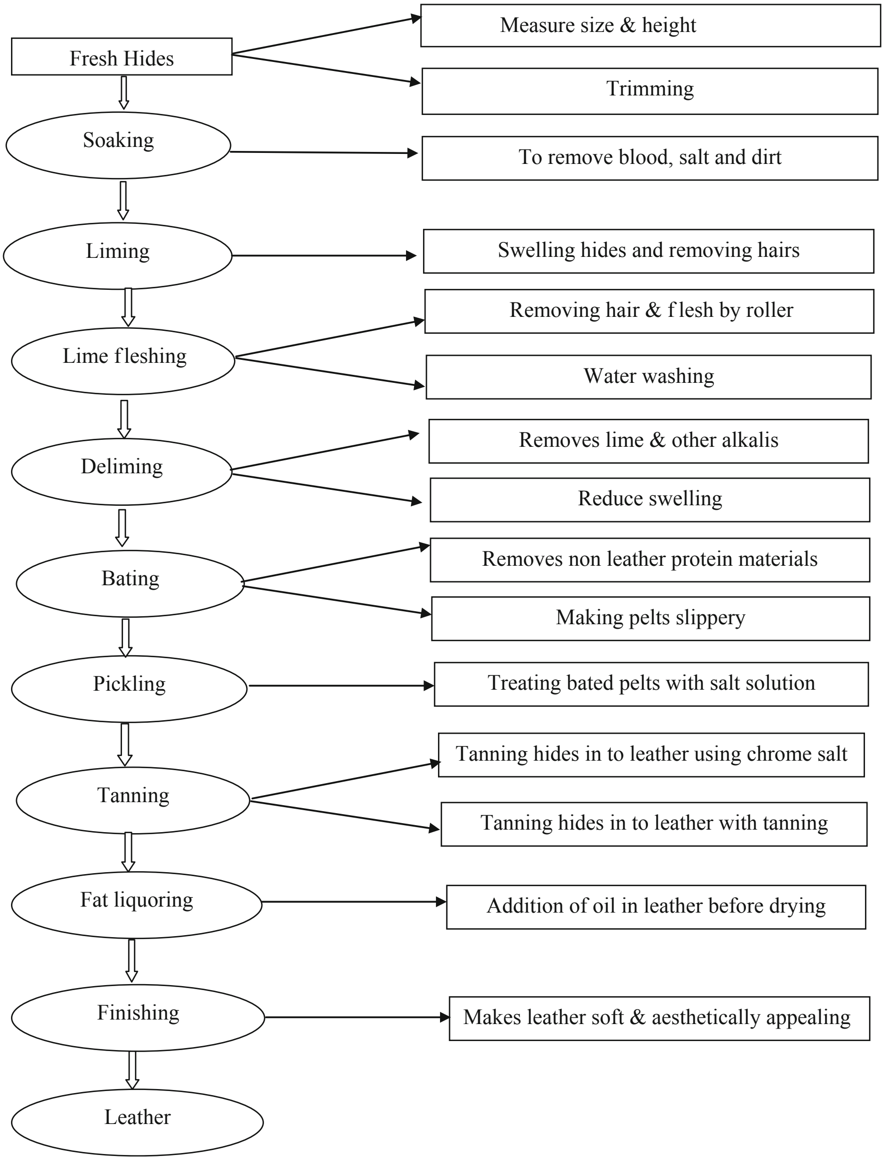


Fig. 16.1 Leather manufacturing process

before the leather is dried in order to replace the natural oil that had been lost in beam house and tan yard processes. Subsequent finishing operations are performed after drying, such as buffing, embossing, and plating, which are done to make leather soft and aesthetically appealing (Midha and Dey 2008). In the tanning industry

Table 16.1 Various chemicals consumed in leather processing (Murad et al. 2018)

Name of Chemical	In kg/ton of Hides or Skin Process
Soaking aids	1.0–2.5
Preservatives	2.5–5.0
Lime	80–200
Sodium sulphide	20–30
Sodium chloride	80–100
Ammonium salts	10–15
Sulphuric acid	12–20
Sodium formate	5–12.5
Basic chromium sulphate	60–120
A1uminium (A12O3)	1–20
Zirconium (ZrO2)	0–15
Vegetable tanning	10–220
Synthetic tanning a	20–60
Fatliquores	25–100
Dyes	2.5–20
Binders	20–45
Pigments	10–25
Top coats	20–45
Wax emulsions	2.5–5.0
Feel modifier	1.0–2.0

putrescible hides or skin is converted into leather; tanning agents provide permanent stabilization of skin against biodegradation.

16.3 Characteristics of Waste Generated

The waste generated from tannery industries consists of a mixture of organic and inorganic pollutants and is characterized by strong color, high biological oxygen demand (BOD), high dissolved salts, and high pH. Tanning agents are responsible for processing of hides into leather; during this process, effluent having turbidity, color, and foul smell generates (Dargo and Ayalew 2014), (Buljan and Kral 2011). Studies associated with tannery industries found that chlorinated phenols and chromium were found as a part of tannery effluents (Reemtsma and Jekel 1997). Chromium is an inorganic pollutant and found in oxidation state, having trivalent and hexavalent as most common form (Kotaś and Stasicka 2000). On the other hand, chlorinated phenols are organic pollutants associated with this industry and are proved to be toxic for cellular compounds of animals which may come under influence of this compound (Pasco et al. 2001).

Other notable concerned pollutants include cadmium compounds, azo dyes, copper, cobalt, antimony, lead, pesticide residues, barium, selenium, zinc, arsenic,

Table 16.2 Types of pollutants released at various leather processing

Leather Process	Liquid Pollutants	Solid Pollutants	Gaseous Pollutants
Fresh hides			
Socking	Salt, BOD, COD, DS, and organic nitrogen		
Liming/ unhairing		Hair, lime, and organic sludge	H_2S
Lime fleshing	BOD, COD, TDS, SS, alkanity, and sulphides	Fat containing lime	
Lime splitting		Lime split and organic matter	
Bating/ deliming	BOD, COD, TDS, and ammonia N		NH_3
Tanning	Acidity, vegetable tans, and syntans		
Chrome splitting		Organic matter containing Cr	
Shaving		Chrome containing organic matter	
Retaining	BOD, COD, DS, SS, fats, dyes, vegetable tans, and syntans		
Bating/ trimming		Formaldehyde and chrome trimming	
Leather product	All other finished agents, solvents, and formaldehyde		CH_2O and solvents

polychlorinated biphenyls, mercury, nickel, and formaldehyde resins (Mwinyihija 2010). Effluents are ranked top as the highest pollutants among the entire industrial wastewater tannery process (Shen 1995). Table 16.2 shows various wastes that arise because of tanning process.

Different wastes generated during tannery can be classified as:

16.3.1 Liquid Waste

Tanneries are one of the major water-consuming industries, and a large portion of water goes into waste. Approximately, 30–40 litres of water are required for the processing of 1 kg of raw hide into finished leather that is the reason why most of the tanneries are located near river banks. A study reveals that in India alone 1,75,000 cubic metre per day of liquid waste is generated by 3000 large, medium, and small scale tanneries (Kaul et al. 2005). Characteristics of liquid waste generated not only vary from tannery to tannery but also vary from time to time. Water generated from beam house after soaking, liming, and deliming is highly alkaline in nature and contains lime, hair, decomposed organic matter, organic nitrogen with high BOD, sulphide, and chemical oxygen demand (COD). Due to presence of organic matter in waste, reduction in dissolved oxygen takes place by microbial decomposition which adversely affects the life of aquatic animals (Balasubramanian and Pugalenthi 2000), (Song et al. 2000), (Mwinyihija et al. 2006).

Tanyard process viz. pickling, chrome tanning, leads to generation of acidic and colored wastes. During vegetable tanning, waste consists of organic matter, whereas high amounts of chromium are formed as waste in case of chrome tanning.

16.3.2 Solid Waste

As per European Commission, the amount of solid waste produced depends on different type of factors, such as type of leather produced, technique applied, and source of hides and skins (Basegio et al. 2002). Waste in solid form generated in tannery can be divided into following forms:

- Non-proteinous waste.
- Non-collagenous protein waste.
- Tanned collagen.
- Untanned collagen.

On average, only 20% weight of hide is transformed into leather, and the remaining goes as waste. Only 200 kg out of 1 ton of hides gets converted into finished leather, whereas the remaining gets discharged as waste in form of waste that contains blood, manure, protein, greases, and fat (Cooray 1999). A part of solid waste or byproducts fixed consumers in the gelatin, textile, glue, and artificial leather industry. Approximately, 35% of the original protein material comes out as effluent tannery sludge, flashings, showings, and brimming. Only a small fraction of solid waste produced in different tannery steps is utilized due to insufficient market (Cheda et al. 1984).

16.3.3 Gaseous Waste

Tanneries are well known to discharge dust, odorous gases, and smoke into the atmosphere (Shastri 1977). Nitrogen and sulfur are the main source of foul smell in the tannery industries. Decay of hides of animals starts immediately after its removal from animal body before its proper curing (Kiernan 1985). Hides which have given delayed curing may not smell bad in salted condition, but curing salt is removed during soaking, and it increases chances of protein putrefaction and possibility of bacterial growth (Mckinney 1969).

Chrome tanning or mineral tanning has an advantage of having no foul smell generation unlike vegetable tanning which suffers from bad smell as tanning agent comes from variety of plants and found in bark, twigs, nuts, and leaves which have their own peculiar smell.

16.4 Effect of Waste on Environment

Pollution due to tannery industries causes horrible ecological crisis to which we are subjected in the modern time. Due to improper management practices, tannery industry is polluting the environment day by day, and further condition becomes worsen as nearly 95% of tannery industries are built in unplanned way throughout the world (Kaul et al. 2005). Wastes generated from tanneries are the primary pollutant to the environment and has potential to pollute both soil and water because of its properties, such as discoloration, toxic chemical constituents, and high oxygen demand (Song et al. 2000).

Most of the tanneries throughout the world use chromium salts for tanning purpose in order to provide better leather water resistance, flexibility, and high shrinkage temperature, but chromium salts are not fixed completely by hides, and the remaining nearly 70% joins the spent tanning liquor (Cassano et al. 2007). High amount of chromium has mutagenic, carcinogenic, and teratogenic effects on animals, humans, and many plants along with bacteria inhabiting aquatic environments (Naik et al. 2007). This may lead to effects, such as headache; dizziness; irritation to skin, eyes, and lungs; poisoning of kidney, liver, or nervous system; or collapse due to insufficient oxygen (Lippmann 2000).

Chromium pollution is increasing in the world due to the increase in tannery industries and can be notably observed in countries, such as India, Pakistan, South Africa, Latin America, Burkina Faso, Ethiopia, and Sudan, where a large number of tannery industries are operating, and all of them are releasing waste containing toxic chromium and phenolics (Felsner and Kiruthu 1996). More specifically, adverse effect of tannery effluents can be studied in the following:

16.4.1 Soil Profiles

We all know the importance of soil in our ecosystem, as it is crucial for plant and animal life due to its vitality as a growth substrate for their development and continual growth. But this crucial resource of life is adversely affected by the presence organic and inorganic contaminants that are produced during tannery operation and discharge with effluent waste. The area of soil adjacent to tanneries are adversely affected by pollutants and lead to heavy metal contamination in the agricultural soil notably shown in areas of Kanpur, Jajmau in India. Continuous application of sludge for irrigation causes accumulation of heavy metals in soil, such as cadmium, zinc, lead, chromium, manganese, and many more, and it will lead to the release of heavy metal into groundwater or soil solution available for plant intake due to reduction in soil capacity to retain heavy metal. Soil contamination with heavy metal or micronutrients in phytotoxic concentrations affects adversely both human health as well as plants (Avudainayagam et al. 2003). As the land is irrigated with the wastewater rich in chromium sulphate, it leads to the increase in the amount of harmful chromium in the soil (Babyshakila and Usha 2009). At high level, chromium is mutagenic, noxious, carcinogenic, and teratogenic in nature and subsists as an extremely poisonous anion. Apart from chromium, chlorides and nitrates also released as the end product, when sodium chloride is used as a raw material (Mondal et al. 2005) in the tanning process. Increase in pH of the soil results due to alkalization caused by presence of sodium carbonate, sodium bicarbonate, sodium chloride, and calcium chloride produced during the tanning process (Tadesse and Guya 2017).

16.4.2 *Water Profile*

Effluents produced during tannery operations release color and diminish the quality of the water that is why they are of a large scale environmental concern (Pepper et al. 1996). Waste produced during the tannery process is consists of biodegradable organic matter, such as carbohydrates and proteins, which is responsible for the depletion of dissolved oxygen level of the water body, resulting from microbial decomposition of organic matter (Mwinyihija et al. 2006).

Due to reduction in oxygen level, anaerobic activity starts in the water system, and it will lead to the release of toxic gases into the water body which is harmful for the survival of aquatic species (Mwinyihija et al. 2006), (Barman and Lal 1994). Fishes and other aquatic animals are badly affected by the presence of sulphide released during the tannery process.

16.4.3 *Vegetable and Plant Growth*

Crop growth and yield gets highly affected when water from the tannery is used as source of irrigation (Camplin 2001). Further, it leads to the accumulation of different heavy toxic metals through the food chain at different tropical levels. Wastewater generated from tanneries, if used for irrigating crop, causes phytotoxicity in plants and results in salinity stress in plants. It affects various metabolic activities that lead to reduction of vegetative growth and also reproductive growth loss of plants in long term. Apart from this, it affects activities, such as photosynthesis, respiration, mitotic activities, and shortened germ sprouting and also leads to the increase in number of reactive oxygen species in the system (Camplin 2001). Accumulation of heavy metals depends upon number of factors, such as plant species, pH, redox, cation exchange capacity, dissolved oxygen, secretion of roots, temperature, and its bioavailability and element present in waste.

Studies suggest that all the parameters responsible for vegetative growth and biomass are reduced in sunflower due to the increase in effluent discharge from tanneries, and this adversely affects sunflower's root and shoot development (Rusan et al. 2007). Similarly, another study had also shown the same adverse growth effect of tannery wastewater on other crops, such as wheat plant, soybeans, and maize (Kılıçel and Dağ 2006, Hewitt and Keller 2003, Nath 2009). Due to high level of salts in tannery waste, such as chlorides and sulphates, the average growth of crop and development of maize were reduced (Hewitt and Keller 1999). Due to the excess amount of dissolved solids, chromium, sulphides, chlorides, high COD, and BOD in the effluents make it unsuitable for crop growth (Mishra and Bera 1995), and lower dilution of effluents inhibits seed germination and seeding growth (Khan and Ghouri 2011). More than 80% concentrations of effluent are harmful for both reproductive and vegetative stages of plants.

16.4.4 Atmospheric System

Air plays an important role in the life of everyone, as it is required for respiration, and no one can live without air. But disappointingly, the whole world is under the influence of air pollution, and the condition further deteriorates in developing countries. One or more hazardous substances are generally present in the polluted air which imparts problem to its belongings. Polluted air contains particulate matters, polycyclic aromatic hydrocarbons (PAHs), ground-level ozone, carbon monoxide, heavy metals, benzene, sulphur dioxide, nitrogen dioxide, ammonia, hydrogen sulphide which are readily present in the waste, originating from tannery industries during liming, deliming, unhearing, and bating processes and mix with the air and cause air problems (Classification of wastes 2009). Chromium is another harmful ingredient which is being released in the atmosphere. 60–70% of chromium in the atmosphere is mainly because of anthropogenic activities. Retention of chromium in the lungs leads to high health risks because of its carcinogenic nature. Till now, industries remains as major source of environmental pollution.

16.4.5 Human and Animal Health

Microorganisms are generally sensitive to chromium (VI) toxicity; tannery worker’s exposure to chromium for a period of five months to fourteen years represents a relevant risk factor for the development of disease associated with the genetic damage. Initial exposure to toxic effluents, such as chromium, lead, zinc, hydrogen sulphide, formaldehyde, and cadmium, leads to headache, dizziness, damage in skin or lungs, irritation of eyes as temporary symptoms. Further exposure leads to poisoning of the liver and collapse of the kidney or nervous system due to limited availability of oxygen and in long term leads to illness, such as ulcers, occupational asthma, genetic defects, bronchitis, and dermatitis, in human as well as animal health (Tare et al. 2003).

16.5 Tannery Waste Treatment Technologies

Generally, various physico-chemical and biological methods or combination of both are used for treatment of tannery waste effluent. Tannery waste can be treated by various methods. In general practice, individual tannery applies only to pre-treatment or a part pre-treatment, and sometimes there is no treatment, and they simply send the effluent to a centralist treatment plant, but a treatment is necessary due to toxicity of the effluent at each and every level (Midha and Dey 2008). Generally, for treatment of tannery effluent, physical and chemical methods are generally employed, but they often are unable to remove the contaminants, and they are found to be costly in comparison to biological methods. That is why biological methods are more favorable and cost-effective for treatment of tannery effluents. A group of organisms work together in the presence or absence of oxygen to carry out decomposition of pollutants, as they utilize them as a source of energy or nutrients (Buljan and Kral 2011). Many research works have reported that tannery effluent can be treated by using activated sludge process (Ahmad 2002, Srivastava and Thakur 2006). By using activated sludge process, BOD_5 removal of tannery effluent can be attained to 90–97% as suggested by these studies, which indicate that this process of treatment is highly efficient. We have already discussed the necessity of removal of chromium and other heavy metals from industrial waste effluent not only due to its toxicity to human beings but also its adverse effect on soil fertility. For carrying out removal of heavy metals, a number of physico-chemical methods have been employed, such as precipitation by hydrolysis, use of ion-exchange resins, carbonates and sulphides, membrane separation, adsorption on activated carbon, and bioremediation, despite that effluents emerging out of leather industries (Spiegel et al. 2012).

In recent times, low-cost industrial proven advanced methods have been applied which includes hair-save liming, salt-free preserved raw hides and skins, advanced chrome management system, ammonia free or low ammonia bating, deliming methods and many more. By using above mentioned methods, it is possible to reduce pollution load significantly as BOD5 and COD by more than 30%, ammonia nitrogen by 80%, sulphides by 80–90%, total kjeldahl nitrogen (TKN) by 50%, sulphates by 65%, chlorides by 70%, and chromium by up to 90%.

Generally, in the following different phases, treatment of tannery effluents takes place:

16.5.1 Preliminary Treatment

It is often used in developing countries where common effluent treatment plants is used for examining the tannery clusters and for removal of not only sand/grit, grease, and large particles but also helps in the reduction of sulphides and chromium before the effluent gets discharged into the collection tank.

16.5.2 Primary Treatment

Primary treatment is associated with physico-chemical processes where sedimentation and skimming are used for the removal of settleable organic and inorganic solids. Moreover, the extra advantage of this method includes satisfaction of 25–50% of BOD_5, 65% of oil and grease, and 50–70% of total suspended solids (TSS). The sludge generated from primary sedimentation is known as primary effluent or sludge.

16.5.3 Secondary Treatment

Secondary treatment is related with the biological treatment of the waste, which is carried out in the presence or absence of oxygen by aerobic and anaerobic microorganisms, respectively, or in some cases by facultative microorganisms.

16.5.4 Tertiary Treatment

Tertiary method is employed for the removal of waste constituents that cannot be removed by using primary and secondary treatment methods. This method gets associated with the advanced treatment methods for reduction of residual COD.

Choice of treatment method depends upon a number of factors, such as location of plant in respect to neighboring use of land; if a number of tanneries exist together then cooperative treatment will prove to be more economical as compared with the individual tannery waste treatment. It also depends on the final tannery and discharge standard specified by the law (Dixit et al. 2015).

16.6 Tannery Waste Management Process

After discussing all the harmful impact of tannery industry on the environment, it is the need at present hour to work together in order to find a suitable solution that will help to satisfy our needs of leather and causing minimal/zero effect on the environment. For this, we have to adopt following waste management practices.

16.6.1 Waste Management

Fundamental control practices have to be adopted in order to reduce the harmful impact of tannery industry; the general waste management hierarchy must include prevention and reduction of waste, recycle and reuse along with treatment, and disposal of waste (Tare et al. 2003).

16.6.2 Cleaner Technology for Leather Manufacturing

It will reduce the cost of environmental compliance due to reduction in effluent loadings and saving in chemical cost used in manufacture of leather. The need to adopt cleaner technology emerges environmental imperatives, such as reduction in treatment cost, need to meet specific discharge needs, and to provide occupational safety and health standards (Germann 1999). It is good to see that now a days every tannery industry has developed some wastewater management systems and use several on site cleaning equipments (Mizan et al. 2016).

16.6.3 Management and Disposal of Sludge

The main purpose of sludge management or disposal is not only limited to reduction of material by the weight or volume that has to be transported but also to attain the dry matter content. Sludge coming from primary clarification, secondary clarification, and tertiary clarification is transferred to the sludge thickener by the help of a pumping system. After that, water is removed by sludge drying beds, or in some cases, mechanical dewatering is done by centrifuge. And finally, solid is obtained which can be processed more easily (Dixit et al. 2015).

16.6.4 Utilization of Sludge

Sludge generated from tanneries consists of greater heavy metal content, and greater inorganic matter content especially compound content of chromium and sulfur. A number of methods for disposal or utilization of safe tannery sludge have been proposed, practiced, tested, and applied at industrial scale that consists of vitrification, land filling, composting, stabilization, and anaerobic digestion. But none of the abovementioned methods have been founded to be satisfactory enough, and no effective universal solution has been provided for sludge utilization, till now. So, detailed investigation has to be done in order to provide a solution for sludge utilization.

16.6.5 Some Developed Techniques for Treatment of Tannery Effluents

In recent time, some techniques have been proposed for effective treatment of tannery effluent. Some of them are as follows:

- Application of low-cost absorbent for mitigation of pollution caused by tannery effluents in water (Mottalib et al. 2014).
- Treatment of tannery effluents must be simple and effective (Alvarez et al. 2004).
- Characterization of tannery effluents (beam house) and study of chromium recovery by water hyacinth (Panov et al. 2003).
- Exhausted chrome tanning solution regeneration method (Usha et al. 2017).
- Application of gamma radiation for treatment of wastewater from leather industry (Fettig et al. 2017).
- Use of membrane bioreactor for treatment of wastewater from leather industry (Yusuf 2018).
- Nonconventional application of basic chromium sulphate for wet blue production (Muralidhara et al. 1982).

16.6.6 Tannery Byproduct

Apart from principal product, if we are able to produce some product which has utility to us, it is known as byproduct. In case of tannery some solid waste are produced during processing of skins, as well as in trimming and fleshing process are termed as tannery byproducts.

16.7 Conclusion

Tannery operation is growing rapidly due to its application in the leather manufacturing which acts as a source of foreign exchange. But at the same time, it is imparting a huge burden on environmental agencies to treat them due to its potential to pollute the environment and its belongings. Complex characteristics, such as COD, BOD, chromium, sulphide, suspended matters, and heavy metals, are the main reasons because of which there is difficulty in treating waste associated with tanneries. A series of different methods have been used worldwide, but only few of them have given fruitful results. Efficiency of these methods can be improved by using them in combination of one another, as compared with the application of individual method.

To stop tannery operation for the sake of our environment is not the solution. As it is possible to reduce the pollution potential of the waste effluent below a level so that it can’t create a disastrous situation for its inhabitants and provide a safe environment. So active work has to be done by the government agencies to strict the norms and regulations on the permissible level of effluent discharge into the environment. Furthermore, systematic approaches have to be made in order to not only reduce the pollutant but also to recover useful things from it which leads to sustainable development.

Acknowledgements The authors wish to acknowledge the cooperation and assistance received from NIT Agartala. The corresponding author, Naveen Patel, is thankful Assistant Professor Biswanath Bhunia, NIT, Agartala, India, Assistant Professor Vinod Kumar Chaudhary, Dr. RMLAU, Ayodhya and other anonymous reviewers for their valuable suggestions to improve this chapter.

Conflict of Interest The authors declare no conflicts of interest regarding the publication of their chapter.

References

Ahmad MS. (2002) Biological treatment of tannery wastewaters. Doctoral dissertation, M. Sc Thesis, Institute of Environmental Engineering and Research, UET, Lahore.

Alvarez SG, Maldonado M, Gerth A, Kuschk P (2004) Characterization of tannery effluents and study of the water hyacinth in chromium recovery. Inf Tecnol 15:75–80. https://doi.org/10.4067/S0718-07642004000300012

Avudainayagam S, Megharaj M, Owens G, Kookana RS, Chittleborough D, Naidu R (2003) Chemistry of chromium in soils with emphasis on tannery waste sites. In: Reviews of environmental contamination and toxicology. Springer, New York, pp 53–91. https://doi.org/10.1007/0-387-21728-2_3

Babyshakila P, Usha K (2009) Effect of diluted effluent on soil properties and plant growth. Adv Stud Biol 1(8):391–398

Balasubramanian S, Pugalenthi V (2000) A comparative study of the determination of sulphide in tannery waste water by ion selective electrode (ISE) and iodimetry. Water Res 34(17): 4201–4206. https://doi.org/10.1016/S0043-1354(00)00190-1

Barman SC, Lal MM (1994) Accumulation of heavy metals (Zn, cu, cd and Pb) in soil and cultivated vegetables and weeds grown in industrially polluted fields. J Environ Biol 15(2): 107–115

Basegio T, Berutti F, Bernardes A, Bergmann CP (2002) Environmental and technical aspects of the utilisation of tannery sludge as a raw material for clay products. J Eur Ceram Soc 22(13): 2251–2259. https://doi.org/10.1016/S0955-2219(02)00024-9

Bibi S, Khan RL, Nazir R, Khan P, Rehman HU, Shakir SK, Jan R (2016) Heavy metals analysis in drinking water of Lakki Marwat District, KPK, Pakistan. World Appl Sci J 34(1):15–19. https://doi.org/10.5829/idosi.wasj.2016.34.1.10252

Buljan J, Kral I (2011) Introduction to treatment of tannery effluents. UNIDO, Vienna

Camplin WC (2001) Effect of paper and pulp factory of Indonesia on the growth and yield potential of cereal crops. Environ Pollut 33:324–331

Cassano A, Molinari R, Romano M, Drioli E (2001) Treatment of aqueous effluents of the leather industry by membrane processes: a review. J Memb Sci 181(1):111–126. https://doi.org/10.1016/S0376-7388(00)00399-9

Cassano A, Della PL, Drioli E (2007) Integrated membrane process for the recovery of chromium salts from tannery effluents. Ind Eng Chem Res 46(21):6825–6830. https://doi.org/10.1021/ie070144n

Cheda PV, Mandlekar UV, Handa BK, Khanna P (1984) Joint wastewater management for a cluster of tanneries at Kanpur. In: Proceedings of the industrial waste conference. Purdue University (USA)

Cooman K, Gajardo M, Nieto J, Bornhardt C, Vidal G (2003) Tannery wastewater characterization and toxicity effects on Daphnia spp. Environ Toxicol 18(1):45–51. https://doi.org/10.1002/tox.10094

Cooray N (1999) Cleaner production assessment in small and medium industries of Sri Lanka. Global competitiveness through cleaner production. Second Asia Pacific Cleaner Production Roundtable

Dargo H, Ayalew A (2014) Tannery waste water treatment: a review. Int J Emrg Trends Sci Technol 1(9):1488–1494

Dixit S, Yadav A, Dwivedi PD, Das M (2015) Toxic hazards of leather industry and technologies to combat threat: a review. J Clean Prod 87:39–49. https://doi.org/10.1016/j.jclepro.2014.10.017

Felsner G, Kiruthu S (1996) Status of the leather industry in eight African countries. Pt. 2: Tanzania, Uganda, Zambia and Zimbabwe. J Soc Leath Tech Chem 80(6):187–190

Fettig J, Pick V, Oldenburg M, Phuoc NV (2017) Treatment of tannery wastewater for reuse by physico-chemical processes and a membrane bioreactor. J Water Reuse Desai 7(4):420–428. https://doi.org/10.2166/wrd.2016.036

Germann HP (1999) Science and technology for leather into the next millennium. Tata McGraw-Hill Publishing Company

Hewitt F, Keller T (2003) Water pollution impacts on bean and cereals. J Agron 11(3):175–185

Joseph K, Nithya N (2009) Materials flows in the life cycle of leather. J Clean Prod 17(7):676–682. https://doi.org/10.1016/j.jclepro.2008.11.018

Kaul SN, Nandy T, Szpyrkowicz L, Gautam A, Khanna DR (2005) Waste water management*:* with special reference to tanneries. Discovery Publishing House New Delhi

Khan MA, Ghouri AM (2011) Environmental pollution: its effects on life and its remedies. Res World - J Arts Sci Commer 2(2):276–285

Khan N, Hussain ST, Saboor A, Jamila N, Kim KS (2013) Physico-chemical investigation of the drinking water sources from Mardan, Khyber Pakhtunkhwa, Pakistan. Int J Phys Sci 8(33): 1661–1671. https://doi.org/10.5897/IJPS2013.3999

Kiernan JA (1985) The action of chromium (III) in fixation of animal tissues. Histochem J 17(10): 1131–1146. https://doi.org/10.1007/BF01002538

Kollar KL, MacAuley P (1980) Water requirements for industrial development. J Am Water Works Assoc 72(1):2–9. https://doi.org/10.1002/j.1551-8833.1980.tb04456.x

Kotaś J, Stasicka Z (2000) Chromium occurrence in the environment and methods of its speciation. Environ Pollut 107(3):263–283. https://doi.org/10.1016/S0269-7491(99)00168-2

Leta S, Assefa F, Dalhammar G (2003) Characterization of tannery wastewater and assessment of downstream pollution profiles along Modjo River in Ethiopia. Ethiop J Biol Sci 2(2):157–168

Lippmann M (ed) (2000) Environmental toxicants*:* human exposures and their health effects. Wiley

Mckinney RE (1969) Micro-biology for sanitary engineering. McGraw Hill, New York

Midha V, Dey A (2008) Biological treatment of tannery wastewater for sulfide removal. Int J Chem Sci 6(2):472–486

Mishra P, Bera AK (1995) Effect of tannery effluent on seed germination and early seedling growth in wheat. Seed Research 23:129–131

Mizan A, Zohra FT, Ahmed S, Nurnabi M, Alam MZ (2016) Low cost adsorbent for mitigation of water pollution caused by tannery effluents at Hazaribagh. Bangladesh J Sci Ind Res 51(3): 215–220. https://doi.org/10.3329/bjsir.v51i3.29433

Mondal NC, Saxena VK, Singh VS (2005) Impact of pollution due to tanneries on groundwater regime. Curr Sci 88(12):1988–1994

Montgomery MA, Elimelech M (2007) Water and sanitation in developing countries: including health in the equation 41:17–24. doi:https://doi.org/10.1021/es072435t

Mottalib MA, Khan T, Abser MN (2014) A simple effective treatment of tannery effluents. J Bangladesh Acad Sci 38(2):235–239. https://doi.org/10.3329/jbas.v38i2.21348

Murad ABMW, Mia MAS, Rahman MA (2018) Studies on the waste management system of a tannery: an overview. Int J Sci Eng and Technol Res 7(4):254–268

Muralidhara HS, Maggin B, Phipps H Jr (1982) Conversion of tannery waste to useful products. Resour Conserv Recycl 8(1):43–59. https://doi.org/10.1016/0166-3097(82)90052-9

Mwinyihija M (2010) Main pollutants and environmental impacts of the tanning industry. In: Ecotoxicological diagnosis in the tanning industry. Springer, New York, pp 17–35. https://doi.org/10.1007/978-1-4419-6266-9_2

Mwinyihija M, Meharg A, Dawson J, Strachan NJ, Killham K (2006) An ecotoxicological approach to assessing the impact of tanning industry effluent on river health. Arch Environ Contam Toxicol 50(3):316–324. https://doi.org/10.1007/s00244-005-1049-9

Naik SJK, Pawar AC, Vani K, Madhuri K, Devi VV (2007) Cytogenetic analysis in human to assess the impact of metal pollution from Jeedimetla industrial area, Hyderabad, AP, India. Pollut Res 26(2):263

Nath K (2009) Long term effect of tannery effluent toxicity on crops and modulation of toxicity through zinc, iron and potassium. Res Environ Life Sci 2(4):193–200

O'Flaherty F, Roddy WT, Lollar RM (1965) The chemistry and technology of leather, Vol. 4. Evaluation of leather

Panov VP, Gyul'khandan'yan EM, Pakshver AS (2003) Regeneration of exhausted chrome tanning solutions from leather production as a method preventing environmental pollution with chromium. Russ J Appl Chem 76(9):1476–1478. https://doi.org/10.1023/B:RJAC.0000012670.09621.44

Pasco N, Joanne H, Webber J (2001) Biosensors: MICREDOX-a new biosensor technique for rapid measurement of BOD and toxicity. Biomarkers 6(1):83–89. https://doi.org/10.1080/135475001452832

Pawari MJ, Gawande S (2015) Ground water pollution & its consequence. Int J Eng Res Gen Sci 3(4):773–776

Pepper IL, Gerba CP, Brusseau ML (1996) Pollution science. Academic Press, New York

Reemtsma T, Jekel M (1997) Dissolved organics in tannery wastewaters and their alteration by a combined anaerobic and aerobic treatment. Water Res 31(5):1035–1046. https://doi.org/10.1016/S0043-1354(96)00382-X

Rusan H, Kamre L, Manser T (2007) Wastewater irrigation impacts on crops with respect to heavy metals. Crop Sci 5:114–118

Shastri CA (1977) Noxious smell and other air pollution problem in tanneries, symposium 12th tanners get together. CLRI, Madras

Shen TT (1995) Industrial pollution prevention. Springer, Heidelberg, pp 15–35

Song Z, Williams CJ, Edyvean RGJ (2000) Sedimentation of tannery wastewater. Water Res 34(7):2171–2176. https://doi.org/10.1016/S0043-1354(99)00358-9

Spiegel J, Alegret M, Clair V, Pagliccia N, Martinez B, Bonet M, Yassi A (2012) Intersectoral action for health at a municipal level in Cuba. Int J Public Health 57(1):15–23. https://doi.org/10.1007/s00038-011-0279-z

Srivastava S, Thakur IS (2006) Evaluation of bioremediation and detoxification potentiality of Aspergillus Niger for removal of hexavalent chromium in soil microcosm. Soil Biol Biochem 38(7):1904–1911. https://doi.org/10.1016/j.soilbio.2005.12.016

Stein K, Schwedt G (1994) Chromium speciation in the wastewater from a tannery. Fresenius J Anal Chem 350:38–41. https://doi.org/10.1007/BF00326250

Tadesse GL, Guya TK (2017) Impacts of tannery effluent on environments and human health. J Environ Earth Sci 7(3):88–97

Tare V, Gupta S, Bose P (2003) Case studies on biological treatment of tannery effluents in India. J Air Waste Manage Assoc 53(8):976–982. https://doi.org/10.1080/10473289.2003.10466250

Usha ZR, Mia A, Islam MR, Manir MS, Khan RA (2017) Treatment of waste water from leather industry in Dhaka, Bangladesh. Bangladesh j sci ind res. 52 (Sp. Issue):36

Yusuf M (2018) Handbook of textile effluent remediation. Pan Stanford

Zywicki B, Reemtsma T, Jekel M (2002) Analysis of commercial vegetable tanning agents by reversed-phase liquid chromatography–electrospray ionization–tandem mass spectrometry and its application to wastewater. J Chromatogr A 970(1–2):191–200. https://doi.org/10.1016/s0021-9673(02)00883-x

Kılıçel F, Dağ B (2006) The relationship between some heavy metal concentrations in soils, leaves and fruits of Starking delicious (Malus communis lam.) in Van, Turkey. Rev Anal Chem 25(4):271–284. https://doi.org/10.1515/REVAC.2006.25.4.271

Chapter 17
Methods for the Treatment of Wastewaters Containing Dyes and Pigments

Raja Shahid Ashraf, Zeeshan Abid, Munazza Shahid, Zia Ur Rehman, Gulzar Muhammad, Muhammad Altaf, and Muhammad Arshad Raza

Contents

Abstract Dyes and pigments are complex organic molecules that are widely utilized in different industries leading to effluent discharge, thus polluting water and disturbing the aquatic life. A wide range of physicochemical and biological methods have been introduced for the dye remediation. Constant research developments over the last decade resulted in the evolution of traditional physiochemical methods into advanced oxidation processes. Likewise, biological treatments have also advanced from using microorganisms to biocatalysts and integrated biochemical approaches for dye remediation.

R. S. Ashraf (✉) · Z. Abid · Z. U. Rehman · G. Muhammad (✉) · M. Altaf (✉) · M. A. Raza
Department of Chemistry, Government College University Lahore, Lahore, Pakistan
e-mail: rajashahid@gcu.edu.pk; muhammad.altaf@gcu.edu.pk; mgulzar@gcu.edu.pk

M. Shahid
Department of Chemistry (SSC), University of Management and Technology, Lahore, Pakistan

Inamuddin et al. (eds.), *Water Pollution and Remediation: Organic Pollutants*, Environmental Chemistry for a Sustainable World 54,
https://doi.org/10.1007/978-3-030-52395-4_17

We reviewed a large number of research articles to provide a connoisseur scientific insight based on the existing methodologies and recent advancements in the treatment of dye-contaminated wastewaters. All physical, chemical, and biological methods show the capability to remove selective dyes; however, the mechanisms, conditions, and limitations of each procedure are different. The use of adsorbents, nanofiltration, coagulation-flocculation, and ion-exchange methods have gained popularity because of feasible operational measures, flexibility, low cost, and harmless end products. Chemical, photocatalytic, and electrochemical processes are considered equally useful but involve sludge production, causing a secondary pollution problem. Biological methods, on the other hand, utilize microorganisms or biocatalysts for dye remediation and provide cost-competitive and eco-friendly alternatives to other methods. Current research is focused on improving the specificity, robustness, and scalability of individual practices as well as designing the novel approaches based on integrated and emerging techniques.

Keywords Wastewater treatment · Pollution control · Dyes and pigments · Remediation · Dye degradation · Dye decolorization · Adsorption · Chemical oxidation · Biosorption · Environment

17.1 Introduction

The intensive industrialization and rampant modern textile production facilities coupled with inadequate wastewater treatment have enhanced the discharge of poisonous, baleful, and carcinogenic pollutants, which include dyes and pigments into the environment. Pigments are generally insoluble substances with no chemical affinity to the substrate to be colored; however, dyes being soluble or partially soluble compounds interact with the leather or fiber to impart color. The classification of various dyes is given in Fig. 17.1.

Recently, the risks of dye pollution have reached an all-time high in a multitude of industries, especially in the textile industry. With the annual production of over 700,000 tons, industrial consumption of 10,000 types of dyes and pigments, approximately, releases about 20% as effluent at some point in textile dyeing processes (Almeida and Corso 2019; Ogugbue and Sawidis 2011). Figure 17.2 shows structures of some prominent dyes.

Adulterated water affects human health and aquatic life severely on direct contact with the water bodies or hydrosphere through different mutagenic and carcinogenic effects. Toxic chemicals present in dyes and pigments show lethal effects by damaging the reproductive system, liver, brain, and renal failure (Baskaralingam et al. 2006).

The development of novel treatments for dyes and pigments before discharging to safeguard our ecosystem and natural resources is crucial. Biological degradation,

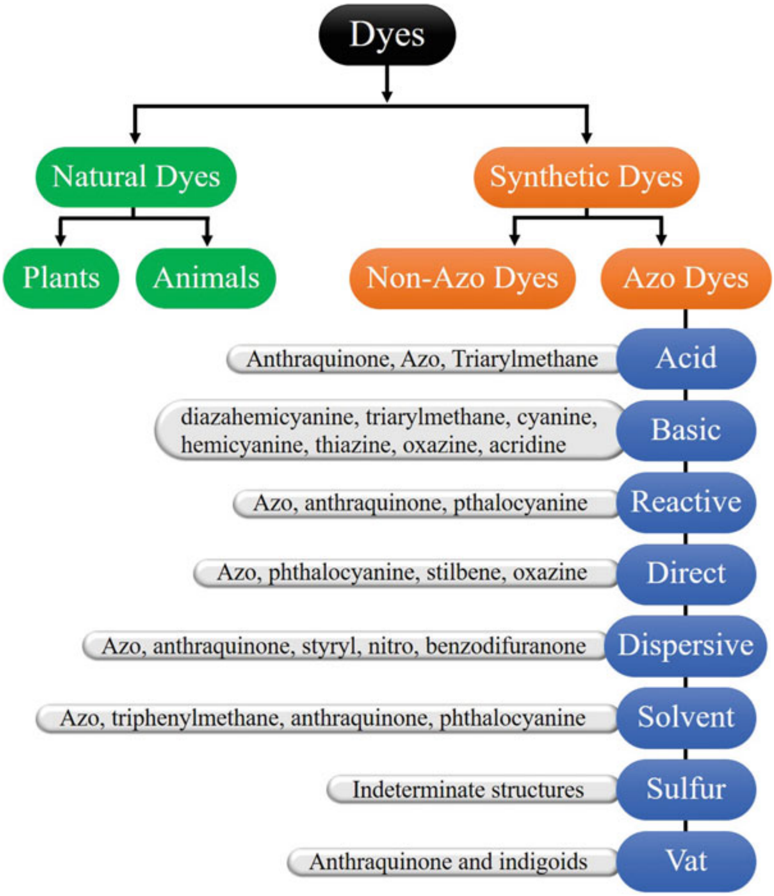


Fig. 17.1 Major classes and subclasses of dyes with the extended list of azo dyes and constituting chemical compounds. (Modified after Ajmal et al. (2014))

physical separation, or chemical processes can be used for the dye removal from wastewater by employing widely used techniques such as membrane filtration, coagulation-flocculation, adsorption, oxidation, biological, and electrochemical treatment (Jebapriya and Gnanadoss 2013).

The implementation of a single or combination of techniques for the removal or degradation of dyes and pigments depends on the composition of wastewater, nature of dyes, and other impurities. Among anionic, non-ionic, and cationic dyes with various chromophoric and auxochromic groups, water-soluble anionic dyes are hard to remove using conventional methods. Similarly, biological treatments are insufficient to remove acidic dyes altogether. The disperse nonionic dyes do not ionize in an aqueous solution and pose resistance to the degradation owing to fused aromatic ring structure. However, advanced oxidation and adsorption processes can easily remove a few cationic dyes such as methyl blue (Robinson et al. 2001). The chapter

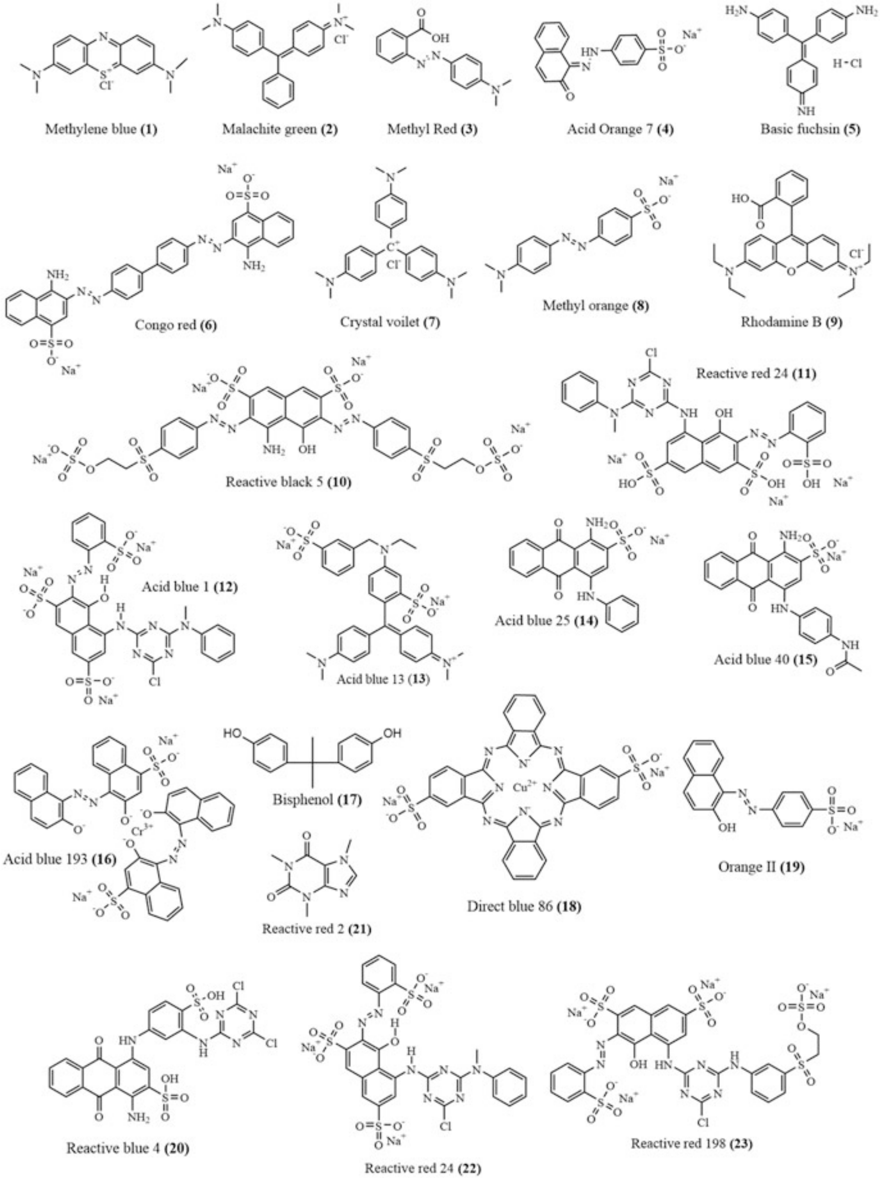


Fig. 17.2 Structures of some prominent organic dyes

presents reports on physical, chemical, and biological techniques for dye degradation from wastewater published in the recent decade with merits and demerits of each technique (Kumar et al. 2012) (Table 17.1).

Table 17.1 Physical, chemical, and biological methods of dye removal with advantages and disadvantages

Treatment	Method	Advantages	Disadvantages
Physical	Adsorption	Effective for a vast range of dyes Waste treatment and waste management	Costly adsorbents and nonselectivity to adsorbents
	Ion exchange	Regeneration and produces high-quality water	Not applicable for all the dyes
	Nanofiltration	Effective removal of mineral salts and all types of dyes	Costly, energy-consuming, and shorter life span. High pressure is needed
	Coagulation-flocculation	Cheap and effective for removing insoluble dyes	Enormous sludge production and pH-dependent
Chemical	Advanced oxidation process	Facile method and easy to apply	H_2O agent needs activation by some means
	Photo Fenton	Highly effective and selective for soluble and insoluble dyes	Sludge production
	Ozonation	Effective for color removal and dealing in a gaseous state	High cost and non-sensitivity to chemical oxygen demand values
	Photocatalytic	No sludge	Not specific in action Produces many by-products
Biological	From bacterial strains	Eco-friendly and 90% efficiency for the oxidizable matter	Less biodegradability of dye with no reduction in salt concentration
	From algal strains	Eco-friendly and special binding affinity for certain dyes	Not effective for all dyes
	From fungal strains	Eco-friendly and degrade dyes by releasing enzymes	No release of enzymes in certain cases

17.2 Physical Methods

Alongside other methods being adapted for degradation or decolorization of dyes from wastewater, significant contributions come from physical methods (Yagub et al. 2014). Based on the reported literature, various physical methods, i.e., adsorption (Gök et al. 2010), coagulation-flocculation (Szyguła et al. 2009), ion exchange (Bayramoglu et al. 2009), and nanofiltration (Gönder et al. 2011), are discussed. Physical methods find most of the worth in the industry and are widely used because of higher effectiveness in dye removal and low operating cost. The most viable physical methods being used are adsorption, ion exchange, and nanofiltration to treat different dye-contaminated industrial effluents (Monika 2012). Among the methods mentioned above, literature reports disclosed that adsorption stands tall due to feasible operational measures, simplicity of design, flexibility, low cost, insensitivity to toxic pollutants, and no harmful products (Gupta 2009). Adsorption carries dual benefits, i.e., waste treatment and waste management, thus, killing two birds with one stone (Rafatullah et al. 2010; Salleh et al. 2011).

Besides adsorption, the ion-exchange method is also reported in different studies but carries a significant drawback of limited efficiency in the removal of dyes from textile effluents. Moreover, recent studies have also used different anion-exchange resins (Greluk and Hubicki 2011), ion-exchange membrane adsorbers (Labanda et al. 2009), and organic hybrid anion-exchange resins (Chiu et al. 2009). Membrane processes such as nanofiltration possess a major drawback of shorter life span with periodic replacement and less favorability for scalable usage against dyes and pigments (Ejder-Korucu et al. 2015).

17.2.1 Adsorption

The adsorption being a surface phenomenon is the accumulation of material at the interface of liquid-solid or gas-solid phases, thus providing adsorbate (accumulated at the interface) and adsorbent (solid surface carrying adsorption). Chemical sorption is based on strong chemical interaction between adsorbate and the adsorbent surface, and physical sorption results from weak van der Waals interaction between adsorbent and adsorbate (Yagub et al. 2014). With time, equilibrium is established between solute (from bulk material) and solution or adsorbent. The following equation is used to measure the adsorption at the equilibrium stage:

$$q_e = \frac{V(C_0 - C_e)}{M} \tag{17.1}$$

where V represents mixture volume in liters, M is adsorbent's mass in grams, and C_o denotes initial and C_e equilibrium concentrations of the adsorbate. Adsorption provides an attractive solution to wastewater treatment provided that the chosen adsorbent must be inexpensive and readily available (Rafatullah et al. 2010). The efficiency of adsorption depends upon the usefulness of different adsorbents, adsorbate to adsorbent ratio, adsorbate-adsorbent interaction, adsorbent particle size, adsorbent surface area, contact time, pH, and temperature (Gupta et al. 2013; Toor and Jin 2012).

Adsorption Isotherms

The adsorption isotherm models represent the amount of solute being absorbed at a constant temperature, per unit weight of adsorbent as a function of equilibrium concentration. Langmuir adsorption isotherm and Freundlich adsorption isotherm are generally used to present absorption data. The equation is given as follows:

$$\frac{C_e}{q_e} = \frac{1}{bX_m} + \frac{C_e}{X_m} \tag{17.2}$$

where C_e and q_e and X_m refer to the solute's equilibrium concentration (mmol//L), the quantity of solute adsorbed by per unit weight of adsorbent (mmol/g of adsorbent), and adsorption capacity (mmol/g), respectively.

Whereas Freundlich adsorption isotherm explains heterogeneous surface adsorption and is formulated as

$$\log q_e = \log k + \frac{1}{n \log C_e} \tag{17.3}$$

where k (mmol g^{-1}) and $1/n$ are the constants (Mittal et al. 2009; Nandi et al. 2009; Yagub et al. 2014).

Types of Adsorbents

There are three types of adsorbent, respectively:

1. Agricultural waste material as adsorbent
2. Industrial waste material as adsorbent
3. Naturally occurring adsorbents

Agricultural Waste Material as Adsorbent

The adsorption process not only treats wastewater but also manages the waste material at a time (Yagub et al. 2014). To get rid of all types of coloring reagents, including dyes and pigments from wastewater, different agricultural waste materials are applied as adsorbents. In all types of adsorbents involving agricultural waste materials, the process of adsorption mainly involves physical forces with a few exceptions of chemisorption (Fig. 17.3) (Yagub et al. 2014; Demirbas 2009).

Methylene blue (**1**) and malachite green (**2**) were removed using *Annona squamosa* seeds with a removal efficiency of over 24.33 and 75.66% for **1** and **2,** respectively, at 27 ± 2 °C and an optimum pH of 6.0. The equilibrium data followed Langmuir adsorption isotherm and pseudo-second-order kinetics with q_{max} values of **1** and **2** on *A. squamosa* seeds as 25.91 and 8.52 mg g^{-1}, respectively (Santhi et al. 2016). Several reports suggest the preparation of activated carbon from agriculture residues following physical and chemical treatments as shown in Fig. 17.4.

Similarly, *Annona squamosa* shell was applied to prepare activated carbon which removed methyl red (**3**) from wastewater successfully using the batch method by optimizing influencing parameters. The isotherm modeling of the adsorption data versus concentration range (80–130 mg L^{-1}) at 303, 313, and 323 K was performed using nonlinear regression analysis suited well with Langmuir adsorption isotherm.

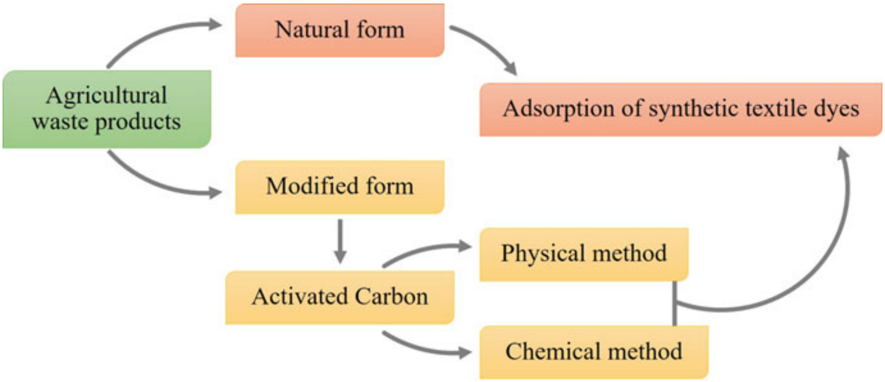


Fig. 17.3 Dye adsorption mechanism by agriculture waste products. Adsorption may take place naturally, or otherwise waste products are modified to allow physical and chemical adsorption of dyes. (Modified after Rangabhashiyam et al. (2013))

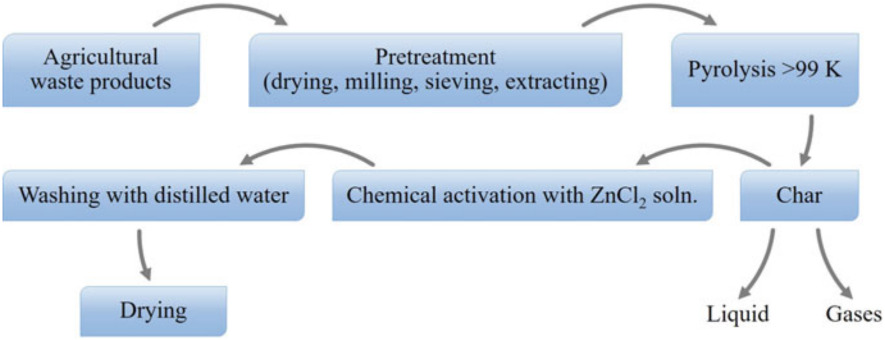


Fig. 17.4 Process flow diagram of activated carbon preparation from agriculture residue. Agricultural waste products are turned into char by physical pretreatments and pyrolysis, followed by chemical activation, washing, and drying. (Modified after Demirbas (2009))

Kinetic modeling confirmed pseudo-first-order and pseudo-second-order rate expressions suggesting activated carbon made from *Annona squamosa* shell a strong adsorbent for decolorization of other industrial effluents as well (Khan and Khan 2018). Likewise, adsorbent prepared from *Annona squamosa* shell adsorbed Orange II (**19**) from aqueous solution using a batch process at optimum contact time and pH. Results from all evaluated concentrations from 5 to 40 mg L^{-1} followed the pseudo-second-order kinetics. Both Langmuir and Freundlich adsorption isotherms confirmed utilization of *Annona squamosa* seeds as an economic adsorbent for dye remediation from effluents (Sonawane and Shrivastava 2011).

Another adsorbent, chemically modified barley straw obtained by treating barley straw with NaOH and a cationic surfactant hexadecyl pyridinium chloride monohydrate, removed anionic dyes such as Acid Blue 40 (**15**) and Reactive Blue 4 (**20**) with q_{max} determined from the Langmuir adsorption isotherm at 250 °C of

51.95 and 31.5 mg g^{-1}, respectively. Experimental work revealed the pseudo-second-order reaction proving the fitness of adsorbent for dye-containing wastewater. In a similar study, surfactant modified barley straw adsorbed **15** (1.02×10^{-4} mol g^{-1}) more effectively than Reactive Black 5 (**10**) (~2.54×10^{-5} mol g^{-1}) (Ibrahim et al. 2010; Oei et al. 2009). Peel of breadnut, *Artocarpus camansi* adsorbed **1** with q_{max} values of 409 mg g^{-1} according to Langmuir adsorption isotherm under pH 4.8. Rapid kinetics of **1** with a pseudo-second-order kinetics model suggested provided an alternative biosorbent to obstruct dyes from wastewater (Lim et al. 2017; Lim et al. 2016).

In the same way, coconut husk and activated carbon adsorbed cyanosine from the aqueous solutions following Langmuir adsorption isotherm and Freundlich adsorption isotherm models with first-order kinetics. Batch studies advocated 86 and 98% dye adsorption by coconut husk and activated carbon with a decrease in chemical oxygen demand from 1650 to 215 mg L^{-1} after adsorption by coconut husk, proving an environmentally benign and low-cost adsorbent (Gupta et al. 2010). *Cucumis sativus* fruit peel adsorbed Acid Red 1 dye from textile wastewater with q_{max} value of 18.76 mg g^{-1} following Langmuir adsorption isotherm and Dubinin-Radushkevitch isotherm models thus showcasing *Cucumis sativus* fruit peel as an effective and cheap adsorbent for industrial wastewater treatment (Khanna and Rattan 2017). Moreover, *Cucumis sativus* fruit peel also adsorbed **1** from wastewater showing pseudo-second-order kinetics while spontaneity and exothermicity were evident from negative values of $\Delta S°$ and $\Delta H°$ (Shakoor and Nasar 2017).

Agricultural solid waste activated by sulfuric acid was employed to remove crystal violet (**7**) and Rhodamine B (**9**) from aqueous solution. Langmuir adsorption isotherm provided the best relativity for isotherm data to adsorb **7** and **9** onto the activated solid waste (Smitha et al. 2017). The applicability of *Cucumis sativus* fruit peel waste as a cheap biosorbent was evaluated by optimizing various reaction parameters. The comprehensive isotherm analysis showed that the crystal violet-*Cucumis sativus* fruit peel system correlated with Langmuir adsorption isotherm model having q_{max} of 149.25 mg g^{-1}. The kinetic and thermodynamic results showed pseudo-second-order and endothermic nature, respectively (Shakoor and Nasar 2019).

Adsorption of Acid Black 25 onto *cempedak durian* peel followed Langmuir adsorption isotherm model with q_{max} of 0.064 mmol g^{-1} at 60 °C. The pseudo-second-order kinetics was obeyed, and thermodynamics process was endothermic (Dahri et al. 2016). Durian rind powder, an agricultural waste material, also adsorbed **1** (95.91%) and brilliant green (87.46%) dyes effectively, and data correlated to Langmuir adsorption isotherm model well (Nuithitikul et al. 2010; Anisuzzaman et al. 2015).

Similarly, activated carbon produced from durian seeds effectively removed remazol brilliant blue reactive dye from water in the batch process. Adsorption data correlated to the Freundlich adsorption isotherm model with the highest removal capacity at pH 2 (Ahmad et al. 2015a). Similarly, chemically modified durian seed with activated carbon also exhibited prominent adsorption of **2** in a batch process by keeping in mind various parameters. Adsorption conformed Freundlich adsorption isotherm model with 97% dye removal at pH 8. Adsorption kinetics matched pseudo-second-order and thermodynamic process being endothermic and spontaneous for the entire adsorption process (Ahmad et al. 2014).

In another study, modified durian seeds were evaluated for removing **3** from aqueous solution with 92.52% efficiency at pH 6.0 and followed the abovementioned adsorption isotherms, kinetics, and thermodynamic analysis (Ahmad et al. 2015b). Papaya seed was chemically modified to eliminate **1** and Congo red (**6**) from aqueous solution. The adsorption data for **1** fitted to Langmuir and Freundlich adsorption isotherm models, while the adsorption kinetics obeyed pseudo-second-order with high values of coefficient of correlation ($R^2 \geq 0.99$) (Nasuha et al. 2011). Likewise, adsorption data of **1** by papaya seeds from aqueous solutions correlated to the Langmuir adsorption isotherm model with a q_{max} of 556 mg g^{-1} with an initial concentration of 50–360 mgL^{-1}, adsorbent dose and pH in the range of 0.05–1.00 g to 3–10, respectively, at 30 °C. The adsorption kinetics followed pseudo-second-order kinetics (Hameed 2009; Mukhlish et al. 2012; Unuabonah et al. 2009).

The papaya seeds also exhibited adsorption of 440 mg g^{-1} to remove Direct Black 38, a tannery dye, following the Langmuir adsorption isotherm model and second-order kinetic equation (Weber et al. 2013). Dye removal and decolorization potential of rice husk against textile wastewater have been studied for **7**, direct orange, and magenta by optimization of influencing factors. Freundlich adsorption isotherm and pseudo-first-order kinetics were obeyed (Verma and Mishra 2010; Chakraborty et al. 2011).

Sorption of **1** was carried with rice husk activated carbon, which achieved adsorption efficiency of over 97% at pH 10 and the initial concentration of 4 mg L^{-1} (Rahman et al. 2012). Likewise, another study reported that activated carbon developed from rice husk removed **2** from aqueous solutions and wastewaters using batch adsorption process with over 63 mg g^{-1} adsorption efficiency following Freundlich adsorption isotherm and Langmuir adsorption isotherm models (Chowdhury et al. 2011; Sharma 2009).

In addition to the use of rice husk, rice husk ash has also demonstrated excellent adsorption capability for **1** from aqueous medium (Sharma et al. 2010; Ahmaruzzaman and Gupta 2011). Rice straw fly ash removed 85% of Reactive Blue 19 (30–100 mg L^{-1}) at highly acidic pH within 1.0 h following Langmuir adsorption isotherm and Freundlich adsorption isotherm models and pseudo-second-order kinetics (Chakraborty et al. 2013b). **1** was removed from organo-modified rice straw using batch adsorption process in which adsorption data correlated to the Langmuir adsorption isotherm model with q_{max} values of 296 and 145 mg/g for modified and unmodified rice straw at 303 K following pseudo-second-order kinetics (Ebrahimian Pirbazari et al. 2016).

Another research endorsed the combination of white-rot fungus *Phanerochaete chrysosporium* and rice straw as an efficient adsorbent for **1** with 88% uptake efficiency from 400 mg/L of initial dye concentration (Cheng et al. 2015). The adsorption process of *Casuarina equisetifolia* needle for methyl violet 2B followed the Langmuir adsorption isotherm model with q_{max} value of 164.99 mg/g with pseudo-second-order kinetics (Dahri et al. 2013). Potential of *Casuarina equisetifolia* needle against **1** and **2** was also according to Langmuir adsorption isotherm model with q_{max} values of over 110 and 77 mg/g, respectively, under optimum conditions (Dahri et al. 2015b).

9 was removed using adsorbent *Casuarina equisetifolia* cone in a batch process and considering the same experimental parameters. Adsorption data correlated completely with Langmuir adsorption isotherm model showcasing pseudo-second-order kinetics, *Casuarina equisetifolia* cone q_{max} value as 49.5 mg g^{-1}, and endothermic nature (Dahri et al. 2016). The *Casuarina equisetifolia* needle was also employed in a study to remove **9** using a similar process resulting in q_{max} value of 82.34 mgg^{-1} (Kooh et al. 2016).

Industrial Waste as Adsorbent

Activated carbon and multiwalled carbon nanotubes were employed to remove Arsenazo (III) and **3** under optimized conditions. The system followed pseudo-second-order adsorption kinetics, while thermodynamically the process was spontaneous and endothermic (Ghaedi et al. 2011). Figure 17.5 illustrates the production of activated carbon from industrial sludge via chemical, physiochemical, and physical methods.

Micro-sized activated carbon was prepared from lather wastage to evaluate adsorption kinetics and equilibrium of Reactive Red 31 and Reactive Red 2 (**21**). The system followed Langmuir adsorption isotherm model and provided q_{max} from 23.15 to 39.37 and 47.62 to 55.87 mg g^{-1} for Reactive Red 31 and **21**, respectively, following pseudo-second-order model (Geethakarthi and Phanikumar 2011).

Coconut coir activated carbon was applied as biosorbent for the removal of **1**. Uptake of **1** from wastewater followed Langmuir, Freundlich, Temkin, and Dubinin-Radushkevitch adsorption isotherm models, and first-order kinetics with the adsorption rate constant of 1.15×10^{-2} min^{-1} and thermodynamic analysis reconfirmed the spontaneous and endothermic nature of the system. Similar findings were obtained when activated carbon prepared from rice husk was examined to adsorb

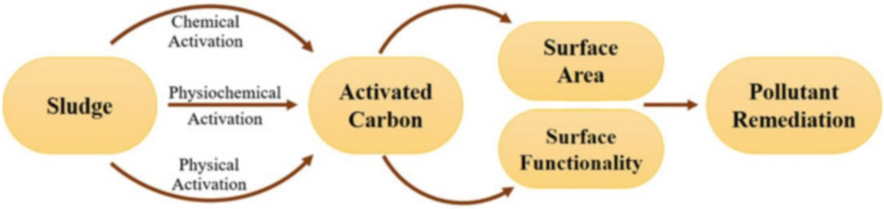


Fig. 17.5 Activation of sludge to activated carbon for pollutant remediation. Chemical, physical, and combined activation methods are used to activate sludge with activated carbon. Large surface area and improved functionality of activated sludge allow an effective pollutant remediation. (Modified after Hadi et al. (2015))

1 (Sharma and Upadhyay 2009; Rahman et al. 2012). Similarly, activated carbon prepared from apricot stones by carbonization and activation with a mixture of phosphoric acid and nitric acid displayed efficient adsorption (99.5%) of methyl orange (**8**) and **1** (Djilani et al. 2015).

Activated carbon prepared from the epicarp of *Ricinus communis* also effectively removed **2** at pH 7 following Langmuir adsorption isotherm model and pseudo-second-order kinetics (Santhi et al. 2010). The activated carbon based on sludge and prepared by pulp wastewater was subjected to fixed-bed adsorption column to remove **1** and Reactive Red 24 (**11**). The results showed weaker desorption for **1** as compared to **11** because of the stability onto the sorbent, but overall analysis proved sludge-based activated carbon to be much better than commercial activated carbon (Li et al. 2011c). The activated carbon prepared from the cotton stalk with microwave radiations proved as good adsorbent for removal of **1** in another study, and adsorption data followed the Langmuir adsorption isotherm. Optimum pH range for absorption was from 9.0 to 10.0, and adsorption efficiency as determined from Langmuir adsorption isotherm was 315.04 mg g^{-1} (Deng et al. 2009).

Activated carbon has also been applied to remove **19**, **1**, and many anionic and cationic dyes in wastewater treatment (Rodríguez et al. 2009). Different other sludge-based activated carbons are also reported for dye removal from aqueous media (Li et al. 2011a). Silver nanoparticle-loaded activated carbon also depicted significant adsorption affinity (98%) toward Direct Yellow 12 under optimized conditions. Adsorption data followed Langmuir adsorption isotherm model and provided q_{max} value of 454 mg g^{-1}. The thermodynamics studies disclosed the process as endothermic, while kinetics studies revealed pseudo-second-order kinetics (Ghaedi et al. 2012).

Another study employed activated carbon extracted from pineapple waste biomass to adsorb **1,** and adsorption data was analyzed based on the goodness-of-fit to Langmuir adsorption isotherm with q_{max} of 288 mg g^{-1}. The study supported the potential of pineapple waste biomass as efficient and cheap raw material to produce activated carbon for dye removal (Mahamad et al. 2015). Likewise, activated carbon prepared from orange peels is reported to have good efficacy for Direct Blue 86 removal from simulated wastewater. Adsorption data based on Langmuir adsorption isotherm with pseudo-second-order kinetics showed 92% removal of Direct Blue 86 (100 mg/L) on 25 °C, pH 2 for 6 g L^{-1} adsorbent dose (El Nemr et al. 2009).

Using fly ash as an adsorbent, the maximum absorption for Reactive Red 23, Reactive Blue 171, Acid Black 1, and Acid Blue 193 (**16**) was noted as 2, 1.8, 11, and 10 mg g^{-1}, respectively, in basic medium with Langmuir adsorption isotherm. Moreover, adsorption kinetics followed pseudo-second-order, and thermodynamics analysis showed the spontaneous and endothermic nature (Sun et al. 2010). Another study revealed that the fly ash or fly ash-based adsorbent might be easily applied for the photocatalytic degradation or removal of **1** along with other heavy metals from the aqueous solutions, and the results were quite optimistic (Visa et al. 2011).

Using fly ash and photo-Fenton system, the possibility of simultaneous removal of hazardous dyes like **8** increases, and fly ash composition assists the adsorption process (Visa and Duta 2013). Besides, hydrothermally modified fly ash can also be applied for dye removal as well as the removal of heavy metals (Visa and Chelaru 2014). An interesting study represented the usage of fly ash synthesized from natural adsorbent zeolite to remove **1** from wastewater using a batch method. Adsorption data followed Langmuir adsorption isotherm, and kinetics obeyed the pseudo-second-order model (Chunfeng et al. 2009).

Further, alkaline-treated biomass fly ash demonstrated noteworthy removal of **10** with adsorption efficiency of 107.53 mg g^{-1} at pH 8.2–10.4 as provided by the Langmuir adsorption isotherm model with pseudo-second-order kinetics (Pengthamkeerati et al. 2010). In another study, activated carbon and fly ash were optimized to remove lignin-based materials from industrial effluents. The experimental data of adsorption correlated well to the Langmuir and Freundlich adsorption isotherm models for both adsorbents. The adsorbent capacities obtained from the Langmuir adsorption isotherm equation were 256 mg g^{-1} (activated carbon) and 17 mg g^{-1} (fly ash) at 60 °C. The thermodynamic studies revealed the sorption onto fly ash as exothermic and activated charcoal as endothermic (Andersson et al. 2011). Another study involving the combined usage of fly ash adsorption and Fenton oxidation for the removal of **9** showed good results. The chemical oxygen demand (98%) was removed by the combined method, and chemical oxygen demand removal capacity of fly ash for Fenton-treated **9** solution was 41 times greater than that for untreated **9** solution (Chang et al. 2009).

Modified red mud was applied against bisphenol (**17**), and optimal results of 82% adsorption were obtained by increasing the experiment duration and dose of adsorbent at pH 3. The results were following the Freundlich adsorption isotherm model and provided the pseudo-second-order kinetics (Zazouli et al. 2013a). Acid-activated sintering process red mud also successfully adsorbed **2** and **7** using batch experiment at a pH of 3.2. Adsorption data suited well to Langmuir adsorption isotherm model and q_{max} of over 60 and 336 mg/g for **7** and **2** were obtained, respectively, with pseudo-second-order kinetics and endothermic nature for **2** and exothermic for **7** (Zhang et al. 2014).

In another investigation, CO_2-neutralized activated red mud was applied to remove Safranin O by response surface methodology at an optimal pH of 8.3 following Langmuir adsorption isotherm model and provided the q_{max} value of 9.7680 mg g^{-1} (Sahu et al. 2015). The adsorptive removal of remazol brilliant blue solution using red mud was studied considering the basic experimental parameters. The results correlated with the Langmuir adsorption isotherm model with an adsorption capacity of red mud as 28.0 mg g^{-1} at 40 °C and pseudo-second-order kinetics (Ratnamala et al. 2012).

Using activated red mud, Acid Blue 113 and **10** removal was studied with different reaction parameters. The red mud was found to have a higher removal efficiency of Acid Blue 113 than **10** at pH 3.0. The results obeyed pseudo-second-order kinetics and Freundlich adsorption isotherm model with maximum adsorption capacities as 83.3 and 35.5 mg/g for Acid Blue 113 and **10**, respectively (Shirzad-Siboni et al. 2014).

Another study opened the horizons of wastewater decolorization containing dyes using $MgCl_2$/red mud as an adsorbent with an efficiency of 98% against reactive blue, acid red, and direct dye. Adsorption data was best correlated to both the Langmuir adsorption isotherm and Freundlich adsorption isotherm models. Langmuir adsorption capacities of reactive blue, acid red, and direct dye were around 28, 9, and 23 mg g^{-1}, respectively (Wang et al. 2009). Reactive Red 198 (**23**) was adsorbed onto active red mud, providing 90% efficiency of dye removal at pH 2–3. The increasing adsorbent dose and contact time lead to more removal efficiency. Adsorption data suited well to Freundlich adsorption isotherm and Temkin isotherms (Zazouli et al. 2013b). Another study revealed significant removal efficiency of phenol, enhanced by an increase in pH. The results showed coherence to Freundlich adsorption isotherm model and pseudo-second-order kinetics (Shirzad-Siboni et al. 2013).

Iron-zeolitic tuff and carbonaceous substances were employed to remove indigo carmine from water, and the latter was more efficient regarding adsorption and pH-independent nature. Adsorption data fitted to the Langmuir-Freundlich adsorption isotherm model, and kinetics was reported to be pseudo-second-order (Gutiérrez-Segura et al. 2009). The granular activated carbon based on sewage sludge was employed to remove **1** following Langmuir adsorption isotherm model with maximum **1** adsorption amount of 132.0 mg g^{-1} and the overall adsorption process as heterogeneous, spontaneous, and endothermic with pseudo-second-order kinetics (Liu et al. 2013b). Another study disclosed that activated carbon prepared from sewage sludge could be efficiently applied for the removal of 4-chlorophenol, as inexpensive, environmentally benign, and cheap adsorbent (Monsalvo et al. 2011; Monsalvo et al. 2012).

Biochar prepared from sewage sludge was opted to remove **1** and **2,** and results conformed with Langmuir adsorption isotherm model and pseudo-second-order kinetics with spontaneous and endothermic nature (Leng et al. 2015). Activated carbon-based sludge derived from paper mill waste had been optimized to remove **1** from the aqueous solution (Li et al. 2011b). In another study, activated carbon-based sludge from paper mill waste was applied for adsorptive removal of **1** and **11**. Experimental data provided the q_{max} values of 263 and 34 mg g^{-1} for **1** and **11**, respectively, following Langmuir adsorption isotherm model (Li et al. 2011a, c). The removal of **1** from palm oil effluent remediation plant by waste-activated sludge was studied considering the reaction parameters. The adsorption data was best fit to both the Langmuir adsorption isotherm and the Freundlich adsorption isotherm models, and kinetics confirmed with pseudo-second-order reaction (Gobi et al. 2011; Zaini et al. 2014).

Natural Adsorbents

Owing to high adsorption capacity, excellent selectivity, greater surface area, and negative charge density, mesoporous silica materials have gained considerable attention as adsorbents to remove basic dyes from wastewater (Anbia et al. 2010).

Mesoporous silica SBA-3 was used to remove **8**, Orange G, and brilliant red X-3B, and adsorption results were compared with calcined and uncalcined silica and later showed higher absorption capacity for dyes following Freundlich adsorption isotherm model and pseudo-second-order kinetics (Anbia et al. 2010). Mesoporous SiO_2 nanoparticles modified with SnO_2 quantum dots provided 100% adsorption of **1** in 5 min conforming to Langmuir adsorption isotherm model and pseudo-second-order kinetics. The q_{max} value of the nanocomposite was reported to be 73.15 mg g^{-1}.

The adsorbent was regenerated after being washed with Milli-Q water, maintaining the adsorption capacity. The environment-friendly nature and reusability established quantum dots/mesoporous silica nanocomposite as potential adsorbent for dyes form wastewater (Dutta et al. 2015). Another study used modified silica nanoparticles to remove anionic dyes (Patra et al. 2016). Silica fume waste material modified with laccase from *Russulaceae* was employed against **10** in a batch process at an optimal pH 9.0. The adsorption process was following the Langmuir adsorption isotherm model and showed q_{max} value of 323.0 mg g^{-1} with spontaneous and endothermic system (Kalkan et al. 2014). Quaternary ammonium polyethylenimine was modified using silica nanoparticle to remove **8**. Adsorption kinetics correlated well to the Langmuir adsorption isotherm model with q_{max} value of 105.4 mg g^{-1} (Liu et al. 2013a).

The peat was also used for adsorptive removal of **9** from aqueous solutions (Chieng et al. 2015). A study on the peat obtained from Panaga, Brunei Darussalam, to remove **6** from aqueous solution was validated by Redlich-Peterson isotherm model and kinetics followed pseudo-second-order equation (Chieng et al. 2014). Similar findings have been confirmed for the adsorption of **7** using yeast peat following the abovementioned kinetics (Zehra et al. 2016; Chieng et al. 2013). Chemically modified fabric peat removed **17** A with q_{max} value of 31.40 mg g^{-1} and pseudo-second-order kinetics, while Freundlich adsorption isotherm model best explained the experimental data (Zhou et al. 2011).

The brown peat was tested against Astrazone blue dye, and removal efficiency of 93.0% was achieved by fitting adsorption data to Langmuir adsorption isotherm model with q_{max} value of 24.0 mg g^{-1}, and adsorption followed pseudo-second-order kinetics (Rusu et al. 2014). The Sphagnum peat moss was employed to adsorb **2** at pH 6.5. Experimental outcomes suited extremely well to the Langmuir adsorption isotherm model, and q_{max} value of 122.0 mg g^{-1} at 20 °C was reported with pseud-second-order kinetics with the spontaneous and exothermic system (Hemmati et al. 2016). Peat was employed to remove p-nitrophenol from aqueous solutions using batch adsorption experiment. Langmuir adsorption isotherm provided q_{max} value of 23.4 mg g^{-1} and followed pseudo-second-order kinetics (Jaerger et al. 2015).

Surface modifications of alumina were carried out using sodium dodecyl sulfate for the removal of phenol and showed 90% removal efficiency as was determined from Langmuir adsorption isotherm model with pseudo-second-order kinetics (Adak and Pal 2009). In another study, surface modifications of alumina were carried using sodium dodecyl sulfate and employed to remove **1**, **2,** and **7** from aqueous solution.

Better removal efficiencies are reported in the pH range of 7.9 to 8.6 (Saitoh et al. 2014). Alumina-coated multiwalled carbon nanotubes adsorbed **23** and Reactive Blue 19 with adsorption coherence to Langmuir and Freundlich adsorption isotherm model, respectively, showing pseudo-second-order kinetics (Malakootian et al. 2015).

The adsorption of **2** from aqueous solution with γ-Al_2O_3 nanoparticles modified by sodium dodecyl sulfate exhibited linear calibration graph over the range of 1.2–250 μg L^{-1} with a relative standard deviation of 1.50% at 100 μg L^{-1}, and Langmuir adsorption isotherm model explained data appropriately with reasonable adsorption efficiency, 72.4 mg g^{-1} (Mohammadifar et al. 2015). Nano-alumina adsorbed Reactive Red 120 dye from aqueous solution significantly at pH 3.0 ensuing Langmuir adsorption isotherm model and pseudo-second-order kinetics (Nadafi et al. 2014). Similarly, aluminum-modified activated carbon as an adsorbent removed **1** from aqueous solution with q_{max} value of 182 mg g^{-1} following Langmuir adsorption isotherm and pseudo-second-order kinetics (Kazeem et al. 2018).

Natural clay was used to remove nile blue and brilliant cresyl blue from the water with a q_{max} values of 25 and 42 mg g^{-1} calculated from Freundlich adsorption isotherm with pseudo-first-order kinetics (İyim and Güçlü 2009). Moroccan natural clays removed **1**, **2,** and **8** from water when adsorption data of **1** and **2** correlated well to Langmuir adsorption isotherm model and **8** to Dubinin-Radushkevitch isotherm model with pseudo-second-order kinetics for dyes (Elmoubarki et al. 2015). The ultrasound-assisted polymerization was carried out to synthesize poly(acrylic acid) hydrogel composite by incorporating kaolin to remove brilliant green from solution at pH 7. Adsorption data followed both Freundlich adsorption isotherm and Langmuir adsorption isotherm with pseudo-second-order kinetics (Shirsath et al. 2013).

Naturally occurring red clay also showed significant adsorption capacity (125 mg g^{-1}) for brilliant green when extracted by batch process, and Redlich-Peterson isotherm model explained the adsorption well. Moreover, adsorption data followed pseudo-second-order kinetics (Rehman et al. 2013). The removal of brilliant red H-EGXL and Procion Yellow H-EXL dyes was studied using synthetic talc and kaolin as adsorbents. A study showed that synthetic talc and kaolin performed well in acidic conditions rather than neutral or alkaline media. The adsorption data was best suited to Langmuir adsorption isotherm (Rahman et al. 2013). Similarly, amino-functionalized attapulgite clay nanoparticle adsorbent uptake **1** from water followed pseudo-second-order kinetics, and according to Langmuir adsorption isotherm model provided q_{max} value as 215.73 mg g^{-1} (Zhou et al. 2015).

The uptake of cationic dye **1** and anionic dye **6** from wastewater by malachite@clay nanocomposites was reasonable with q_{max} value of 277.77 and 238.09 mg g^{-1} following Langmuir adsorption isotherm model and pseudo-second-order kinetics. The results encouraged the application of malachite@clay nanocomposite for better adsorption and dye removal from wastewater (Srivastava and Sillanpää 2017). Another study on **6** was carried out using mixed adsorbents with natural clay materials. The results showed coherence to Freundlich adsorption isotherm and pseudo-second-order kinetics. Overall results were satisfactorily true for the usage of mixed adsorbents with natural clay materials (Vimonses et al. 2010).

Another study revealed the potential usage of organoclay for the maximum removal (99.6%) of **2** (60 mg L^{-1}) from aqueous effluents at pH of 6 and room temperature followed by Langmuir adsorption isotherm model and pseudo-second-order kinetics (Arellano-Cárdenas et al. 2013). Another investigation confirmed the successful removal of basic red 46 by Moroccan crude clay where results complied with Langmuir adsorption isotherm model with pseudo-second-order kinetics (Karim et al. 2009). Similar investigations were carried out to adsorb methyl violet by Moroccan natural clay except for the endothermic nature of the process (Rafati et al. 2016). Montmorillonite clay also exhibited good adsorptive affinity for **1**, and astrazon red violet 3RN and data followed Langmuir adsorption isotherm model with pseudo-second-order kinetics, endothermic, and spontaneous nature.

Nano-clay was used as an adsorbent with further modification to enhance the adsorptive uptake of naproxen from wastewater. Adsorption data fitted to all the applied isotherm models except Langmuir adsorption isotherm and Temkin with q_{max} value of adsorbent as 1.1 mg g^{-1} (Rafati et al. 2016).

Palygorskite clay demonstrated adsorption of basic red 2 from water with q_{max} value of 200 mg g^{-1} following the Langmuir adsorption isotherm model (Taha et al. 2013). In a similar study, Iraqi palygorskite clay adsorbed the maximum amount (99.0 mg g^{-1}) of **6** from water when studied using batch experiment and Langmuir adsorption isotherm model (Taha et al. 2013). Surface modification of palygorskite was carried out to enhance the adsorptive behavior against some reactive dyes. The results complied with Langmuir adsorption isotherm model and pseudo-second-order kinetics (Kurniawan et al. 2012). Activated clay removed **8** from aqueous solution following Langmuir adsorption isotherm model and Temkin isotherm model. The kinetics study showed pseudo-second-order kinetics with spontaneous and exothermic nature (Ma et al. 2013). *N*-vinyl-2-pyrrolidone/itaconic acid/organoclay nanocomposite hydrogels removed safranin T dye following Langmuir adsorption isotherm model with pseudo-second-order kinetics (Çöle et al. 2013). A polymeric clay composite presented adsorptive removal of bromophenol blue according to Freundlich adsorption isotherm model with pseudo-first-order kinetics (El-Zahhar et al. 2014).

Bentonite clay modified from cationic surfactant (hexadecyltrimethylammonium chloride) was used to remove **1**, **7,** and **9**. pH 9 is found appropriate to achieve maximum adsorption (83–99%). The adsorption of **2** onto organoclay was performed in batch system. At pH 6 and room temperature, organoclay delivered 99.6% removal efficiency following Langmuir adsorption isotherm model with pseudo-second-order kinetics (Arellano-Cárdenas et al. 2013). Modified KSF-montmorillonite was used to remove remazol brilliant blue R from aqueous solution following Langmuir adsorption isotherm model and pseudo-second-order kinetics with spontaneous and exothermic thermodynamics (Silva et al. 2012). Another study about the adsorptive behavior of clay, activated clay, and modified clay for the removal of Reactive Blue 21 was carried out with a batch experiment. Adsorption data was fitted well to Freundlich, Langmuir, Temkin, and Halsey adsorption isotherms models with pseudo-second-order kinetics (Vanaamudan et al. 2014; Xue et al. 2010).

Self-assembled organobentonite employed to remove Reactive Blue 13 exhibited 93% dye removal in one step process according to Langmuir adsorption isotherm model (Yao et al. 2012). In another study, surfactant-modified bentonite was also evaluated for the removal of **6**, which was reasonably explained by Langmuir adsorption isotherm and pseudo-second-order models with spontaneous and endothermic properties (Akl et al. 2013). Modified clay, phenol, and catechol were removed from water by Na-montmorillonites in the batch adsorption process. Langmuir adsorption isotherm best explained the adsorption process. Pseudo-second-order kinetics, spontaneous, and exothermic nature was observed (Jourvand et al. 2015; Liu et al. 2014b).

Bis-imidazolium cations were used to modify bentonite to adsorb telon-orange, telon-red, and telon-blue dyes, which were explained better by Langmuir adsorption isotherm model with pseudo-second-order kinetics (Makhoukhi et al. 2015). Organobentonite was studied for the adsorptive removal of Acid Green 25 at three different temperatures (30, 40, and 50 °C). Result correlated to the Langmuir adsorption isotherm model with q_{max} 3.7 mmol g^{-1}, and kinetics reported was pseudo-second-order kinetics (Koswojo et al. 2010). Organobentonite prepared from microwave radiation from a natural source, rarasaponin, was investigated for the removal of **1** and **2**. The adsorption data was best suited to Langmuir adsorption isotherm model and provided satisfactory results for the usage of that adsorbent to remove **1** and **2** (Kurniawan et al. 2012).

7 was removed by manganese oxide-coated sepiolite as an adsorbent with q_{max} value of 319 mg g^{-1} described by Langmuir adsorption isotherm. Moreover, adsorbent showed pseudo-second-order kinetics (Eren et al. 2010). Surface modifications of bentonite carried out using benzyltrimethylammonium chloride, hexadecyltrimethylammonium bromide, and tris(hydroxymethyl)aminomethane surfactants showed enhanced adsorption against **6**. The results were explained by Langmuir adsorption isotherm model and pseudo-second-order kinetics with spontaneous and endothermic nature (Fosso-Kankeu et al. 2016). Organobentonite successfully removed Acid Red 1 and **9** from aqueous solutions. The batch adsorption experiments provided the q_{max} values as 157.4 and 173.5 mg g^{-1} for Acid Red 1 and **9** at pH 9. Results correlated with Langmuir adsorption isotherm model and pseudo-second-order kinetics (Huang et al. 2017).

In a similar study, organic modifications of hydroxyapatite with ethylhexadecyldimethyl ammonium bromide were carried out to remove **2**. The results complied with Langmuir adsorption isotherm model showing q_{max} value of 188.0 mg g^{-1} and kinetics studied revealed pseudo-second-order kinetics (El-Zahhar and Awwad 2016). In another study, poly(epicholorohydrin dimethylamine)-modified bentonite was used for removal of direct fast scarlet, eosin Y, and reactive violet K-3R dyes with q_{max} values of 148, 106, and 88 mg g^{-1}, respectively, following Langmuir adsorption isotherm model and pseudo-second-order kinetics (Kang et al. 2009). Montmorillonite-iron oxide was applied to remove **1** from aqueous solution. Results correlated with Langmuir adsorption isotherm model showing q_{max} value of 71.12 mg g^{-1}, and pseudo-second-order kinetics was observed (Cottet et al. 2014).

Zeolite A was used to modify chitosan, and the resulting product was investigated for the potential to remove Bezactive Orange 16 from aqueous solution. The adsorption results are best explained by Langmuir adsorption isotherm model with q_{max} value of 306 mg g^{-1}, and pseudo-second-order kinetics was noted (Nešić et al. 2013). Zeolite-reduced graphene oxide was also tested to remove **2** and **1**. Adsorption data suited well to Langmuir adsorption isotherm model with q_{max} values of over 48 and 53 mg/g for **2** and **1**. The system was reported as endothermic (Zhu et al. 2014). Phenol was removed by a cost-effective adsorbent, namely, zeolitic tuff, at varying temperatures using a batch process. Results were in compliance with Langmuir adsorption isotherm model showing q_{max} as 34.5, 24.9, 23.8, and 23.3 mg g^{-1} at 25, 35, 45, and 55 °C with pseudo-second-order kinetics (Yousef et al. 2011). Benzene carboxylic acid-derivatized graphene oxide zeolite powder exhibited reasonable adsorption of **9** from aqueous solutions, which was in accordance with Langmuir adsorption isotherm model with q_{max} value of 67.56 mg g^{-1} and pseud-second-order kinetics (Yu et al. 2013).

The microwave-assisted synthesis of NaA (clay type) was carried out to remove **1** from aqueous solution with q_{max} value of 65.0 mg g^{-1}, following Langmuir adsorption isotherm. Pseudo-first-order kinetics, spontaneity, and endothermic nature are observed. Reusability study revealed that NaA would be stable even after five cycles (Sapawe et al. 2013). Kaolin and zeolite were opted to remove **1** from water. Results well suited to Temkin and Dubinin-Radushkevitch isotherm models with endothermic and non-spontaneous nature (Rida et al. 2013).

Mesoporous zeolite-activated carbon composite was employed for the removal of **1**. Results were per Freundlich adsorption isotherm model with pseudo-second-order kinetics (Khanday et al. 2017). Zeolites synthesized from electrolytic manganese residue were used to remove **1**. Results followed Langmuir adsorption isotherm model and pseudo-second-order kinetics (Li et al. 2015). In a similar study, NaA zeolite composites removed **1**, **7**, and fuchsine. Over 98% of the removal was achieved, which was close to the predicted values (Shirani et al. 2014). Zeolite tuff was applied to remove basic blue 41 from water. Results were in accordance with the Langmuir adsorption isotherm model with pseudo-second-order kinetics, and q_{max} value of 192.0 mg g^{-1} was obtained (Humelnicu et al. 2017). In another study, zeolitic imidazolate framework-8 removed 5-tolyltriazole and 1H-benzotriazole from aqueous water. Experimental data was in accordance to Langmuir adsorption isotherm model with $q_{\max}$ values of 298.5 and 396.8 mg g^{-1}, respectively, and pseudo-second-order kinetics was observed (Jiang et al. 2013).

17.2.2 Nanofiltration

For nanofiltration of wastewater, microfiltration membranes with different proportions and size of the zeolite, clay, and polyethylene glycol were optimized. For removal of **7** and **8**, a membrane with 30% of zeolite proportion was selected. A change in initial and time-filtered solution concentration was observed by

UV-visible spectrometry to determine the amount of each dye before and after filtration. Over 95 and 90% removal of **7** and **1** was achieved at 1 to 1.5 bar transmembrane pressure with solution concentrations of over 54 and 35 mg/L, respectively. However, in case of negatively charged **8**, removal was not successful. By heating membranes at 300 °C for 1.0 h, adsorbed dyes were eliminated (Foorginezhad and Zerafat 2017). The sequencing batch reactor in a combination of nanofiltration membranes was designed to reuse the industrial waste effluent by removing remazol (yellow, blue, red) RR dyes. Over 90% of decolorization efficiency was achieved for blue and red dye and above 75% for yellow.

However, when a combined feed of aforementioned dyes was used, the rejection percentage was higher than 40%, indicating relatively low and inferior color removal efficiencies for all three dyes (Zuriaga-Agusti et al. 2010). The integration of biological methods with nanofiltration for the better removal and decolorization of the wastewater was successfully studied. In a study, Reactive Red 120 was studied with such an integrated method, and nanofiltration concentrate was significantly decolorized by biological process and endorsed the potential usage of the designed method for textile wastewater (Paździor et al. 2009).

The spiral wound nanofiltration module opted for the elimination/separation of dyes from the textile waste effluents. The effects of feed pressure, dye concentration, and feed flow rate on dye rejection and recovery were studied. The maximum rejection was observed for **20**. The highest reflection coefficient ($\sigma = 0.969$) was observed for **20**, which marks the impermeability of the nanofiltration membrane to the solute. Permeate characteristics were optimized using Spiegler-Kedem-based model and were not in good correlation with experimental data. Thus, for scalable usage in the future, a more accurate module based on Spiegler-Kedem theory could opt for the textile industry (Dash and Kumar 2017). By bringing nanofiltration in combination with reverse osmosis, composite polyamide membrane modules were reported to be highly effective for decolorization of the wastewater containing dyes and salts. Flux rate was comparable to that of pure water. The effect of varied concentration of dyes and salts was also optimized on spiral wound membrane, and results strongly endorsed the potential scalable usage of the designed membranes (Nataraj et al. 2009).

Polyamide thin-film composite was modified by diethanolamine and used to remove **1**, Sunset Yellow, **6**, and natural red. Modified membranes have shown promising results with steady-state water fluxes of an aqueous solution containing dyes mentioned above, which were quite high in a range between 37 and 54%. Meanwhile, flux decline ratio due to membrane fouling was quite low in a range between 37 and 49%. Through nanofiltration, modified composite membranes have demonstrated efficient dye removal from aqueous solutions (Liu et al. 2017). In another study, nanofiltration of textile waste materials with different commercially available membranes such as Desal 5 DK, Desal 5 DL, N30F, and NF PES10 was reported. The impact of temperature change on permeates quality, and membrane fouling was studied from 20 to 70 °C. Up to 80% of color rejection was noted with nanofiltration membranes, and permeate quality was quite satisfactory for recycling the effluents (Xuan Nguyen and Van der Bruggen 2015).

Polyethyleneimine thin-film composite nanofiltration membranes were modified with SiO_2 nanoparticles for good retention of the **7**. SiO_2 nanoparticles were responsible for enhancing the structural properties of the membrane required for better separation of the dye. Best results were achieved with 0.1% by wt. of SiO_2 nanoparticles, a superior flux rate, and a better rejection over 99% was observed for organic solutions (Kebria et al. 2015). For handling biologically treated wastewater from pulp and paper industry, a two-step nanofiltration process was developed. In the first step, FM NP010 membrane was used and the impact of different working environments such as pH, temperature, transmembrane pressure, and decrease in volume retention factors on membrane fouling was studied. Transmembrane pressure played a major role in membrane fouling. Although the permeate was colorless and free from insoluble materials. However, the removal of chloride ions and conductivity was incomplete. In the second step, a different membrane FMNP030 was used for nanofiltration, which provided better-quality processed water (Gönder et al. 2011).

By use of different layer by layer techniques, composite hollow fiber nanofiltration membrane can be prepared. A nanofiltration membrane is prepared by a pressure-driven layer-by-layer assembly of polyethylenimine and polyacrylic acid on a porous substrate. Multilayer polyelectrolyte nanofiltration membrane was studied to treat brilliant green, Victoria blue B, and **6** dyes and inorganic salts. Dynamically deposited cross-linked nanofiltration membrane exhibited over 95% rejection of $MgCl_2$, in comparison to non-cross-linked, which showed a rejection value of less than 70% (Chen et al. 2015). The removal of **1** from wastewater by a positively charged nanofiltration membrane was reported. Novel membrane PA6DT-C exhibited superior membrane flux compared to commercially available membranes. Over 98% rejection of **1**, and approximately three- to fourfold higher membrane flux was reported (Cheng et al. 2012).

The nanofiltration membrane based on Yttria-stabilized zirconia with molecular weight cut-off was employed for removal of organic dyes from water. After filtration, the permeate samples revealed to be almost colorless. At elevated temperature such as 60 °C, the permeate flux was high with a superior dye recovery (Abdi et al. 2017). Nanofiltration of hazardous dye **6** was carried out using polypiperazine amide nanofiltration membranes. The investigation concluded that 100% removal of dye was achieved at pH 9 with minimum flux decline at room temperature 25 °C and transmembrane pressure of 5 bar (Hairom et al. 2014).

Two types of nanofiltration membranes (negatively and positively charged) were prepared to remove Sulfur Black B dye from effluents. The impact of various operational factors was measured, and 92.3% dye rejection was reported with over 14.5 L/m^2 h flux (Han et al. 2009). Novel loose nanofiltration hollow fiber membranes were developed with a small pore size of about 1.0 nm. Novel membranes, unlike other nanofiltration membranes, showed selectively higher rejection for dyes and lower rejection for inorganic salts. Because of high selectivity, low fouling tendency and greater recovery make such membranes ideal candidates for efficient fractionation and wastewater treatment (Han et al. 2018).

Polyamide nanofiltration membranes having molecular weight cut-off of 200–400 Da and 150–300 Da, respectively, were used to remove Lanaset Blue 2R, remazol yellow GR, and remazol turquoise blue G at different temperatures and pressures. DK membrane showed highest permeate flux at higher temperatures with acidic to neutral pH and 100% color removal of the synthetic wastewater (Hildebrand et al. 2014). Poly(m-phenylene isophthalamide)-based nanofiltration membranes were used to remove Eriochrome Blue Black B, Eriochrome Black T, and alizarin red dyes. The designed nanofiltration membrane showed 98% rejection with a high flux at 0.4 MPa (Huang and Zhang 2011). The nanofiltration membranes were prepared by polyethersulfone-based hollow fibers and employed for the removal of indigo carmine. The obtained results endorsed the efficacy of the nanofiltration membranes by showing 96.4% rejection of dye with 12.8 L m^{-2} h^{-1} bar^{-1} (Gao et al. 2017). Similar study was carried out for indigo carmine using nanofiltration membranes prepared for polyethersulfone-based hollow fibers. Nanofiltration membrane possessed a molecular weight cut-off of 1500 Da, the pore diameter of $\approx$1.96 nm, high pure water permeability of 13.2 LMH/bar, and 94.9% rejection of the dye (Thong et al. 2018).

Sulfonated polyphenylene sulfone-based positively charged nanofiltration membranes are reported. Membranes having 1.13–1.2 nm diameter, molecular weight cut-off of 1627–1674 Da, and highly positive surface charge led to the 99.98% rejection of Safranin O (Zhong et al. 2012). In a similar study, a positively charged nanofiltration membrane showed rejection of 99.8, 99.8, and 99.2% of brilliant green, victoria blue B, and **7**, respectively (Zheng et al. 2013). A novel composite nanofiltration membrane was prepared using plant polyphenols and achieved elevated permeability of 76.3 L/(m^2 h MPa) and 99.0% rejection for **1** (Zhao et al. 2018). The synthesized membrane was further cross-linked with $FeCl_3$. The negatively charged membrane was used to remove dyes such as Sunset Yellow, **6**, and **1** and exhibited rejection rates of 82.2, 99.7, and 99.9%, respectively (Yu et al. 2012).

Low-pressure nanofiltration membranes were fabricated having hydroxyl groups ended hyperbranched polyester with polysulfone ultrafiltration membrane as the porous support. Nanofiltration membranes possessed the 100 and 98.4% rejection of the nanofiltration membrane to **9** and xylenol orange, respectively (Wei et al. 2012). Positively charged nanofiltration membranes were prepared from cross-linking polyimide substrate with polyethylenimine, with molecular weight cut-off of 458 Da with a high rejection (>95%), and high fouling resistance against basic dyes was reported (Wang et al. 2018). Table 17.2 shows different parameters for the adsorbents mentioned in the above section.

17.2.3 Coagulation-Flocculation

Coagulation-flocculation could be applied as a primary treatment or even before and after the major process. Unfortunately, a lot of commercially available coagulants, including aluminum chloride, aluminum sulfate, and polyacrylamide-based materials, are reported to have bad impacts on human health. The dilemma led to the

Table 17.2 List of dyes and adsorbents with different adsorption parameters reported in literature

Dye	Adsorbent	q_{max} (mg/g)	Percentage removal	Isotherm modeling	Kinetics	Thermodynamic studies	Optimum pH	References
2	*A. squamosa* seed	8.52	24.33	Langmuir	Pseudo-second-order	–	6.0	Santhi et al. (2016)
1		25.91	75.66					
3	*A. squamosa* shell	435.25	64%	Langmuir	Pseudo-first-order and pseudo-second-order	Spontaneous and endothermic	–	Khan and Khan (2018)
19	*A. squamosa* shell	–	–	Freundlich, Langmuir	Pseudo-second-order	–	4.0	Sonawane and Shrivastava (2011)
Acid blue	Modified barley straw	51.95	95%	Langmuir	Pseudo-second-order	–	3–8	Ibrahim et al. (2010)
20		31.5	100%					
15	Modified barely straw	–	–	Langmuir	–	Spontaneous and endothermic	–	Oei et al. (2009)
10								
1	*A. camansi*	409	–	Langmuir	Pseudo-second-order	Spontaneous and exothermic	4.8	Lim et al. (2017)
1	*A. camansi* Blanco	369	50%	Langmuir	Pseudo-second-order	Spontaneous and exothermic	2–10	Lim et al. (2016)
		328		Sips				
Acid Blue 113	*C. sativus* peel	59.81	97.65%	Langmuir	Pseudo-second-order	Spontaneous and endothermic	2.0	Lee et al. (2016)
2	*C. sativa* fruit	25	99.86%	Langmuir	Pseudo-second-order	–	6.0	Santhi and Manonmani (2011)
7	*C. sativa* peel	149.25	96.2%	Langmuir	Pseudo-second-order	Spontaneous and endothermic	8.0	Shakoor and Nasar (2019)

(continued)

Table 17.2 (continued)

Dye	Adsorbent	q_{max} (mg/g)	Percentage removal	Isotherm modeling	Kinetics	Thermodynamic studies	Optimum pH	References
Acid Blue 25 (**14**)	*C. durian* peel	26.62	60%	Langmuir	Pseudo-second-order	Spontaneous and endothermic	2.0	Dahri et al. (2016)
2	Durian seed-based activated carbon	–	97%	Langmuir	Pseudo-second-order	Spontaneous and endothermic	8.0	Ahmad et al. (2014)
3	Durian seed	–	92.52%	Langmuir	Pseudo-second-order	Spontaneous and endothermic	6.0	Ahmad et al. (2015b)
Methyl violet	*C. durian* peel	0.606 mmol g-1	95%	Langmuir	–	Spontaneous and endothermic	6.0	Dahri et al. (2015a)
1	Papaya seeds	555.557	80%	Langmuir	Pseudo-second-order	–	3–10	Hameed (2009)
1	Papaya seeds	637.29	–	Langmuir	Pseudo-second-order	–	12.0	Paz et al. (2013)
1	Organo-modified rice straw	296	93%	Langmuir	Pseudo-second-order	Spontaneous and endothermic	7.0–12.0	Ebrahimian Pirbazari et al. (2016)
Methyl violet 2B	*C. equisetifolia* needle	164.99	69%	Langmuir	Pseudo-second-order	Spontaneous and endothermic	6.70	Dahri et al. (2013)
1	*C. equisetifolia* needle	110.8	93%	Langmuir	Pseudo-second-order	Spontaneous and endothermic	4.0	Dahri et al. (2015b)
2		77.6	89%					
9	*C. equisetifolia* needle	49.5	75%	Langmuir	Pseudo-second-order	Spontaneous and endothermic	2.0	Dahri et al. (2016)
9	*C. equisetifolia* needle	82.34	–	Langmuir	Pseudo-second-order	Spontaneous and endothermic	2.9	Kooh et al. (2016)
Reactive Red 31	Activated carbon	39.37	–	Langmuir	Pseudo-second-order	–	2–11	Geethakarthi and Phanikumar (2011)
21		55.87						

2	Activated carbon	27.78	99.04%	Langmuir	Pseudo-second-order	–	7.0	Santhi et al. (2010)
1	Activated carbon from cotton stalk	315.04	95%	Langmuir	–	–	9.0–10.0	Deng et al. (2009)
Direct Yellow 12	Silver nanoparticle-loaded activated carbon	454.54	98%	Langmuir	Pseudo-second-order	Spontaneous and endothermic	1.0	Ghaedi et al. (2012)
Direct Blue 86 (**18**)	Activated carbon prepared from orange peels	33.78	92%	Langmuir	Pseudo-second-order	–	2.0	El Nemr et al. (2009)
Reactive Red 23	Fly ash	2.102	97%	Langmuir	Pseudo-second-order	Spontaneous and endothermic	7.5–8.5	Sun et al. (2010)
Reactive Blue 171		1.860	75%					
Acid Black 1		10.937	97%					
16		10.331	90%					
10	Alkaline-treated fly ash	107.53	–	Langmuir	Pseudo-second-order	–	8.2–10.4	Pengthamkeerati et al. (2010)
17	Modified red mud	–	82%	Freundlich	Pseudo-second-order	–	3.0	Zazouli et al. (2013a)
2	Acid-activated sintering process red mud	336.4	98.5%	Langmuir	Pseudo-second-order	Spontaneous, endothermic, and exothermic	3.2	Zhang et al. (2014)
7		60.5	63.1%					
Remazol brilliant blue dye	Red mud	27.8	90%	Langmuir	Pseudo-second-order	Spontaneous and endothermic	2–6	Ratnamala et al. (2012)
2	Bio chars from sewage sludge	–	–	Langmuir	Pseudo-second-order	Spontaneous and endothermic	~ 5	Leng et al. (2015)
1								
1	Mesoporous SiO_2 nanoparticles decorated with SnO_2 quantum dots	73.15	99.4%	Langmuir	Pseudo-second-order	Spontaneous and exothermic	6.1	Dutta et al. (2015)

(continued)

Table 17.2 (continued)

Dye	Adsorbent	q_{max} (mg/g)	Percentage removal	Isotherm modeling	Kinetics	Thermodynamic studies	Optimum pH	References
1	SBA-16	561	98.6%	Langmuir	Pseudo-second-order	Spontaneous and exothermic	9.0	Tsai et al. (2016)
Phenosafranine		519						
10	Silica fume waste material	322.58	–	Langmuir	–	Spontaneous and endothermic	9.0	Kalkan et al. (2014)
2	Coco peat	276.8	–	Langmuir	Pseudo-first-order	Spontaneous and endothermic	7.0	Vijayaraghavan et al. (2016)
7		119.2						
7	Yeast-treated peat	108	98%	Sip	Pseudo-second-order	Spontaneous and endothermic	5.2	Chieng et al. (2013)
Bisphenol A	Chemically modified fabric peat	31.40	–	Freundlich	Pseudo-second-order	–	6	Zhou et al. (2011)
2	Sphagnum peat moss	121.95	99.75%	Langmuir	Pseudo-second-order	Spontaneous and endothermic	6.5	Hemmati et al. (2016)
p-Nitrophenol	Peat	23.4	56.76%	Langmuir	Pseudo-second-order	Spontaneous and endothermic	8.0	Jaerger et al. (2015)
Reactive Red 120	Nano-alumina	20.3	~ 35%	Langmuir	Pseudo-second-order	–	3.0	Nadafi et al. (2014)
1	Aluminum-modified activated carbon	181.82	98%	Langmuir	Pseudo-second-order	Spontaneous and endothermic	–	Kazeem et al. (2018)
	Natural clay	25	–	Freundlich	Pseudo-first-order	–	5	İyim and Güçlü (2009)
Brilliant cresyl blue		42						
1	Cellulose-clay nanocomposite hydrogels	1065	98%	Freundlich	Pseudo-second-order	Spontaneous and endothermic	1–11	Peng et al. (2016)
		782.9		Langmuir				

1	Amino-functionalized attapulgite clay nanoparticle adsorbent	215.73	~ 80%	Langmuir	Pseudo-second-order	Spontaneous and exothermic	3.0–10.0	Zhou et al. (2015)
1	Malachite@clay nanocomposite	277.77	99.82%	Langmuir	Pseudo-second-order	Spontaneous, exothermic, and endothermic, respectively	2.5–10.5	Srivastava and Sillanpää (2017)
6		238.09	88.55%					
Methyl violet	Moroccan natural clay	625	–	Langmuir	Pseudo-second-order	Spontaneous and endothermic	3–10	Elass et al. (2011)
8	Activated clay	13.624–16.779	94%	Langmuir, Temkin	Pseudo-second-order	Spontaneous and endothermic	3–7	Ma et al. (2013)
2	Organoclay	56.82	99.6%	Langmuir	Pseudo-second-order	Spontaneous and endothermic	6.0	Arellano-Cárdenas et al. (2013)
Reactive Blue 13	Organobentonite	714.28	93%	Langmuir	–	–	–	Yao et al. (2012)
Neutral red	Hectorite	393.70	90%	Langmuir	Pseudo-second-order	Spontaneous and exothermic	3–13	Yue et al. (2011)
Phenol	Na-montmorillonite	104.49	–	Langmuir	Pseudo-second-order	Spontaneous and exothermic	10	Liu et al. (2014b)
Catechol		112.23						
Acid Green 25	Organobentonite	3.7230 mmol g^{-1}	–	Langmuir	Pseudo-second-order	Spontaneous and exothermic	6.0	Koswojo et al. (2010)
7	Manganese oxide-coated sepiolite	319	–	Langmuir	Pseudo-second-order	–	6.5	Eren et al. (2010)
9	Bentonite	173.5	94.2%	Langmuir	Pseudo-second-order	Spontaneous and endothermic	9.0	Huang et al. (2017)
Acid Red 1		157.4						
1	Montmorillonite	71.12	–	Langmuir	Pseudo-second-order	Spontaneous and endothermic	8.0	Cottet et al. (2014)

(continued)

Table 17.2 (continued)

Dye	Adsorbent	q_{max} (mg/g)	Percentage removal	Isotherm modeling	Kinetics	Thermodynamic studies	Optimum pH	References
Bezactive Orange 16	Zeolite A	305.8		Langmuir	Pseudo-second-order			Nešić et al. (2013)
1	NaA clay	64.8	92.9%	Langmuir	Pseudo-second-order	Spontaneous and endothermic	7.0	Sapawe et al. (2013)
6	Surface-modified natural zeolite	69.94	97.4%	Langmuir	Pseudo-second-order	Spontaneous and exothermic	6.0	Liu et al. (2014a)
Basic blue 41	Zeolite tuff	192.31	95.7%	Langmuir	Pseudo-second-order	Spontaneous and endothermic	8.0	Humelnicu et al. (2017)
Acid Blue 92	Zeolitic imidazolate framework	633.4	95.0%	Langmuir	Pseudo-second-order	–	2.1	Abdi et al. (2017)
Direct Red 80		500.2						

demand of environmentally benign technologies and found the way in the usage of natural coagulants extracted from waste, being biodegradable, safer for human health, and capable of causing flocculation in colloidal solutions on different concentrations (Moussas et al. 2011; Szyguła et al. 2009).

The main aim of coagulation-flocculation is the agglomeration of tiny colloids into larger masses to reduce turbidity (Szyguła et al. 2009). Most of the natural coagulants are polysaccharides in nature and are known as polymeric coagulants and show two types of mechanisms, i.e., adsorption and charge cancellation and adsorption and interparticle bridging due to an interaction between π-electrons of dyes and hydroxyl groups of polymeric coagulants (Renault et al. 2009; Verma et al. 2012). Ferric chloride sludge was employed to remove Acid Red 119. Response surface methodology revealed over 96% of the degradation was achieved at pH 3.5, ferric chloride sludge dosage 236 mg L^{-1}, and initial dye concentration of over 65 mg L^{-1} (Moghaddam et al. 2010).

The generic behavior of the coagulation-flocculation technique was evaluated using different coagulants against brilliant green and **6**, respectively. However, the addition of lime to magnesium chloride and ferrous sulfate improved decolorization to 99% for both dyes (Mane and Babu 2011). In a similar study, coagulation-flocculation process was evaluated for textile wastewater treatment before release, which contains hydron blue dye using $Al_2(SO_4)_3$. The maximum dye removal of 64% was achieved under optimized conditions (Chenna et al. 2016).

Direct Red 23 azo dye was removed from textile effluents by *Moringa stenopetala* seed extract, alum, and *M. stenopetala-alum* hybrid coagulant to evaluate and compare efficacy. All the three coagulants showed over 98% dye removal at pH 7. However, the dosage of hybrid coagulant (80 mg L^{-1}) was lesser than seed extract (240 mg L^{-1}) and alum (120 mg L^{-1}), thus proving the higher efficacy (Dalvand et al. 2016). The potential of cationic polyelectrolyte based on lignin was also evaluated by the removal of anionic dyes, namely, acid black, reactive red, and direct red, from simulated dye effluent. A 100% dye removal was achieved with 5.4% sludge production. The obtained results showed the commercialization potential of the adsorbent (Fang et al. 2010).

The coagulation-flocculation potential of poly-aluminum chloride and bentonite clay was evaluated for **3** and **7** removal considering various parameters. Bentonite clay exhibited higher attraction to **7**, resulting in over 99 and 98% removal of **7** and **3**, respectively while poly-aluminum chloride showed an optimum removal efficiency of over 99% for **7** and 97% for **3** (Fosso-Kankeu et al. 2017). The efficiency of natural polymer coagulants, *Vigna unguiculata*, *Telfairia occidentalis*, *Brachystegia eurycoma*, *Vigna* subterranea, and *Moringa oleifera*, for decolorization of crystal Ponceau 6R dye has been studied. Four variables of the coagulation-flocculation process, namely, pH, coagulant dosage, dye concentration, and time, were optimized using response surface methodology. The color removal efficiencies obtained from the optimization analysis were in the range of 97–99% at pH 2, coagulant dosage of 1000 mg L^{-1}, and dye concentration of 20 mg L^{-1} in 7 h (Obiora-Okafo and Onukwuli 2015).

The Reactive Blue19 dye was subjected to poly-aluminum chloride, alum, and ferric chloride for the removal from aqueous solution. An anionic polyelectrolyte and kaolin were also added to aid the coagulation process. Alum showed highest dye removal efficiency (92%) followed by poly-aluminum chloride (91%) and ferric chloride (81%) at 300, 200, and 400 mg L^{-1} dosages, respectively (Assadi et al. 2013). In another study, the degradation of Acid Orange 7 (**4**) was reported using laterite soil in the coagulation process. Over 98% color removal was achieved at pH 2 (Lau et al. 2014).

Similar studies were carried for the degradation of **1** and **8** using natural coagulant-laterite soil with aluminum-ferric ions acting as an auxiliary agent in the degradation process, and the results were quite satisfying (Lau et al. 2015). Magnesium hydroxide was applied as a coagulant to eliminate reactive dyes from wastewater aided by kaolin at a pH of 12 (Li et al. 2016).

Moringa oleifera waste was used as a coagulant to remove black, orange, blue, crimson, and navy dyes. The coagulant effect of *Moringa* solutions was enhanced by NaCl than $FeCl_3$ at an optimum pH of 9.0. However, above 95% of blue, crimson, and navy dyes and 85% of black dye and 80% of orange dye were removed using *M. oleifera* waste (Vilaseca et al. 2014).

To decompose **6** from wastewater, coagulants of natural origins, i.e., surjana seed powder, maize seed powder, and chitosan, were employed. With a coagulant dose of 25 mg L^{-1}, pH 4, 66.85 °C temperature, and 1.0 h of flocculation, surjana seed powder removed 98% color, whereas maize seed powder and chitosan removed over 89% and 94%, respectively (Patel and Vashi 2012). $FeSO_4 \cdot 7H_2O$ was employed as a coagulant to decolorize synthetic effluents simulating the cotton, acrylic, and polyester dyeing wastewaters. Results disclosed complete decolorization of polyester effluent, whereas over 91 and 94% removal of cotton and acrylic wastewaters was achieved (Rodrigues et al. 2013).

Chitosan was used as a coagulant in assistance with different Al species (Al_a/Al_b/Al_c) for the treatment of disperse yellow wastewater. Larger color removal efficiencies were obtained with chitosan at pH 6.0–7.0 (Wang et al. 2017). Poly-aluminum chloride-poly(3-acrylamido-isopropanol chloride, a hybrid polymer, was used in coagulation-flocculation process against reactive cibacron blue F3GA and disperse Terasil Yellow W-4G dyes, which decolorized both dyes up to 92 and 95% with 50 and 20 mg l^{-1} dosage, and pH of 7.5 and 3, respectively (Yeap et al. 2014).

A facile and simple design strategy was reported for the isolation of cellulose nanocrystals with carboxylic groups from microcrystalline cellulose. Cellulose nanocrystals as adsorbent decomposed **1** showing coagulation-flocculation capability to kaolin suspensions with over 99% reduction in turbidity (Yu et al. 2016). Poly-aluminum chloride and alum were used to decompose dye Acid Blue 292 from aqueous solution resulting in 85% decomposition at pH of 7.0 and 5.0 for poly-aluminum and alum, respectively (Zonoozi et al. 2009).

Bittern salt was found to be efficient and cheap coagulant for saline wastewaters as 95% turbidity and 80% color of an effluent containing 200 mg Mg^{2+} L^{-1} was removed (Albuquerque et al. 2013). Hybrid $Al(OH)_3$-polyacrylamide polymer in coagulation-flocculation process and iron scrap were separately applied for the treatment of Reactive Blue 19. At 700 mg L^{-1} of dosage and pH of 5–6, hybrid polymer achieved 82 and 90% removals of chemical oxygen demand and color, respectively (Al-Ani and Li 2012).

Natural coagulants *Vigna unguiculata*, *Telfairia occidentalis*, *Brachystegia eurycoma*, *Vigna subterranean*, and *Moringa oleifera* were used to decolorize Acid Red 101 dye with maximum color removal efficiencies of 99.7, 99.4, 89, and 98, respectively, at pH 2, dye concentration of over 22 mg/L, and coagulant amount of 375 mg/L in 9.0 h (Obiora-Okafo and Onukwuli 2017). A study was carried out with poly-aluminum chloride and bentonite clay as coagulants to eliminate cationic **7** and anionic **3** dyes. Poly-aluminum chloride showed better removal for **7** with efficiency of 99.2% at a pH of 12 and bentonite clay for **3** at a pH of 2.0 with a removal efficiency of 97.6% (Fosso-Kankeu et al. 2015).

Tanfloc, a tannin-based coagulant, was employed to eliminate Palatine Fast Black and Alizarin Violet 3R dyes. High-percentage removal was obtained with low coagulant doses and removed 80% of Alizarin Violet 3R and 100% of Palatine Fast Black with initial concentration of 0.16 mmol L^{-1} and 0.06 mmol L^{-1}, respectively (Beltrán-Heredia et al. 2010). Alum and ferric chloride as coagulant with NaOH and lime were used as softener agents. With 12 g L^{-1} concentration of lime, over 94 and 86% color was removed from Eriochrome Black T and **1**, respectively (Malakootian and Fatehizadeh 2010).

17.2.4 Ion Exchange

A strong cation-exchange resin was used to adsorb **7** and basic fuchsin (**5**) at pH of 2 and 7 with adsorption capacities of 76.8 and 127.0 mg g^{-1} following Langmuir adsorption isotherm and Temkin isotherms. The desorption ratio of 97% was achieved as a result of seven adsorption/desorption cycles (Bayramoglu et al. 2009). Anion-exchange membranes having quaternary ammonium groups were employed for the adsorptive removal of anionic cibacron blue 3GA dye with membrane ion-exchange capacity of 6.8 mol cm^{-2} (or 104.2 mol cm^{-3}). The adsorption data was best correlated to Langmuir adsorption isotherm with an adsorption capacity of 2.12 mg cm^{-3} and 70% performance with ten adsorption/desorption cycles (Chiu et al. 2009).

Azocarmine B dye was removed with pullulan microspheres using batch adsorption experiment resulting in 90% removal of the dye following Langmuir adsorption isotherm model with q_{max} of 113.63 mg g^{-1} and pseudo-second-order kinetics with spontaneity and exothermic thermodynamics (Constantin et al. 2013). Remazol black-B was removed using weakly basic anion-exchange resins of phenol-formaldehyde, polyacrylate, and polystyrene with q_{max} values of 66.4, 282, and 796 mg g^{-1}, respectively, following Langmuir adsorption isotherm model (Wawrzkiewicz and Hubicki 2011).

To remove basic blue 3 dye, a different type of cation-exchange resin polymeric sorbents such as Lewatit MonoPlus SP-112, Dowex Optipore SD-2, and Amberlite

XAD-1180 were used. Adsorption data followed Langmuir adsorption isotherm model with q_{max} values of 560.7, 270.9, and 35.7 mg g^{-1} for Lewatit MonoPlus SP-112, Dowex Optipore SD-2 and Amberlite XAD-1180, respectively. Kinetically, the system followed pseudo-second-order, and 100% performance was reported with four cycles of sorption-desorption (Wawrzkiewicz 2013).

17.3 Chemical Methods

Chemical methods for dye decolorization and degradation from wastewater mainly include advanced oxidation processes and photocatalytic and electrochemical treatments. All methods mentioned above involve the use of chemicals and chemical reactions between reagents and dye molecules, which often results in hazardous by-products. Nevertheless, many novel approaches have been designed to unlock the potential and safety of chemical methods. Below is the detail of all the major dye removal chemical methods.

17.3.1 Advanced Oxidation Processes

Because of the simple handling, oxidation is the most commonly used chemical decolorization process. Constant developments and improved understanding of the oxidation mechanism enabled the evolution of advanced oxidation processes. The advanced oxidation processes are suitable for the removal of chemically stable and non-biodegradable wastewater constituents. Advanced oxidation processes transform the pollutants by mineralization into carbon dioxide, water, and salts (Poyatos et al. 2010).

Advanced oxidation processes involve the production of hydroxyl ($^\bullet OH$) radicals destroying pollutants until mineralization. All types of advanced oxidation processes, including photochemical degradation (O_3/UV, UV/H_2O_2), photocatalysis (UV/TiO_2), and chemical oxidation methods (O_3, O_3/H_2O_2, H_2O_2/Fe^{2+}), share the same mechanism (Rosenfeldt et al. 2007; Skoumal et al. 2006; Ollis 1993).

$$\text{Advanced oxidation processes} \rightarrow {}^{\cdot}OH \overset{pollutant}{\rightarrow} CO_2 + H_2O + \text{salts}$$

Ultraviolet-Assisted Ozonation

Ozone interacts with dye molecules in an aqueous medium by a free radical attack which may be direct or indirect. In the simplest form, the reaction can be summarized as below (Hsu et al. 1998):

Direct reaction:

$$O_3 + \text{dye} \rightarrow \text{dye}_{\text{oxid}}(\text{oxidation product of dye})$$

Indirect reaction:

$$O_3 + H_2O \overset{OH^-}{\rightarrow} OH^{\bullet} + O_2$$

$$OH^{\bullet} + \text{dye} \rightarrow \text{dye}_{\text{oxid}}$$

Three oxidative processes, including UV-assisted ozonation (UV/O_3), ultrasound-assisted ozonation (US/O_3), and simple ozone systems, were compared against each other for the treatment of **9** aqueous solution. All the processes performed successful oxidation in the acidic medium. The UV/O_3 process, however, proved to be the most efficient and eco-friendly with 99% decolorization efficiency and chemical oxygen demand removal rate of 47% after 15-min reaction and nontoxic by-products (Cuiping et al. 2011).

The performances of ozonation and H_2O_2/UV-C (hydrogen peroxide with ultraviolet radiation of shortest wavelength) processes were compared against Reactive Red 194, reactive yellow, and textile wastewater. The results revealed that decolorization via H_2O_2/UV-C process was greatly influenced by pH. Contrarily, ozonation was found to be free of any dependences, more effective, and feasible for reactive dyes (Gül and Özcan-Yıldırım 2009).

The major benefit of ozone oxidation is that gaseous ozone used resists the rise in mixture volume and avoids sludge production. The drawbacks of ozonation include high cost of installation plant, the limited half-life of ozone, and the sensitivity to pH and temperature change. For the best results, ozonation is assisted with radiations (Zaharia et al. 2009) or with a membrane separation method (Bechtold et al. 2005).

UV-Assisted Oxidation with Hydrogen Peroxide

The use of H_2O_2 for the decomposition of non-biodegradable organic contaminants in textile effluents has many technical and economic benefits. H_2O_2 is stable, cost-friendly, and commercially available. From the chemical perspective, H_2O_2 is completely miscible with water, requires the ambient temperature to function, and prevents sludge formation during the different stages of treatment (Aleboyeh et al. 2003; Shu and Chang 2005; Daneshvar et al. 2008; Zaharia et al. 2009). The mechanism of H_2O_2/UV involves the creation of hydroxyl radicals and subsequent oxidation of dye molecules (Gül and Özcan-Yıldırım 2009; Georgiou et al. 2002).

$$H_2O_2 + UV \rightarrow 2OH^{\bullet}$$

$$OH^{\bullet} + \text{dye} \rightarrow H_2O + \text{dye}^{\bullet} \rightarrow \text{further oxidation}$$

H_2O_2/UV process was employed in a lab-scale reactor to decolorize textile wastewater containing reactive Yellow 84 and Reactive Red 141. At the original pH, wastewater was decolorized in 5.0 h. Acidification to pH 3 reduced the decolorization time to 2 h and chemical oxygen demand removal up to 70% (Racyte et al. 2009). The photo-oxidation of **9** was carried out by H_2O_2/UV, and parameters were optimized. At 10 μM dye concentration, 1.67 mM H_2O_2, and neutral pH, 73% decoloration was achieved (AlHamedi et al. 2009).

Similarly, H_2O_2/UV process decolorized Reactive Blue 181 effectively under conditions of 500 mg/L of both dye and H_2O_2 and pH 3 in less than 30 min (Basturk et al. 2015). UV/ H_2O_2/microwave process has also been reported as a modified system with higher efficiency. By taking 2.0 mmol L^{-1} initial concentration of H_2O_2, pH of 2.6, and 30 °C temperature, over 92% decolorization was achieved in less than half an hour of irradiation. In addition, chemical oxygen demand and biological oxygen demand were significantly removed. Comparison between microwave, H_2O_2, H_2O_2/microwave, and UV/microwave revealed the superiority of UV/ H_2O_2/microwave process by eightfold in terms of speed (Parolin et al. 2013).

Photo-Fenton

The advanced oxidation of textile industry effluents with Fenton and photo-Fenton processes provides high decolorization efficiency, simple handling, and cost-friendliness (Bigda 1995). Fenton's reagent (Fe^{2+}/H_2O_2) utilizes Fe^{2+} ions for the catalytic breakdown of H_2O_2 (Barbeni et al. 1987; Walling 1975). The process has evolved into photo-Fenton (Fe^{2+}/H_2O_2/UV) and photo-Fenton-like (Fe^{3+}/H_2O_2/UV) techniques that involve the use of irradiation and improved efficiency of the process (Ruppert et al. 1993; Bauer and Fallmann 1997). Some other variations of the process include the application of zero-valent iron with H_2O_2 (Nazari et al. 2013; Kusic et al. 2006) and Fe^{2+}/ultrasound combinations to further facilitate the process efficiency (Ghodbane and Hamdaoui 2009). **16** and Reactive Black 39 taken from rinsing and purification stages and treated with photo-Fenton-like advanced oxidation processes. Response surface methodology confirmed 100% decolorization, 78% chemical oxygen demand, and 59% total organic carbon removal, respectively. Optimization of chloride content was suggested to remove the potential limit the technique (Arslan-Alaton et al. 2009).

Despite the success, several limitations of the Fenton process, such as the dramatic inhibition caused by hydrogen phosphate ions and sludge production, are common. Iron oxide-coated granular activated carbon with H_2O_2 has been suggested as an alternative oxidation process to cope with limitations. The newly developed process was applied to degrade **7**, a triphenylmethane dye, responsible for toxicity to mammalian cells. Not only the proposed process minimized the sludge problem but also increased the adsorption capacity of dyes and oxidation ability of H_2O_2. The removal efficiency of the proposed process was over 70% which was far better than efficiencies of H_2O_2 (10%), granular activated carbon (44%), granular activated carbon/H_2O_2 (43%) under acidic conditions, and 7.4 mM concentration of H_2O_2 (Chen et al. 2011).

In a combined chemical-biological process designed for biodegradability enhancement and operating cost reduction, Fenton's reaction was used to assist biological oxidation in a sequential batch reactor to remove color and organic matter from synthetic textile effluents. The combined approach successfully removed over 99% of color and 88–98% of organic matter. Additional benefits included meeting the wastewaters discharge limits and reduction of the individual operating costs of individual processes (Rodrigues et al. 2014).

Electrochemical Oxidation

Electrochemical oxidation or electro-oxidation is an effective technique to remove contaminants from effluents that are rich in anionic content (Abdessamad et al. 2013; Guzmán-Duque et al. 2014). The mechanism of electrochemical oxidation involves a redox reaction initiated by electric current leading to the transformation of organic components into CO_2 and H_2O. The electrochemical treatment of dyeing wastewater comprises of direct and indirect oxidation processes. The direct oxidation process starts with adsorption of pollutants on the surface of anode followed by degradation through electron transferring reaction. On the other hand, the indirect oxidation process electrochemically generates strong oxidizing agents to breakdown contaminants with oxidation reactions (Zhan et al. 2001).

An important factor that defines the efficiency of electrochemical oxidation is the type and properties of the electrode. Boron-doped diamond is known to be the most efficient electrode materials for the electro-oxidation of wastewaters. The success of boron-doped diamond electrode is attributed to the physicochemical stability, reliable oxidative strength, controllable adsorption, and the convenient water discharge (Peralta-Hernández et al. 2012; Shen et al. 2006). Doped boron-doped diamond films with boron grown on titanium plates by hot filament chemical vapor technique were used to remove **10** from dyeing wastewater. Complete decolorization of **10** was achieved with boron-doped diamond/Ti electrode at 100 mA cm^{-2} current density. Electrodes also showed the capacity to transform aromatic hydrocarbons into aliphatic species, which may further degrade into CO_2 (Vasconcelos et al. 2015). Boron-doped diamond anodes were employed for galvanostatic electrolysis by anodic oxidation of mixtures contaminated with containing Alphazurine A. Electrolysis caused 100% color and chemical oxygen demand removal at varying reaction parameters (Bensalah et al. 2009).

Large-scale application of the electrochemical method is hampered by the single great disadvantage of high operational cost. Some researchers have suggested an indirect electrochemical process using Cl^- and UV irradiation-assisted electrochemical process. Synthetic textile wastewater polluted with reactive dyes subjected to low current density electrochemical oxidation followed by UV irradiation with Ti/Pt oxide electrodes. The integration of techniques resulted in full decolorization with a minute concentration of Cl^-, which was reduced by 75% as a result of UV irradiation (Riera-Torres and Gutiérrez 2010). Another solution has been proposed as the replacement of traditional one-cell reactor with a double-section electrolytic cell partitioned with anion-exchange membrane. So-called dual-electrode oxidation reactor allows simultaneous oxidation at both electrodes, thereby reducing the energy demand by multiple folds (Raghu et al. 2009).

Ozonation in an Alkaline Medium

Most of the organic compounds can be degraded and decolorized with ozone, mainly because oxidation potential of 2.07 V allows ozone to break the unsaturated bonds in complex hydrocarbons and chromophores constituting humic and colored substances (Alaton et al. 2002). Ozone works in one of the two ways known as direct and indirect mechanism; the former involves the action of molecular ozone, and the latter corresponds to the action of free radicals generated by the decomposition of ozone in aqueous solution (Shu and Huang 1995).

Ozone was used to decolorize Sirius blue SBRR, a direct dye, in a batch bubble column reactor. A high inlet gas flow at highly basic pH resulted in a large amount of bubble and complete color removal in less than 30 min. Toxicity tests performed on the dye decolorization breakdown products revealed that breakdown products are nontoxic (Turhan and Turgut 2009). The residual dyes from the tanning industry were also successfully decolorized by ozone. A high pH value and low dye concentrations were recommended for faster processing (Srinivasan et al. 2009).

Ozonation of **19** and Acid Red 27 at different salt concentrations and pH values has been studied. The process yielded 98% color removal in half an hour with 45 and 20% mineralization of dyes **19** and Acid Red 27, respectively (Silva et al. 2009). Reactive Blue 19 was also decolorized and degraded with ozone in a cylindrical batch reactor. With a concentration of 800 mg/L dye solution and duration of 1.5 h, 55% removal of chemical oxygen demand and 17% of total organic carbon reduction were achieved. The addition of other oxidative agents was suggested to cope with the challenge of incomplete degradation and partial mineralization (Tehrani-Bagha et al. 2010).

Anionic sulfonated azo dye and a suspected carcinogen, Reactive Orange 16, was decolorized and degraded via ozonation in a bubble column reactor. At pH value of 12, about 70% decolorization and 100% degradation were achieved within 8-min duration (Turhan and Ozturkcan 2013). Another study reported over 98% decolorization efficiency of azo dye Reactive Red 120 at a contact time of half an hour by ozonation method, emphasizing the suitability of ozonation for dyeing effluents and wastewater treatment (Abidin et al. 2015).

The performance of three different processes involving O_3, namely, ozonation, O_3/H_2O_2, and O_3/activated carbon, was compared against Acid Blue 92 dye. First two processes worked best in basic conditions; however, the third one caused the maximum degradation at a low pH. Open reflux analysis revealed the chemical oxygen demand removal in ozonation, O_3/H_2O_2, and O_3/activated carbon processes were 30, 80, and 100%, respectively (Parsa and Negahdar 2012).

Catalytic Ozonation

Several reports have suggested the use of catalyzed ozonation of dye for the decolorization and chemical oxygen demand removal from industrial wastewater. Catalyzed ozonation of Procion Red MX-5B was carried out at an ozone dose of 260 mg h^{-1} and pH 11.0. The results revealed the successful removal of color, chemical oxygen demand, and total organic carbon with maximum values in the range of 75–97%. The presence of ionic and acidic species in the solution indicated the mineralization caused by ozonation. Mn^{2+} was considered to the best metal ion for decolorization and chemical oxygen demand removal compared to the rest (Pachhade et al. 2009).

The solution of an azo dye **23** was subjected to MgO nanocrystal-catalyzed ozonation using a lab-scale batch reactor. At optimized pH of 8 and catalyst dosage of 5 g/L, clear improvements in both reaction time and decolorization efficiency were noticed. Complete decolorization of 200 mg/L dye solution was achieved in 9 min only, which may take up to half an hour without the addition of catalyst (Moussavi and Mahmoudi 2009). Overall, catalytic ozonation was regarded as a reasonable process for treating dye wastewater prior and later to the discharge.

17.3.2 Photocatalytic Treatment

A photocatalyst absorbs energy from light to produce electron-hole pairs which is used to impart chemical transformations in the reaction participants (Natarajan et al. 2018; Davis et al. 1994). Ammonium oxalate fiber surface was modified with silver nanoparticles of different sizes and shapes and tested for photodegradation of **8** in aqueous solution. The study revealed successful degradation of **8**, particularly under sunlight, a capability that can be extended to dye removal from wastewater streams under the normal sunlight conditions (Wu et al. 2010). A mesoporous-assembled TiO_2 nanocrystal photocatalyst was used to remove acid yellow and acid black dyes with mono and diazo groups. At photocatalyst dose of 10/L, initial pH of 4.5, and acid yellow and acid black concentrations of 2.5 and 5 mg L^{-1}, highest degradation efficiency was achieved. Although water hardness hampered the degradation, pH optimization can resolve the issue to resist a decrease in efficiency (Wongkalasin et al. 2011).

3, 8, and methyl yellow were degraded to demonstrate the catalytic and magnetic activity of palladium/hydroxyapatite/Fe_3O_4 nanocatalyst. The effective degradation of dyes by the novel catalyst was attributed to the formation of Pd hydroperoxide as a result of a reaction between catalyst and dissolved oxygen under acidic condition followed by oxidation of azo dyes under hydroxyapatite catalysis (Safavi and

Momeni 2012). Another novel photocatalyst based on silver nanoparticles and colemanite ore waste was employed to remove reactive Yellow 86 and **21** in single and multiple dye mixtures. Ag-colemanite ore waste proved to be a reusable and cheap photocatalyst causing the removal of dyes from both single and binary systems under optimized conditions of highly acidic pH, 100 mg/L beginning concentration, duration of 1.25 h, and photocatalyst dose of 1.0 g L^{-1} (Yola et al. 2014).

17.3.3 Electrochemical Treatment

Electrochemical methods such as electrocoagulation offer many advantages over existing physiochemical and membrane separation methods. For instance, electrocoagulation utilizes the electron as a unique reagent, thus reducing the cost sludge production while increasing safety and selectivity. In a typical electrocoagulation method, a metal electrode functions as anode where electrolytic oxidation produces the coagulant (Singh et al. 2013). Iron or aluminum electrodes have gained popularity not only because of economic and commercial advantages but also due to the favorable mechanism of action, i.e., the formation of metal oxides and hydroxides that increases adsorption (Zidane et al. 2008). Aluminum and stainless steel electrodes employed for a simulated reactive dyebath solution revealed the superiority of stainless steel electrodes, particularly for decolorization. The mechanism behind color and chemical oxygen demand removal was attributed to coagulation and adsorption at extremely basic pH (Kabdaşlı et al. 2009).

Reactive Blue 140 and disperse red 1 were subjected to decolorization via electrochemical technique both in single and mixed form using iron and aluminum electrodes. The experiment optimized several parameters such as type and distances of the electrode, current density, and process duration to achieve effective color removal. At a particular current density, iron displayed better treatment of both Reactive Blue 140 and disperse red 1 than aluminum, and the energy consumption was 1kWh.m^{-3} for over 96% decolorization of both dyes (Phalakornkule et al. 2010). Another report suggested superior efficiency and operating cost of aluminum over iron electrodes in the application of electrocoagulation for decolorization of Levafix brilliant blue E-B. The aluminum electrode achieved 99% decolorization in less than 30 min at a current density of 100 A/m^2, electrolyte concentration of 5 mM, and initial pH of 5.5. The operational cost and energy usage were calculated to be as \$2.9 per m^3 and 16.9 kWh/m^3, respectively (Akbal et al. 2011).

Aluminum electrodes were applied in the electrocoagulation of **19** dye in a flow-through cell under varying reaction parameters. Optimum values for electrolyte (NaCl) concentration, dye concentration, current density, and pH are 4.0 g L^{-1}, 10 ppm, 160A m^{-2}, and 6.5, respectively, to achieve about 95% decolorization (Mollah et al. 2010). The feasibility of electrocoagulation was compared with ozonation to decolorize diazo-, anthraquinone-, and aniline-based colorants. Both processes removed nearly 99% of diazo and aniline dyes, whereas the ozonation also decolorized 89% of anthraquinone colorant (Lambert et al. 2013). Although electrocoagulation treatment has a series of benefits, some disadvantages are also encountered, to name a few, the operational control, ineffectiveness on non-ionic components, sludge production, and treatment costs.

17.4 Biological Methods

A series of physical and chemical techniques for dye remediation have been developed. However, none has satisfied the criteria of economic feasibility, technological mastery, and environmental safety all at the same time. Biological treatments for dye remediation have been proposed as cost-competitive and eco-friendly alternatives to physical and chemical methods (Robinson et al. 2001; Vikrant et al. 2018). Biological treatments or so-called bioremediation utilize microorganisms or biocatalysts for dye degradation and decolorization. Advantages and disadvantages and/or limitations of both microorganisms and biocatalysts are often compared in terms of feasibility, efficiency, and working conditions (process control, the concentration of dye, pH, and temperature).

Microorganism strains of various kinds and origins uptake or produce enzymes that can biotransform or eliminate recalcitrant compounds from compounds (Xiang et al. 2016; Vikrant et al. 2018; Kandelbauer and Guebitz 2005). The mechanism behind the decolorization and degradation of dyes caused by microorganisms involves the chemical breakdown of chromophore molecules (Ghosh et al. 2017; Ito et al. 2016). Microorganisms that can decolorize or degrade dyes include bacteria (Jadhav et al. 2010; Saranraj et al. 2010; Saratale et al. 2010; Mahmood et al. 2011; Ponraj et al. 2011; Saratale et al. 2011; Alalewi and Jiang 2012; Buthelezi et al. 2012; Cheriaa et al. 2012; Khalid et al. 2012; Khouni et al. 2012; Sriram et al. 2013; San et al. 2014; Singh et al. 2014; Lalnunhlimi and Krishnaswamy 2016), fungi (Akar et al. 2009a, b; Couto 2009; Kaushik and Malik 2009; Prigione et al. 2009; Yang et al. 2009; Diwaniyan et al. 2010; Vaithanomsat et al. 2010; Zhang et al. 2011; Chakraborty et al. 2013a; Daâssi et al. 2013; Hadibarata et al. 2013; Jebapriya and Gnanadoss 2013; Almeida and Corso 2014; Ma et al. 2014; Rani et al. 2014), algae (Bekçi et al. 2009; Chu et al. 2009; El-Sheekh et al. 2009; Khataee et al. 2010; Lim et al. 2010; Rubín et al. 2010; Khataee et al. 2011; Cardoso et al. 2012; Esmaeli et al. 2013; Khataee et al. 2013; Salima et al. 2013; San Keskin et al. 2015; Wang et al. 2016), etc.

17.4.1 Dye Removal via Bacterial Strains

Bacteria have been extensively employed for dye degradation and decolorization, especially for the azo dyes. Generally, bacteria decolorize azo dyes by cleaving azo bonds either using electron donor moieties or enzymes such as laccase and azo reductase and laccase (Brüschweiler and Merlot 2017). The researchers have mainly focused on investigating the capability of textile effluent-adapted bacteria to cause biodegradation of dyes, effects and bioremediation of secondary metabolites generated from bacterial reactions, and use of bacterial isolations from industrial wastewater and drains as low-cost dye biodegradation raw materials (Alalewi and Jiang 2012).

Removal of Orange 3R was carried out by *Pseudomonas sp.* and *Bacillus sp.* which showed maximum dye decolorization of 89% under optimized conditions (Ponraj et al. 2011). There are a large number of reports on extensive microbial screening to discover more efficient dye decolorizing strains. In a comprehensive study, about 200 pre-concentrated bacterial isolates were evaluated for capability to eliminate remazol black-B azo dye from the solution. Out of 200, 5 most efficient bacterial isolates with more than 75% decolorizing efficiency were selected for experimentation on modified mineral salt medium. Of which, one isolate completely removed the remazol black-B (100 mg L^{-1}) from solution in less than a day at neutral pH and 35 °C using yeast extract as carbon source (Mahmood et al. 2011).

Two purified bacterial isolations *Comamonas acidovorans* and *Burkholderia cepacia* were identified as the most potent decolorizers for **4** and Direct Blue 75 (Alalewi and Jiang 2012). Many studies compared the decolorizing potential of various bacteria. *Bacillus sp.*, *E. coli*, and *P. fluorescens* isolated from soil contaminated by textile wastewater were tested for decolorization of Reactive Orange M2R. The results revealed that all three bacteria decolorized *P. fluorescens* effectively with highest efficiency followed by *Bacillus* and *Escherichia coli* (Sriram et al. 2013). A bacterial strain, *Staphylococcus hominis* RMLRT03, was isolated from soil affected by textile effluent for decolorization of textile dye acid orange in Bushnell and Haas medium which amended the mentioned dye. The bacterial strain produced good results at incubation for 2 1/2 days at neutral pH and 35 °C with glucose and yeast extract as co-substrate. The tolerance of acid orange was found to be as high as 600 mg L^{-1} (Singh et al. 2014).

The bioflocculant-producing bacteria have been extracted from activated sludge to decolorize whale, mediblue, fawn, and mixed dye. Decolorization rate of bacteria, namely, *B. subtilis*, *E. acetylicum*, *K. terrigena*, *S. aureus*, *P. pseudoalcaligenes*, and *P. plecoglossicida* was found to be in the range of 80 to 97% (Buthelezi et al. 2012).

The use of marine-derived bacteria has also been suggested since such bacteria possess a higher tolerance to the extreme conditions which may be useful in the treatment of industrial effluents. In a study, around 60 bacterial isolates from seawater sediment and saline soil were subjected to a mineral salt medium containing dyes. Two of the study isolates *P. alimentarius* and *S. equorum* efficiently decolorized reactive (black 5, blue BRS, Golden Ovifix) dyes from solution at salt concentration 0–100 g NaCl L^{-1} (Khalid et al. 2012). Table 17.3 enlists notable bacteria isolates and dyes which mentioned bacterial isolates are capable to decolorize.

The use of bacterial isolates produces reliable and reproducible data which ensures convenient interpretation of experiments. Nevertheless, microbial consortia carry additional benefits in contrast to the individual isolates for dye degradation and

Table 17.3 Adsorption of various dyes using bacterial strains

Dye(s)	Bacteria	References
Direct green-PLS	*B. subtilis*	Saranraj et al. (2010)
Direct violet-BL	*K. pneumonia*	
Direct sky blue-FF	*E. coli*	
Direct black-E	*K. pneumonia*	
Orange 3R	*Pseudomonas sp.* and *Bacillus sp.*	Ponraj et al. (2011)
4, Direct Blue 75	*C. acidovorans*, *B. cepacia*	Alalewi and Jiang (2012)
Whale, mediblue, fawn	*B. subtilis*, *E. acetylicum*, *K. terrigena*, *S. aureus*, *P. pseudoalcaligenes*, *P. plecoglossicida*	Buthelezi et al. (2012)
Reactive (black 5, blue BRS, Golden Ovifix)	*P. alimentarius*, *S. equorum*	Khalid et al. (2012)
Acid orange	*S. hominis* RMLRT03	Singh et al. (2014)

decolorization. Different strains may lead to a multisite attack on dye molecules or may assist each other by providing decomposition products (Saratale et al. 2011; Esther et al. 2004). A microbial consortium consisting *Pseudomonas* bacterial sp. decolorized textile dyestuff and Reactive Orange 16 dye (100 mg L^{-1}) by the metabolic activity in 2 days, much faster and safer than the individual bacteria, under pH 7 and 30 °C temperature. The role of laccase and reductase enzyme in biodegradation was confirmed. Bio-treated samples were found nontoxic in cytotoxicity analysis (Jadhav et al. 2010).

Green HE4BD dye and alike reactive dyes were decolorized and degraded to nontoxic products by oxidoreductive enzymes produced from bacterial consortium of *Proteus vulgaris* NCIM-2027 and *Micrococcus glutamicus* NCIM-2168. In addition to much faster and higher decolorization efficiency than individual bacteria, the consortium offered use of low-cost co-substrates, i.e., rice straw and rice husk (Saratale et al. 2010). Such reports inspired the researchers to develop novel bacterial consortia. One such example is an acclimated novel microbial consortium “Bx,” introduced to decolorize Blue Bezaktiv S-GLD 150. Under optimized conditions, the consortium showed 88–97% decolorization rates and 95–98% chemical oxygen demand removal. The process holds many advantages over traditional wastewater treatments concerning investment, process control, operative convenience, and environmental safety (Khouni et al. 2012).

A consortium consisting bacterial strains *A. radiobacter*, *Bacillus spp.*, *S. paucimobilis*, and *A. hydrophila* was obtained from activated sludge of a dyeing industry plant. The potential of individual bacteria was tested for the degradation and color removal of triphenylmethane dyes and then compared to the combined treatment as a consortium. Individual bacterial decolorized **7** and **2**, 50 mg L^{-1} each, in 1 day, whereas consortium showed a high decolorization for **7** (91%) and **2** (99%) in just 2 h (Cheriaa et al. 2012). Direct Red 31 and Direct Blue 151 dyes were decolorized by an alkaliphilic bacterial consortium consisting of *Bacillus flexus* strain NBN2, *Bacillus cereus* strain AGP-03, *Bacillus cytotoxicus* NVH 391–98 and *Bacillus sp*. L10 isolated from saline soil samples. At 200 mg L^{-1} concentration, the consortium decolorized 97 and 95% of Direct Blue 151 and Direct Red 31 dyes, respectively, within 5 days at pH 9.5 (Lalnunhlimi and Krishnaswamy 2016).

Overall, bacterial treatment has gained momentum as an efficient technique for dye degradation and decolorization. However, further developments are required to cope with some challenges such as toxicity of the treated effluents and scale-up applications of bacterial techniques in real industrial sewage and drains. The solution to the mentioned challenges lies in advanced knowledge of fundamental biological sciences coupled with the revolutionary analytical techniques based on genomics and proteomics.

17.4.2 Dye Removal via Algae Strains

Biosorption of malachite green oxalate dye was attempted using *Caulerpa racemosa* var. *cylindracea*. The system suggested an alternative to recently reported cyclodextrin-based adsorbent for **2** because of the lower equilibrium time and high adsorption capacity (Bekçi et al. 2009). In another study, *Chlorella vulgaris* UMACC 001 was used to remove Supranol Red 3BW and textile wastewater using high-rate algal ponds. Decolorization reached up to 41–50% and chemical oxygen demand removal 38–62%, and biomass was found to be 0.17–2.26 mg chlorophyll a/L. Additional benefits of high-rate algal ponds were proposed in the form of a polishing system for textile wastewater prior to the disposal and use of algal biomass as feedstock for biofuel generation (Lim et al. 2010). **1** was adsorbed using raw and dried Mediterranean green alga *Enteromorpha spp.* (Ncibi et al. 2009). Some reports suggested chemical and surface modifications in algae to enhance sorption capacity, for instance, removal of lipid fraction from *Sargassum muticum* biomass increased the sorption efficiency (Rubín et al. 2010). Likewise, marine alga *Ulva lactuca* and *Systoceira stricta* modified with activated carbon showed significantly improved adsorption capacities for **2** (400 mg g^{-1}) and Safranin O (526 mg g^{-1}) (Salima et al. 2013).

Reactive Red 120 dye was removed by adsorption using *Spirulina platensis* microalgae as sorbent. Microalgae successfully removed nearly 97% of dye, thus indicating the suitability of SP for bioremediation of simulated dyestuff effluents (Cardoso et al. 2012). Biosorption of Acid Black 1 was carried out using brown marine macroalga, *Nizamuddin zanardini*, which utilized hydroxyl and amine surface functional groups for biosorption (Esmaeli et al. 2013). Textile dyes **4**, basic red 46, and basic blue 3 taken from polluted water were subjected to biosorption using filamentous green alga *Spirogyra sp.* Equilibrium was achieved in 1 h and biosorption of dyes in 72 h was highest for basic red 46, the average for basic blue 3, and lowest for **4** (Khataee et al. 2013).

Immobilization of microalgae has been suggested to cope with a low resistance to temperature and chemicals. A study used 1% κ-carrageenan and 2% sodium alginate

Table 17.4 Adsorption of various dyes using algal strains

Dye(s)	Algae	References
Malachite green oxalate	*C. racemosa* var. *cylindracea*	Bekçi et al. (2009)
Supranol Red 3BW, Lanaset Red 2GA, Levafix Navy Blue EBNA	*C. vulgaris* UMACC 001	Chu et al. (2009)
3, **19**, G-red	*C. vulgaris*, *L. lagerlerimi*, *N. lincki*, *O. rubescens*, *E. viridis*, *V. aureus*	El-Sheekh et al. 2009)
(1	*Enteromorpha spp.*	Ncibi et al. (2009)
1	*S. muticum*	Rubín et al. (2010)
2	*Chlorella, Euglena*	Khataee et al. (2010)
Supranol Red 3BW	*C. vulgaris* UMACC 001	Lim et al. (2010) and Khataee et al. (2011)
Reactive Red 120	*S. platensis*	Cardoso et al. (2012)
Acid Black 1	*N. zanardinii*	Esmaeli et al. (2013)
4, Basic Red 46, Basic Blue 3	*Spirogyra sp.*	Khataee et al. (2013)
2, Safranin O	*U. lactuca*, *S. stricta*	Salima et al. (2013)
Remazol black 5, Reactive Blue 221	*C. reinhardtii* polysulfone nanofibrous web	San Keskin et al. (2015)

matrices for the immobilization of *Chlorella vulgaris* UMACC 001 to decolorize Lanaset Red 2GA dye and textile wastewater. Decolorization up to 44 and 49% was achieved for Lanaset Red 2GA and textile wastewater, respectively. The system was suggested for the final polishing of textile wastewater prior to discharge (Chu et al. 2009). Likewise, immobilization of microalgae *Chlamydomonas reinhardtii* on polysulfone nanofibrous web showed significantly better decolorization capacities against remazol black 5 and Reactive Blue 221 as compared to pristine polysulfone nanofibrous web. Owing to nanoporous structure and reusability, microalgae/ polysulfone nanofibrous web biocomposite could be a suitable membrane material for the textile wastewater treatment (San Keskin et al. 2015). Table 17.4 presents notable accounts of decolorizing algae with respective dyes.

17.4.3 Dye Removal via Fungi Strains

The application of fungi in bioremediation and decolorization of dyes has been regarded as advantageous over competitive bacterial techniques. Certain types of fungi, such as whit-rot fungi, produce laccase and lignin/manganese peroxidase enzymes that can degrade and mineralize complex dye molecules (Wesenberg et al. 2003). Ligninolytic enzyme produced by basidiomycetous fungi was responsible for 90% or higher decolorization percentages of Xylidine Ponceau 2R, indigo carmine, Poly R-478, and Lissamine Green B dyes and 54% of textile effluent (Diwaniyan et al. 2010).

Another study reported the capability of white-rot fungus *Datronia sp.* KAPI0039 to decolorize Reactive Blue 19 and **10** by virtue of laccase production.

Periodical evaluation of color degradation revealed 86% decolorization of Reactive Blue 19 (1000 mg L^{-1}) and 88% decolorization of **10** (600 mg L^{-1}) by 2% (w/v) *Datronia sp.* KAPI0039 at pH 5. Laccase activity was measured to be 759.81 U L^{-1} and 178.57 U L^{-1} for remazol brilliant blue R and **10**, respectively (Vaithanomsat et al. 2010). Another white-rot fungus, *P. eryngii* F032, culture decolorized about 94% of **10** (10 mg L^{-1}) dye within 3 days of incubation in dark condition with agitation. However, fungus faced reproducibility limitations and required immobilization to overcome the issue (Hadibarata et al. 2013). Owing to the crude enzyme production, *Ganoderma sp.* En3 effectively decolorized Reactive Orange 16 (Ma et al. 2014).

Lanaset Gray G (200 mg L^{-1}) was decolorized by four Tunisian-isolated white-rot fungi immobilized onto Ca-Alg which achieved decolorization percentages up to 89, 89, 82, and 81%. Immobilized fungi exhibited reusability by removing dyes with high percentages in subsequent cycles suggesting the suitability for metal dye-contaminated effluents in continuous systems (Daâssi et al. 2013). **6** (600 mg L^{-1}) was completely decolorized by *Alternaria alternata* within 2 days in yeast extract-glucose medium with excellent dye retention capacity and nontoxic final products (Chakraborty et al. 2013a).

The fungal isolates, *Aspergillus niger* and *Phanerochaete chrysosporium*, isolated from dye-contaminated soil were used for the removal of **2**, nigrosin, and **5**. *Aspergillus niger* effectively decolorized **5**, nigrosin, and **2** up to 82%, 77%, and 73%, respectively. Whereas decolorization percentages of *P. chrysosporium* for nigrosin, **5, 2,** and dye mixture were found to be around 90%, 90%, 83%, and 78%, respectively. Both fungi were regarded as appropriate for detoxification of complex textile dyes (Rani et al. 2014).

Despite the multitude of successful experiments, the use of fungi for biodegradation is not entirely risk-free. Filamentous fungi *Aspergillus niger* and *Aspergillus terreus* were capable of completely removing Procion Red MX-5B dye from solution with a drawback of toxic metabolite production leading to the growth inhibition and death of *A. salina* larvae (Almeida and Corso 2014). The efforts have been made to modify the physicochemical properties of fungi and/or appropriate selection of fungal strains. Biosorbents based on macro-fungi type were found to be advantageous in terms of chemical stability, morphological favorability, and excellent mechanical performance in different pH conditions. Acid Red 44 dye was efficiently removed by macro-fungus *Agaricus bisporus* from aqueous solutions (Akar et al. 2009b).

A biosorbent based on the mixture of macro-fungus *A. bisporus* and *Thuja orientalis* cones eliminated Reactive Blue 49 dye from contaminated solutions in both batch and continuous biosorption processes. The proposed system could be an affordable, efficient, and environmentally favorable option for biosorption of reactive dyes from solutions (Akar et al. 2009a). A biofilm reactor was introduced that combined bacteria-fungi coupled system for biodegradation of textile wastewater. Results revealed the key role of yeasts belonging to genus *Candida* in the success of the proposed system (Yang et al. 2009). Table 17.5 enlists notable fungal strains along with dyes.

Table 17.5 Adsorption of dyes by fungi

Dye(s)	Fungi	Decolorization efficiency (%)	References
Acid Red 44	*A. bisporus*	95.24	Akar et al. (2009b)
Reactive Blue 49	*A. bisporus*, *T. orientalis*	–	Akar et al. (2009a)
Reactive Blue 19	*Datronia sp.* KAPI0039	86	Vaithanomsat et al. (2010)
10		88.01	
Reactive Orange 16	*Ganoderma sp.*	88.2	Ma et al. (2014)
10	*Pleurotus eryngii* F032	93.57	Hadibarata et al. (2013)
6	*Alternaria alternata* CMERI F6	78	Chakraborty et al. (2013a)
Lanaset Gray G	*Coriolopsis gallica*	88.7	Daâssi et al. (2013)
	Bjerkandera adusta	89.3	
	Trametes versicolor	82.1	
	Trametes trogii	81.3	
Procion Red MX-5B	*Aspergillus niger*	100	Almeida and Corso (2014)
	Aspergillus terreus		
2	*A. niger*, *P. chrysosporium*	93.33, 71.42	Rani et al. (2014)
Nigrosin	*A. niger*, *P. chrysosporium*	90.05, 70	
5	*A. niger*, *P. chrysosporium*	92.85, 8.33	

Overall, biological methods are comparatively green and sustainable. A major issue associated with the biological method is robustness. Innovative approaches are required to ensure the reproducibility of results. Moreover, there is still room to explore the synergistic effect of microorganisms not only within the domain but in combination with physical and chemical methods.

17.5 Conclusions and Prospects

The natural and synthetic dyes which make our life colorful also cause much pollution of water bodies. Effluents from the dye industry contain very harmful chemicals. The organic dyes should be discharged up to only certain strict limits in final effluents discharged untreated in natural water resources. Removal of dye from textile effluents is an environmental issue that can be solved by use of adequate mechano-physical-chemical and biological treatment of textile effluents. A thorough survey of all the useful data is available for the study and is discussed with the overall impact on the treatment of wastewater. Conclusively, among the different methods opted, adsorption stands good for the removal of dyes and pigments from wastewater due to ease of operation, low cost, and no requirement of the specific pretreatments of the waste material. Chemical methods can offer reliable decolorization and degradation of a large number of dye effluents. Combined with physical and biological techniques, chemical methods can provide sustainable solutions to dye pollution. To unlock the potential of chemical methods, however, there is a dire need to develop strategies to overcome the sludge production which causes a secondary pollution problem. Furthermore, chemical techniques usually have a high cost that hinders large-scale application. Efforts should be made to design materials that can transform chemical methods into economic and convenient approaches. One way to achieve the goal is to introduce integrated approaches based on novel and emerging techniques. For example, the broad specificity of chemical oxidation methods can be coupled with versatile biological methods, which can be further assisted by recombinant DNA approach and bio-engineering. However, the complementarity and compatibility of chemical techniques should be carefully evaluated. Furthermore, there is a gap in the area of structural elucidation and characterization of toxic dye effluents before release from the industrial resources. To address this issue, extensive evaluation of dyestuff material is required before its release. In the future, validation of integrated and coordinated approaches on broader scale will most likely produce an economically feasible, practical, and effective solution.

References

Abdessamad N, Akrout H, Hamdaoui G, Elghniji K, Ksibi M, Bousselmi L (2013) Evaluation of the efficiency of monopolar and bipolar BDD electrodes for electrochemical oxidation of anthraquinone textile synthetic effluent for reuse. Chemosphere 93(7):1309–1316. https://doi.org/10.1016/j.chemosphere.2013.07.011

Abdi J, Vossoughi M, Mahmoodi NM, Alemzadeh I (2017) Synthesis of amine-modified zeolitic imidazolate framework-8, ultrasound-assisted dye removal and modeling. Ultrason Sonochem 39:550–564. https://doi.org/10.1016/j.ultsonch.2017.04.030

Abidin CZA, Fahmi MR, Soon-An O, Makhtar SNNM, Rahmat NR (2015) Decolorization of an azo dye in aqueous solution by ozonation in a semi-batch bubble column reactor. ScienceAsia 41:49–54. https://doi.org/10.2306/scienceasia1513-1874.2015.41.049

Adak A, Pal A (2009) Removal kinetics and mechanism for phenol uptake by surfactant-modified alumina. Desalin Water Treat 6(1–3):269–275. https://doi.org/10.5004/dwt.2009.547

Ahmad MA, Ahmad N, Bello OS (2014) Adsorptive removal of malachite green dye using durian seed-based activated carbon. Water Air Soil Pollut 225(8):2057. https://doi.org/10.1007/s11270-014-2057-z

Ahmad MA, Ahmad N, Bello OS (2015a) Adsorption kinetic studies for the removal of synthetic dye using durian seed activated carbon. J Dispers Sci Technol 36(5):670–684. https://doi.org/10.1080/01932691.2014.913983

Ahmad MA, Ahmad N, Bello OS (2015b) Modified durian seed as adsorbent for the removal of methyl red dye from aqueous solutions. Appl Water Sci 5(4):407–423. https://doi.org/10.1007/s13201-014-0208-4

Ahmaruzzaman M, Gupta VK (2011) Rice husk and its ash as low-cost adsorbents in water and wastewater treatment. Ind Eng Chem Res 50(24):13589–13613. https://doi.org/10.1021/ie201477c

Ajmal A, Majeed I, Malik RN, Idriss H, Nadeem MA (2014) Principles and mechanisms of photocatalytic dye degradation on TiO_2 based photocatalysts: a comparative overview. RSC Adv 4(70):37003–37026. https://doi.org/10.1039/C4RA06658H

Akar ST, Gorgulu A, Kaynak Z, Anilan B, Akar T (2009a) Biosorption of Reactive Blue 49 dye under batch and continuous mode using a mixed biosorbent of macro-fungus Agaricus bisporus and Thuja orientalis cones. Chem Eng J 148(1):26–34. https://doi.org/10.1016/j.cej.2008.07.027

Akar T, Tosun İ, Kaynak Z, Kavas E, Incirkus G, Akar ST (2009b) Assessment of the biosorption characteristics of a macro-fungus for the decolorization of Acid Red 44 (AR44) dye. J Hazard Mater 171(1–3):865–871. https://doi.org/10.1016/j.jhazmat.2009.06.085

Akbal F, Kuleyin A (2011) Decolorization of levafix brilliant blue E-B by electrocoagulation method. Environ Prog Sustain Energy 30(1):29–36. https://doi.org/10.1002/ep.10437

Akl M, Youssef A, Al-Awadhi M (2013) Adsorption of acid dyes onto bentonite and surfactant-modified bentonite. J Anal Bioanal Tech 4(4):3–7. https://doi.org/10.4172/2155-9872.1000174

Alalewi A, Jiang C (2012) Bacterial influence on textile wastewater decolorization. J Environ Prot 3 (08):889. https://doi.org/10.4236/jep.2012.328104

Al-Ani Y, Li Y (2012) Degradation of CI Reactive Blue 19 using combined iron scrap process and coagulation/flocculation by a novel Al (OH) 3–polyacrylamide hybrid polymer. J Taiwan Inst Chem Eng 43(6):942–947. https://doi.org/10.1016/j.jtice.2012.07.005

Alaton IA, Balcioglu IA, Bahnemann DW (2002) Advanced oxidation of a reactive dyebath effluent: comparison of O3, H_2O_2/UV-C and TiO2/UV-A processes. Water Res 36 (5):1143–1154. https://doi.org/10.1016/S0043-1354(01)00335-9

Albuquerque L, Salgueiro A, Melo JS, Chiavone-Filho O (2013) Coagulation of indigo blue present in dyeing wastewater using a residual bittern. Sep Purif Technol 104:246–249. https://doi.org/10.1016/j.seppur.2012.12.005

Aleboyeh A, Aleboyeh H, Moussa Y (2003) Decolorisation of Acid Blue 74 by ultraviolet/H_2O_2. Environ Chem Lett 1(3):161–164. https://doi.org/10.1007/s10311-003-0039-2

AlHamedi FH, Rauf M, Ashraf SS (2009) Degradation studies of Rhodamine B in the presence of UV/H_2O_2. Desalination 239(1–3):159–166. https://doi.org/10.1016/j.desal.2008.03.016

Ali HJ (2010) Biodegradation of synthetic dyes—a review. Water Air Soil Pollut 213 (1–4):251–273. https://doi.org/10.1007/s11270-010-0382-4

Almeida E, Corso C (2014) Comparative study of toxicity of azo dye Procion Red MX-5B following biosorption and biodegradation treatments with the fungi Aspergillus niger and Aspergillus terreus. Chemosphere 112:317–322. https://doi.org/10.1016/j.chemosphere.2014.04.060

Almeida EJR, Corso CR (2019) Decolorization and removal of toxicity of textile azo dyes using fungal biomass pelletized. Int J Environ Scie Technol 16(3):1319–1328. https://doi.org/10.1007/s13762-018-1728-5

Anbia M, Hariri SA, Ashrafizadeh S (2010) Adsorptive removal of anionic dyes by modified nanoporous silica SBA-3. Appl Surf Sci 256(10):3228–3233. https://doi.org/10.1016/j.apsusc.2009.12.010

Andersson KI, Eriksson M, Norgren M (2011) Removal of lignin from wastewater generated by mechanical pulping using activated charcoal and fly ash: adsorption isotherms and thermodynamics. Ind Eng Chem Res 50(13):7722–7732. https://doi.org/10.1021/ie200378s

Anisuzzaman S, Joseph CG, Krishnaiah D, Bono A, Ooi L (2015) Parametric and adsorption kinetic studies of methylene blue removal from simulated textile water using durian (Durio zibethinus Murray) skin. Water Sci Technol 72(6):896–907. https://doi.org/10.2166/wst.2015.247

Arellano-Cárdenas S, López-Cortez S, Cornejo-Mazón M, Mares-Gutiérrez JC (2013) Study of malachite green adsorption by organically modified clay using a batch method. Appl Surf Sci 280:74–78. https://doi.org/10.1016/j.apsusc.2013.04.097

Arslan-Alaton I, Tureli G, Olmez-Hanci T (2009) Treatment of azo dye production wastewaters using Photo-Fenton-like advanced oxidation processes: optimization by response surface methodology. J Photochem Photobiol A Chem 202(2–3):142–153. https://doi.org/10.1016/j.jphotochem.2008.11.019

Assadi A, Nateghi R, Bonyadinejad GR, Amin MM (2013) Application of coagulation process reactive blue 19 dye removal from textile industry wastewater. Int J Environ Health Eng 2(1):5. https://doi.org/10.4103/2277-9183.107913

Barbeni M, Minero C, Pelizzetti E, Borgarello E, Serpone N (1987) Chemical degradation of chlorophenols with Fenton'' reagent (Fe^{2++} H_2O_2). Chemosphere 16(10–12):2225–2237. https://doi.org/10.1016/0045-6535(87)90281-5

Baskaralingam P, Pulikesi M, Elango D, Ramamurthi V, Sivanesan S (2006) Adsorption of acid dye onto organobentonite. J Hazard Mater 128(2–3):138–144. https://doi.org/10.1016/j.jhazmat.2005.07.049

Basturk E, Karatas M (2015) Decolorization of antraquinone dye reactive blue 181 solution by UV/H_2O_2 process. J Photochem Photobiol A Chem 299:67–72. https://doi.org/10.1016/j.jphotochem.2014.11.003

Bauer R, Fallmann H (1997) The photo-Fenton oxidation—a cheap and efficient wastewater treatment method. Res Chem Int 23(4):341–354. https://doi.org/10.1163/156856797X00565

Bayramoglu G, Altintas B, Arica MY (2009) Adsorption kinetics and thermodynamic parameters of cationic dyes from aqueous solutions by using a new strong cation-exchange resin. Chem Eng J 152(2–3):339–346. https://doi.org/10.1016/j.cej.2009.04.051

Bechtold T, Maier P, Schrott W (2005) Bleaching of indigo-dyed denim fabric by electrochemical formation of hypohalogenites in situ. Color Technol 121(2):64–68. https://doi.org/10.1111/j.1478-4408.2005.tb00252.x

Bekçi Z, Seki Y, Cavas L (2009) Removal of malachite green by using an invasive marine alga Caulerpa racemosa var. cylindracea. J Hazard Mater 161(2–3):1454–1460. https://doi.org/10.1016/j.jhazmat.2008.04.125

Beltrán-Heredia J, Sánchez-Martín J, Martín-Sánchez C (2010) Remediation of dye-polluted solutions by a new tannin-based coagulant. Ind Eng Chem Res 50(2):686–693. https://doi.org/10.1021/ie101148y

Bensalah N, Alfaro MAQ, Martínez-Huitle CA (2009) Electrochemical treatment of synthetic wastewaters containing Alphazurine A dye. Chem Eng J 149(1/3):348–352. https://doi.org/10.1016/j.cej.2008.11.031

Bigda RJJCEP (1995) Consider Fentons chemistry for wastewater treatment. 91(12)

Brüschweiler BJ, Merlot C (2017) Azo dyes in clothing textiles can be cleaved into a series of mutagenic aromatic amines which are not regulated yet. Regul Toxicol Pharmacol 88:214–226. https://doi.org/10.1016/j.yrtph.2017.06.012

Buthelezi S, Olaniran A, Pillay B (2012) Textile dye removal from wastewater effluents using bioflocculants produced by indigenous bacterial isolates. Molecules 17(12):14260–14274. https://doi.org/10.3390/molecules171214260

Cardoso NF, Lima EC, Royer B, Bach MV, Dotto GL, Pinto LA, Calvete T (2012) Comparison of Spirulina platensis microalgae and commercial activated carbon as adsorbents for the removal of Reactive Red 120 dye from aqueous effluents. J Hazard Mater 241:146–153. https://doi.org/10.1016/j.jhazmat.2012.09.026

Chakraborty S, Chowdhury S, Saha PD (2011) Adsorption of crystal violet from aqueous solution onto NaOH-modified rice husk. Carbohydr Polym 86(4):1533–1541. https://doi.org/10.1016/j.carbpol.2011.06.058

Chakraborty S, Basak B, Dutta S, Bhunia B, Dey A (2013a) Decolorization and biodegradation of congo red dye by a novel white rot fungus Alternaria alternata CMERI F6. Biosour Technol 147:662–666. https://doi.org/10.1016/j.biortech.2013.08.117

Chakraborty S, Chowdhury S, Saha PD (2013b) Artificial neural network (ANN) modeling of dynamic adsorption of crystal violet from aqueous solution using citric-acid-modified rice

(Oryza sativa) straw as adsorbent. Clean Techn Environ Policy 15(2):255–264. https://doi.org/10.1007/s10098-012-0503-4

Chang S-H, Wang K-S, Li H-C, Wey M-Y, Chou J-D (2009) Enhancement of Rhodamine B removal by low-cost fly ash sorption with Fenton pre-oxidation. J Hazard Mater 172 (2–3):1131–1136. https://doi.org/10.1016/j.jhazmat.2009.07.106

Chen C-C, Chen W-C, Chiou M-R, Chen S-W, Chen YY, Fan H-J (2011) Degradation of crystal violet by an FeGAC/H_2O_2 process. J Hazard Mater 196:420–425. https://doi.org/10.1016/j.jhazmat.2011.09.042

Chen Q, Yu P, Huang W, Yu S, Liu M, Gao C (2015) High-flux composite hollow fiber nanofiltration membranes fabricated through layer-by-layer deposition of oppositely charged crosslinked polyelectrolytes for dye removal. J Membr Sci 492:312–321. https://doi.org/10.1016/j.memsci.2015.05.068

Cheng S, Oatley DL, Williams PM, Wright CJ (2012) Characterisation and application of a novel positively charged nanofiltration membrane for the treatment of textile industry wastewaters. Water Res 46(1):33–42. https://doi.org/10.1016/j.watres.2011.10.011

Cheng M, Zeng G, Huang D, Lai C, Wei Z, Li N, Xu P, Zhang C, Zhu Y, He X (2015) Combined biological removal of methylene blue from aqueous solutions using rice straw and Phanerochaete chrysosporium. Appl Microbiol Biotechnol 99(12):5247–5256. https://doi.org/10.1007/s00253-014-6344-9

Chenna M, Chemlal R, Drouiche N, Messaoudi K, Lounici H (2016) Effectiveness of a physico-chemical coagulation/flocculation process for the pretreatment of polluted water containing Hydron Blue Dye. Desalin Water Treat 57(56):27003–27014. https://doi.org/10.1080/19443994.2016.1165149

Cheriaa J, Khaireddine M, Rouabhia M, Bakhrouf A (2012) Removal of triphenylmethane dyes by bacterial consortium. Sci World J. https://doi.org/10.1100/2012/512454

Chieng HI, Lim LB, Priyantha N, Tennakoon D (2013) Sorption characteristics of peat of Brunei Darussalam III: equilibrium and kinetics studies on adsorption of crystal violet (CV). Int J Earth Sci Eng 6(4):791–801

Chieng HI, Zehra T, Lim LB, Priyantha N, Tennakoon D (2014) Sorption characteristics of peat of Brunei Darussalam IV: equilibrium, thermodynamics and kinetics of adsorption of methylene blue and malachite green dyes from aqueous solution. Environ Earth Sci 72(7):2263–2277. https://doi.org/10.1007/s12665-014-3135-7

Chieng HI, Lim LB, Priyantha N (2015) Sorption characteristics of peat from Brunei Darussalam for the removal of rhodamine B dye from aqueous solution: adsorption isotherms, thermodynamics, kinetics and regeneration studies. Desalin Water Treat 55(3):664–677. https://doi.org/10.1080/19443994.2014.919609

Chiu H-C, Liu C-H, Chen S-C, Suen S-Y (2009) Adsorptive removal of anionic dye by inorganic–organic hybrid anion-exchange membranes. J Membr Sci 337(1–2):282–290. https://doi.org/10.1016/j.memsci.2009.04.004

Chowdhury S, Mishra R, Saha P, Kushwaha P (2011) Adsorption thermodynamics, kinetics and isosteric heat of adsorption of malachite green onto chemically modified rice husk. Desalination 265(1–3):159–168. https://doi.org/10.1016/j.desal.2010.07.047

Chu W-L, See Y-C, Phang S-M (2009) Use of immobilised Chlorella vulgaris for the removal of color from textile dyes. J Appl Phycol 21(6):641. https://doi.org/10.1007/s10811-008-9396-3

Chunfeng W, Jiansheng L, Lianjun W, Xiuyun S, Huang J (2009) Adsorption of dye from wastewater by zeolites synthesized from fly ash: kinetic and equilibrium studies. Chin J Chem Eng 17(3):513–521. https://doi.org/10.1016/S1004-9541(08)60239-6

Çöle G, Gök MK, Güçlü G (2013) Removal of basic dye from aqueous solutions using a novel nanocomposite hydrogel: N-vinyl 2-pyrrolidone/itaconic acid/organo clay. Water Air Soil Pollut 224(11):1760. https://doi.org/10.1007/s11270-013-1760-5

Constantin M, Asmarandei I, Harabagiu V, Ghimici L, Ascenzi P, Fundueanu G (2013) Removal of anionic dyes from aqueous solutions by an ion-exchanger based on pullulan microspheres. Carbohydr Polym 91(1):74–84. https://doi.org/10.1016/j.carbpol.2012.08.005

Cottet L, Almeida C, Naidek N, Viante M, Lopes M, Debacher N (2014) Adsorption characteristics of montmorillonite clay modified with iron oxide with respect to methylene blue in aqueous media. Appl Clay Sci 95:25–31. https://doi.org/10.1016/j.clay.2014.03.023

Couto SR (2009) Dye removal by immobilised fungi. Biotechnol Adv 27(3):227–235. https://doi.org/10.1016/j.biotechadv.2008.12.001

Cuiping B, Xianfeng X, Wenqi G, Dexin F, Mo X, Zhongxue G, Nian X (2011) Removal of rhodamine B by ozone-based advanced oxidation process. Desalination 278(1–3):84–90. https://doi.org/10.1016/j.desal.2011.05.009

Daâssi D, Mechichi T, Nasri M, Rodriguez-Couto S (2013) Decolorization of the metal textile dye Lanaset Grey G by immobilized white-rot fungi. J Environ Manage 129:324–332. https://doi.org/10.1016/j.jenvman.2013.07.026

Dahri MK, Kooh MRR, Lim LB (2013) Removal of methyl violet 2B from aqueous solution using Casuarina equisetifolia needle. ISRN Environ Chem 2013. https://doi.org/10.1155/2013/619819

Dahri MK, Chieng HI, Lim LB, Priyantha N, Mei CC (2015a) Cempedak durian (Artocarpus sp.) peel as a biosorbent for the removal of toxic methyl violet 2B from aqueous solution. Korean Chem Eng Res 53(5):576–583. https://doi.org/10.9713/kcer.2015.53.5.576

Dahri MK, Kooh MRR, Lim LB (2015b) Application of Casuarina equisetifolia needle for the removal of methylene blue and malachite green dyes from aqueous solution. Alex Eng J 54 (4):1253–1263. https://doi.org/10.1016/j.aej.2015.07.005

Dahri MK, Kooh MRR, Lim LB (2016) Remediation of rhodamine b dye from aqueous solution using Casuarina equisetifolia cone powder as a low-cost adsorbent. Adv Phys Chem 2016. https://doi.org/10.1155/2016/9497378

Dalvand A, Gholibegloo E, Ganjali MR, Golchinpoor N, Khazaei M, Kamani H, Hosseini SS, Mahvi AH (2016) Comparison of Moringa stenopetala seed extract as a clean coagulant with Alum and Moringa stenopetala-Alum hybrid coagulant to remove direct dye from textile wastewater. Environ Sci Pollut Res 23(16):16396–16405. https://doi.org/10.1007/s11356-016-6708-z

Daneshvar N, Behnajady M, Mohammadi MKA, Dorraji MS (2008) UV/H2O2 treatment of Rhodamine B in aqueous solution: Influence of operational parameters and kinetic modeling. Desalination 230(1–3):16–26. https://doi.org/10.1016/j.desal.2007.11.012

Dash B, Kumar A (2017) Nanofiltration for textile dye–water treatment: experimental and parameter estimation studies using a spiral wound module and validation of the Spiegler–Kedem-based model. Sep Sci Technol 52(7):1216–1224. https://doi.org/10.1080/01496395.2017.1282965

Davis RJ, Gainer JL, O'Neal G, Wu I-W (1994) Photocatalytic decolorization of wastewater dyes. Water Environ Res 66(1):50–53. https://doi.org/10.2175/WER.66.1.8

Demirbas A (2009) Agricultural based activated carbons for the removal of dyes from aqueous solutions: a review. J Hazard Mater 167(1–3):1–9. https://doi.org/10.1016/j.jhazmat.2008.12.114

Deng H, Yang L, Tao G, Dai J (2009) Preparation and characterization of activated carbon from cotton stalk by microwave assisted chemical activation—application in methylene blue adsorption from aqueous solution. J Hazard Mater 166(2–3):1514–1521. https://doi.org/10.1016/j.jhazmat.2008.12.080

Diwaniyan S, Kharb D, Raghukumar C, Kuhad RC (2010) Decolorization of synthetic dyes and textile effluents by basidiomycetous fungi. Water Air Soil Pollut 210(1–4):409–419. https://doi.org/10.1007/s11270-009-0263-x

Djilani C, Zaghdoudi R, Djazi F, Bouchekima B, Lallam A, Modarressi A, Rogalski M (2015) Adsorption of dyes on activated carbon prepared from apricot stones and commercial activated carbon. J Taiwan Inst Chem Eng 53:112–121. https://doi.org/10.1016/j.jtice.2015.02.025

Dutta D, Thakur D, Bahadur D (2015) SnO2 quantum dots decorated silica nanoparticles for fast removal of cationic dye (methylene blue) from wastewater. Chem Eng J 281:482–490. https://doi.org/10.1016/j.cej.2015.06.110

Ebrahimian Pirbazari A, Fakhari Kisom B, Ghamangiz Khararoodi M (2016) Anionic surfactant-modified rice straw for removal of methylene blue from aqueous solution. Desalin Water Treat 57(39):18202–18216. https://doi.org/10.1080/19443994.2015.1090919

Ejder-Korucu M, Gürses A, Doğar Ç, Sharma SK, Açıkyıldız M (2015) Removal of organic dyes from industrial effluents: an overview of physical and biotechnological applications. In: Green chemistry for dyes removal from wastewater: research trends and applications, pp 1–34. https://doi.org/10.1002/9781118721001.ch1

El Nemr A, Abdelwahab O, El-Sikaily A, Khaled A (2009) Removal of direct blue-86 from aqueous solution by new activated carbon developed from orange peel. J Hazard Mater 161(1):102–110. https://doi.org/10.1016/j.jhazmat.2008.03.060

Elass K, Laachach A, Alaoui A, Azzi M (2011) Removal of methyl violet from aqueous solution using a stevensite-rich clay from Morocco. Appl Clay Sci 54(1):90–96. https://doi.org/10.1016/j.clay.2011.07.019

Elmoubarki R, Mahjoubi F, Tounsadi H, Moustadraf J, Abdennouri M, Zouhri A, El Albani A, Barka N (2015) Adsorption of textile dyes on raw and decanted Moroccan clays: kinetics, equilibrium and thermodynamics. Water Resour Ind 9:16–29. https://doi.org/10.1016/j.wri.2014.11.001

El-Sheekh MM, Gharieb M, Abou-El-Souod G (2009) Biodegradation of dyes by some green algae and cyanobacteria. Int Biodeter Biodegr 63(6):699–704. https://doi.org/10.1016/j.ibiod.2009.04.010

El-Zahhar AA, Awwad NS (2016) Removal of malachite green dye from aqueous solutions using organically modified hydroxyapatite. J Environ Chem Eng 4(1):633–638. https://doi.org/10.1016/j.jece.2015.12.014

El-Zahhar AA, Awwad NS, El-Katori EE (2014) Removal of bromophenol blue dye from industrial waste water by synthesizing polymer-clay composite. J Mol Liq 199:454–461. https://doi.org/10.1016/j.molliq.2014.07.034

Eren E, Cubuk O, Ciftci H, Eren B, Caglar B (2010) Adsorption of basic dye from aqueous solutions by modified sepiolite: equilibrium, kinetics and thermodynamics study. Desalination 252(1–3):88–96. https://doi.org/10.1016/j.desal.2009.10.020

Esmaeli A, Jokar M, Kousha M, Daneshvar E, Zilouei H, Karimi K (2013) Acidic dye wastewater treatment onto a marine macroalga, Nizamuddina zanardini (Phylum: Ochrophyta). Chem Eng J 217:329–336. https://doi.org/10.1016/j.cej.2012.11.038

Esther F, Tibor C, Gyula O (2004) Removal of synthetic dyes from wastewaters: a review. Environ Int 30(7):953–971. https://doi.org/10.1016/j.envint.2004.02.001

Fang R, Cheng X, Xu X (2010) Synthesis of lignin-base cationic flocculant and its application in removing anionic azo-dyes from simulated wastewater. Bioresour Technol 101(19):7323–7329. https://doi.org/10.1016/j.biortech.2010.04.094

Foorginezhad S, Zerafat M (2017) Microfiltration of cationic dyes using nano-clay membranes. Ceram Int 43(17):15146–15159. https://doi.org/10.1016/j.ceramint.2017.08.045

Fosso-Kankeu E, Ntwampe O, Waanders F, Webster A (2015) The performance of polyaluminium chloride and bentonite clay coagulant in the removal of cationic and anionic dyes. In: 7th International Conference on Latest Trends in Engineering and Technology (ICLTET'2015). https://doi.org/10.15242/IIE.E111501

Fosso-Kankeu E, Waanders F, Fourie CL (2016) Adsorption of Congo Red by surfactant-impregnated bentonite clay. Desalin Water Treat 57(57):27663–27671. https://doi.org/10.1080/19443994.2016.1177599

Fosso-Kankeu E, Webster A, Ntwampe I, Waanders F (2017) Coagulation/flocculation potential of polyaluminium chloride and bentonite clay tested in the removal of methyl red and crystal violet. Arab J Sci Eng 42(4):1389–1397. https://doi.org/10.1007/s13369-016-2244-x

Gao J, Thong Z, Wang KY, Chung T-S (2017) Fabrication of loose inner-selective polyethersulfone (PES) hollow fibers by one-step spinning process for nanofiltration (NF) of textile dyes. J Membr Sci 541:413–424. https://doi.org/10.1016/j.memsci.2017.07.016

Geethakarthi A, Phanikumar B (2011) Adsorption of reactive dyes from aqueous solutions by tannery sludge developed activated carbon: kinetic and equilibrium studies. Int J Environ Sci Technol 8(3):561–570. https://doi.org/10.1007/BF03326242

Georgiou D, Melidis P, Aivasidis A, Gimouhopoulos K (2002) Degradation of azo-reactive dyes by ultraviolet radiation in the presence of hydrogen peroxide. Dyes Pigments 52(2):69–78. https://doi.org/10.1016/S0143-7208(01)00078-X

Ghaedi M, Shokrollahi A, Tavallali H, Shojaiepoor F, Keshavarz B, Hossainian H, Soylak M, Purkait M (2011) Activated carbon and multiwalled carbon nanotubes as efficient adsorbents for removal of arsenazo (III) and methyl red from waste water. Toxicol Environ Chem 93 (3):438–449. https://doi.org/10.1080/02772248.2010.540244

Ghaedi M, Sadeghian B, Pebdani AA, Sahraei R, Daneshfar A, Duran C (2012) Kinetics, thermodynamics and equilibrium evaluation of direct yellow 12 removal by adsorption onto silver nanoparticles loaded activated carbon. Chem Eng J 187:133–141. https://doi.org/10.1016/j.cej.2012.01.111

Ghodbane H, Hamdaoui O (2009) Degradation of Acid Blue 25 in aqueous media using 1700 kHz ultrasonic irradiation: ultrasound/Fe (II) and ultrasound/H2O2 combinations. Ultrason Sonochem 16(5):593–598. https://doi.org/10.1016/j.ultsonch.2008.11.006

Ghosh A, Dastidar MG, Sreekrishnan T (2017) Bioremediation of chromium complex dyes and treatment of sludge generated during the process. Int Biodeter Biodegr 119:448–460. https://doi.org/10.1016/j.ibiod.2016.08.013

Gobi K, Mashitah M, Vadivelu V (2011) Adsorptive removal of methylene blue using novel adsorbent from palm oil mill effluent waste activated sludge: equilibrium, thermodynamics and kinetic studies. Chem Eng J 171(3):1246–1252. https://doi.org/10.1016/j.cej.2011.05.036

Gök Ö, Özcan AS, Özcan A (2010) Adsorption behavior of a textile dye of Reactive Blue 19 from aqueous solutions onto modified bentonite. Appl Surf Sci 256(17):5439–5443. https://doi.org/10.1016/j.apsusc.2009.12.134

Gönder ZB, Arayici S, Barlas H (2011) Advanced treatment of pulp and paper mill wastewater by nanofiltration process: effects of operating conditions on membrane fouling. Sep Purif Technol 76(3):292–302. https://doi.org/10.1016/j.seppur.2010.10.018

Greluk M, Hubicki Z (2011) Efficient removal of Acid Orange 7 dye from water using the strongly basic anion exchange resin Amberlite IRA-958. Desalination 278(1–3):219–226. https://doi.org/10.1016/j.desal.2011.05.024

Gül Ş, Özcan-Yıldırım Ö (2009) Degradation of Reactive Red 194 and Reactive Yellow 145 azo dyes by O3 and H2O2/UV-C processes. Chem Eng J 155(3):684–690. https://doi.org/10.1016/j.cej.2009.08.029

Gupta V (2009) Application of low-cost adsorbents for dye removal–a review. J Environ Manag 90 (8):2313–2342. https://doi.org/10.1016/j.jenvman.2008.11.017

Gupta VK, Jain R, Shrivastava M (2010) Adsorptive removal of Cyanosine from wastewater using coconut husks. J Colloid Interface Sci 347(2):309–314. https://doi.org/10.1016/j.jcis.2010.03.060

Gupta VK, Kumar R, Nayak A, Saleh TA, Barakat M (2013) Adsorptive removal of dyes from aqueous solution onto carbon nanotubes: a review. Adv Colloid Interf Sci 193:24–34. https://doi.org/10.1016/j.cis.2013.03.003

Gutiérrez-Segura E, Solache-Ríos M, Colín-Cruz A (2009) Sorption of indigo carmine by a Fe-zeolitic tuff and carbonaceous material from pyrolyzed sewage sludge. J Hazard Mater 170(2–3):1227–1235. https://doi.org/10.1016/j.jhazmat.2009.05.102

Guzmán-Duque FL, Palma-Goyes RE, González I, Peñuela G, Torres-Palma RA (2014) Relationship between anode material, supporting electrolyte and current density during electrochemical degradation of organic compounds in water. J Hazard Mater 278:221–226. https://doi.org/10.1016/j.jhazmat.2014.05.076

Hadi P, Xu M, Ning C, Lin CSK, McKay G (2015) A critical review on preparation, characterization and utilization of sludge-derived activated carbons for wastewater treatment. Chem Eng J 260:895–906. https://doi.org/10.1016/j.cej.2014.08.088

Hadibarata T, Adnan LA, Yusoff ARM, Yuniarto A, Zubir MMFA, Khudhair AB, Teh ZC, Naser MA (2013) Microbial decolorization of an azo dye reactive black 5 using white-rot fungus Pleurotus eryngii F032. Water Air Soil Pollut 224(6):1595. https://doi.org/10.1007/s11270-013-1595-0

Hairom NHH, Mohammad AW, Kadhum AAH (2014) Nanofiltration of hazardous Congo red dye: performance and flux decline analysis. J Water Proc Eng 4:99–106. https://doi.org/10.1016/j.jwpe.2014.09.008

Hameed B (2009) Evaluation of papaya seeds as a novel non-conventional low-cost adsorbent for removal of methylene blue. J Hazard Mater 162(2–3):939–944. https://doi.org/10.1016/j.jhazmat.2008.05.120

Han R, Zhang S, Zhao W, Li X, Jian X (2009) Treating sulfur black dye wastewater with quaternized poly (phthalazinone ether sulfone ketone) nanofiltration membranes. Sep Purif Technol 67(1):26–30. https://doi.org/10.1016/j.seppur.2009.03.006

Han G, Chung T-S, Weber M, Maletzko C (2018) Low-pressure nanofiltration hollow fiber membranes for effective fractionation of dyes and inorganic salts in textile wastewater. Environ Sci Technol 52(6):3676–3684. https://doi.org/10.1021/acs.est.7b06518

Hemmati F, Norouzbeigi R, Sarbisheh F, Shayesteh H (2016) Malachite green removal using modified sphagnum peat moss as a low-cost biosorbent: kinetic, equilibrium and thermodynamic studies. J Taiwan Inst Chem Eng 58:482–489. https://doi.org/10.1016/j.jtice.2015.07.004

Hildebrand C, Kuglin V, Brandao H, Vilar VJ, de Souza SGU, de Souza AU (2014) Insights into nanofiltration of textile wastewaters for water reuse. Clean Techn Environ Policy 16 (3):591–600. https://doi.org/10.1007/s10098-013-0665-8

Hsu YC, Yen CH, Huang HC (1998) Multistage treatment of high strength dye wastewater by coagulation and ozonation. J Chem Technol Biotechnol 71(1):71–76. https://doi.org/10.1002/(SICI)1097-4660(199801)71:1<71::AID-JCTB808>3.0.CO;2-K

Huang J, Zhang K (2011) The high flux poly (m-phenylene isophthalamide) nanofiltration membrane for dye purification and desalination. Desalination 282:19–26. https://doi.org/10.1016/j.desal.2011.09.045

Huang Z, Li Y, Chen W, Shi J, Zhang N, Wang X, Li Z, Gao L, Zhang Y (2017) Modified bentonite adsorption of organic pollutants of dye wastewater. Mater Chem Phys 202:266–276. https://doi.org/10.1016/j.matchemphys.2017.09.028

Humelnicu I, Băiceanu A, Ignat M-E, Dulman V (2017) The removal of Basic Blue 41 textile dye from aqueous solution by adsorption onto natural zeolitic tuff: kinetics and thermodynamics. Process Saf Environ Prot 105:274–287. https://doi.org/10.1016/j.psep.2016.11.016

Ibrahim S, Fatimah I, Ang H-M, Wang S (2010) Adsorption of anionic dyes in aqueous solution using chemically modified barley straw. Water Sci Technol 62(5):1177–1182. https://doi.org/10.2166/wst.2010.388

Ito T, Adachi Y, Yamanashi Y, Shimada YJ (2016) Long–term natural remediation process in textile dye–polluted river sediment driven by bacterial community changes. Water Res 100:458–465. https://doi.org/10.1016/j.watres.2016.05.050

İyim TB, Güçlü G (2009) Removal of basic dyes from aqueous solutions using natural clay. Desalination 249(3):1377–1379. https://doi.org/10.1016/j.desal.2009.06.020

Jadhav J, Kalyani D, Telke A, Phugare S, Govindwar S (2010) Evaluation of the efficacy of a bacterial consortium for the removal of color, reduction of heavy metals, and toxicity from textile dye effluent. Bioresour Technol 101(1):165–173. https://doi.org/10.1016/j.biortech.2009.08.027

Jaerger S, Dos Santos A, Fernandes A, Almeida C (2015) Removal of p-nitrophenol from aqueous solution using Brazilian peat: kinetic and thermodynamic studies. Water Air Soil Pollut 226 (8):236. https://doi.org/10.1007/s11270-015-2500-9

Jebapriya GR, Gnanadoss JJ (2013) Bioremediation of textile dye using white rot fungi: a review. Int J Curr Res Rev 5(3):1

Jiang J-Q, Yang C-X, Yan X-P (2013) Zeolitic imidazolate framework-8 for fast adsorption and removal of benzotriazoles from aqueous solution. ACS Appl Mater Interfaces 5(19):9837–9842. https://doi.org/10.1021/am403079n

Jourvand M, Shams Khorramabadi G, Omidi Khaniabadi Y, Godini H, Nourmoradi H (2015) Removal of methylene blue from aqueous solutions using modified clay. J Basic Res Med Sci 2(1):32–41

Kabdaşlı I, Vardar B, Arslan-Alaton I, Tünay O (2009) Effect of dye auxiliaries on color and COD removal from simulated reactive dyebath effluent by electrocoagulation. Chem Eng J 148 (1):89–96. https://doi.org/10.1016/j.cej.2008.08.006

Kalkan E, Nadaroğlu H, Celebi N, Tozsin G (2014) Removal of textile dye Reactive Black 5 from aqueous solution by adsorption on laccase-modified silica fume. Desalin Water Treat 52 (31–33):6122–6134. https://doi.org/10.1080/19443994.2013.811114

Kandelbauer A, Guebitz G (2005) Bioremediation for the decolorization of textile dyes—a review. In: Environmental chemistry. Springer, pp 269–288. https://doi.org/10.1007/3-540-26531-7_26

Kang Q, Zhou W, Li Q, Gao B, Fan J, Shen D (2009) Adsorption of anionic dyes on poly (epichlorohydrin dimethylamine) modified bentonite in single and mixed dye solutions. Appl Clay Sci 45(4):280–287. https://doi.org/10.1016/j.clay.2009.06.010

Karim AB, Mounir B, Hachkar M, Bakasse M, Yaacoubi A (2009) Removal of Basic Red 46 dye from aqueous solution by adsorption onto Moroccan clay. J Hazard Mater 168(1):304–309. https://doi.org/10.1016/j.jhazmat.2009.02.028

Kaushik P, Malik A (2009) Fungal dye decolorization: recent advances and future potential. Environ Int 35(1):127–141. https://doi.org/10.1016/j.envint.2008.05.010

Kazeem TS, Lateef SA, Ganiyu SA, Qamaruddin M, Tanimu A, Sulaiman KO, Jillani SMS, Alhooshani K (2018) Aluminium-modified activated carbon as efficient adsorbent for cleaning of cationic dye in wastewater. J Clean Prod 205:303–312. https://doi.org/10.1016/j.jclepro.2018.09.114

Kebria MRS, Jahanshahi M, Rahimpour A (2015) SiO2 modified polyethylenimine-based nanofiltration membranes for dye removal from aqueous and organic solutions. Desalination 367:255–264. https://doi.org/10.1016/j.desal.2015.04.017

Khalid A, Kausar F, Arshad M, Mahmood T, Ahmed I (2012) Accelerated decolorization of reactive azo dyes under saline conditions by bacteria isolated from Arabian seawater sediment. Appl Microbiol Biotechnol 96(6):1599–1606. https://doi.org/10.1007/s00253-012-3877-7

Khan EA, Khan TA (2018) Adsorption of methyl red on activated carbon derived from custard apple (Annona squamosa) fruit shell: equilibrium isotherm and kinetic studies. J Mol Liq 249:1195–1211. https://doi.org/10.1016/j.molliq.2017.11.125

Khanday W, Marrakchi F, Asif M, Hameed B (2017) Mesoporous zeolite–activated carbon composite from oil palm ash as an effective adsorbent for methylene blue. J Taiwan Inst Chem Eng 70:32–41. https://doi.org/10.1016/j.jtice.2016.10.029

Khanna S, Rattan VK (2017) Removal of acid red 1 from aqueous waste streams using peel of Cucumis sativus fruit. Equilibrium studies. J Chem Technol Metall 52:803–811

Khataee AR, Zarei M, Pourhassan M (2010) Bioremediation of malachite green from contaminated water by three microalgae: neural network modeling. Clean Soil Air Water 38(1):96–103. https://doi.org/10.1002/clen.200900233

Khataee A, Zarei M, Dehghan G, Ebadi E, Pourhassan M (2011) Biotreatment of a triphenylmethane dye solution using a Xanthophyta alga: modeling of key factors by neural network. J Taiwan Inst Chem Eng 42(3):380–386. https://doi.org/10.1016/j.jtice.2010.08.006

Khataee A, Vafaei F, Jannatkhah M (2013) Biosorption of three textile dyes from contaminated water by filamentous green algal Spirogyra sp.: Kinetic, isotherm and thermodynamic studies. Int Biodeter Biodegr 83:33–40. https://doi.org/10.1016/j.ibiod.2013.04.004

Khouni I, Marrot B, Amar RBJS, Technology P (2012) Treatment of reconstituted textile wastewater containing a reactive dye in an aerobic sequencing batch reactor using a novel bacterial consortium. Sep Purif Technol 87:110–119. https://doi.org/10.1016/j.seppur.2011.11.030

Kooh MRR, Dahri MK, Lim LB (2016) The removal of rhodamine B dye from aqueous solution using Casuarina equisetifolia needles as adsorbent. Cogent Environ Sci 2(1):1140553. https://doi.org/10.1080/23311843.2016.1140553

Koswojo R, Utomo RP, Ju Y-H, Ayucitra A, Soetaredjo FE, Sunarso J, Ismadji S (2010) Acid Green 25 removal from wastewater by organo-bentonite from Pacitan. Appl Clay Sci 48 (1–2):81–86. https://doi.org/10.1016/j.clay.2009.11.023

Kumar P, Agnihotri R, Wasewar K, Uslu H, Yoo C (2012) Status of adsorptive removal of dye from textile industry effluent. Desalin Water Treat 50. https://doi.org/10.1080/19443994.2012.719472

Kurniawan A, Sutiono H, Indraswati N, Ismadji S (2012) Removal of basic dyes in binary system by adsorption using rarasaponin–bentonite: revisited of extended Langmuir model. Chem Eng J 189:264–274. https://doi.org/10.1016/j.cej.2012.02.070

Kusic H, Koprivanac N, Srsan L (2006) Azo dye degradation using Fenton type processes assisted by UV irradiation: a kinetic study. J Photochem Photobiol A 181(2–3):195–202. https://doi.org/10.1016/j.jphotochem.2005.11.024

Labanda J, Sabaté J, Llorens J (2009) Modeling of the dynamic adsorption of an anionic dye through ion-exchange membrane adsorber. J Membr Sci 340(1–2):234–240. https://doi.org/10.1016/j.memsci.2009.05.036

Lalnunhlimi S, Krishnaswamy V (2016) Decolorization of azo dyes (Direct Blue 151 and Direct Red 31) by moderately alkaliphilic bacterial consortium. Braz J Microbiol 47(1):39–46. https://doi.org/10.1016/j.bjm.2015.11.013

Lambert J, Vega MM, Isarain-Chavez E, Peralta-Hernandez JMJIJET, Engineering A (2013) Ozone and electrocoagulation processes for treatment of dye in leather industry wastewater: a comparative study 3(7):1–9

Lau Y-Y, Wong Y-S, Teng T-T, Morad N, Rafatullah M, Ong S-A (2014) Coagulation-flocculation of azo dye Acid Orange 7 with green refined laterite soil. Chem Eng J 246:383–390. https://doi.org/10.1016/j.cej.2014.02.100

Lau Y-Y, Wong Y-S, Teng T-T, Morad N, Rafatullah M, Ong S-A (2015) Degradation of cationic and anionic dyes in coagulation–flocculation process using bi-functionalized silica hybrid with aluminum-ferric as auxiliary agent. RSC Adv 5(43):34206–34215. https://doi.org/10.1039/C5RA01346A

Lee LY, Gan S, Tan MSY, Lim SS, Lee XJ, Lam YF (2016) Effective removal of Acid Blue 113 dye using overripe Cucumis sativus peel as an eco-friendly biosorbent from agricultural residue. J Clean Prod 113:194–203. https://doi.org/10.1016/j.jclepro.2015.11.016

Leng L, Yuan X, Huang H, Shao J, Wang H, Chen X, Zeng G (2015) Bio-char derived from sewage sludge by liquefaction: characterization and application for dye adsorption. Appl Surf Sci 346:223–231. https://doi.org/10.1016/j.apsusc.2015.04.014

Li W-H, Yue Q-Y, Gao B-Y, Ma Z-H, Li Y-J, Zhao H-X (2011a) Preparation and utilization of sludge-based activated carbon for the adsorption of dyes from aqueous solutions. Chem Eng J 171(1):320–327. https://doi.org/10.1016/j.desal.2011.05.020

Li W-H, Yue Q-Y, Gao B-Y, Wang X-J, Qi Y-F, Zhao Y-Q, Li Y-J (2011b) Preparation of sludge-based activated carbon made from paper mill sewage sludge by steam activation for dye wastewater treatment. Desalination 278(1–3):179–185. https://doi.org/10.1016/j.cej.2011.10.049

Li W, Yue Q, Tu P, Ma Z, Gao B, Li J, Xu X (2011c) Adsorption characteristics of dyes in columns of activated carbon prepared from paper mill sewage sludge. Chem Eng J 178:197–203. https://doi.org/10.1016/j.cej.2011.04.012

Li C, Zhong H, Wang S, Xue J, Zhang Z (2015) Removal of basic dye (methylene blue) from aqueous solution using zeolite synthesized from electrolytic manganese residue. J Ind Eng Chem 23:344–352. https://doi.org/10.1016/j.jiec.2014.08.038

Li H, Liu S, Zhao J, Feng N (2016) Removal of reactive dyes from wastewater assisted with kaolin clay by magnesium hydroxide coagulation process. Colloids Surf A Physicochem Eng Asp 494:222–227. https://doi.org/10.1016/j.colsurfa.2016.01.048

Lim S-L, Chu W-L, Phang S-M (2010) Use of Chlorella vulgaris for bioremediation of textile wastewater. Bioresour Technol 101(19):7314–7322. https://doi.org/10.1016/j.biortech.2010.04.092

Lim LB, Priyantha N, Chieng HI, Dahri MK (2016) Artocarpus camansi Blanco (Breadnut) core as low-cost adsorbent for the removal of methylene blue: equilibrium, thermodynamics, and kinetics studies. Desalin Water Treat 57(12):5673–5685. https://doi.org/10.1080/19443994.2015.1007088

Lim LB, Priyantha N, Tennakoon D, Chieng HI, Dahri MK, Suklueng M (2017) Breadnut peel as a highly effective low-cost biosorbent for methylene blue: equilibrium, thermodynamic and kinetic studies. Arab J Chem 10:S3216–S3228. https://doi.org/10.1016/j.arabjc.2013.12.018

Liu J, Ma S, Zang L (2013a) Preparation and characterization of ammonium-functionalized silica nanoparticle as a new adsorbent to remove methyl orange from aqueous solution. Appl Surf Sci 265:393–398. https://doi.org/10.1016/j.apsusc.2012.11.019

Liu L, Lin Y, Liu Y, Zhu H, He Q (2013b) Removal of methylene blue from aqueous solutions by sewage sludge based granular activated carbon: adsorption equilibrium, kinetics, and thermodynamics. J Chem Eng Data 58(8):2248–2253. https://doi.org/10.1021/je4003543

Liu S, Ding Y, Li P, Diao K, Tan X, Lei F, Zhan Y, Li Q, Huang B, Huang Z (2014a) Adsorption of the anionic dye Congo red from aqueous solution onto natural zeolites modified with N, N-dimethyl dehydroabietylamine oxide. Chem Eng J 248:135–144. https://doi.org/10.1016/j.cej.2014.03.026

Liu Y, Gao M, Gu Z, Luo Z, Ye Y, Lu L (2014b) Comparison between the removal of phenol and catechol by modified montmorillonite with two novel hydroxyl-containing Gemini surfactants. J Hazard Mater 267:71–80. https://doi.org/10.1016/j.jhazmat.2013.12.039

Liu M, Chen Q, Lu K, Huang W, Lü Z, Zhou C, Yu S, Gao C (2017) High efficient removal of dyes from aqueous solution through nanofiltration using diethanolamine-modified polyamide thin-film composite membrane. Sep Purif Technol 173:135–143. https://doi.org/10.1016/j.seppur.2016.09.023

Ma Q, Shen F, Lu X, Bao W, Ma H (2013) Studies on the adsorption behavior of methyl orange from dye wastewater onto activated clay. Desalin Water Treat 51(19–21):3700–3709. https://doi.org/10.1080/19443994.2013.782083

Ma L, Zhuo R, Liu H, Yu D, Jiang M, Zhang X, Yang Y (2014) Efficient decolorization and detoxification of the sulfonated azo dye Reactive Orange 16 and simulated textile wastewater containing Reactive Orange 16 by the white-rot fungus Ganoderma sp. En3 isolated from the forest of Tzu-chin Mountain in China. Biochem Eng J 82:1–9. https://doi.org/10.1016/j.bej.2013.10.015

Mahamad MN, Zaini MAA, Zakaria ZA (2015) Preparation and characterization of activated carbon from pineapple waste biomass for dye removal. Int Biodeterior Biodegradation 102:274–280. https://doi.org/10.1016/j.ibiod.2015.03.009

Mahmood S, Arshad M, Khalid A, Nazli ZH, Mahmood TJS, Environment (2011) Isolation and screening of azo dye decolorizing bacterial isolates from dye-contaminated textile wastewater. 30 (1)

Makhoukhi B, Djab M, Didi MA (2015) Adsorption of Telon dyes onto bis-imidazolium modified bentonite in aqueous solutions. J Environ Chem Eng 3(2):1384–1392. https://doi.org/10.1016/j.jece.2014.12.012

Malakootian M, Fatehizadeh A (2010) Color removal from water by coagulation/caustic soda and lime. J Environ Health Sci Eng 7(3):267–272

Malakootian M, Mansoorian HJ, Hosseini A, Khanjani N (2015) Evaluating the efficacy of alumina/carbon nanotube hybrid adsorbents in removing Azo Reactive Red 198 and Blue 19 dyes from aqueous solutions. Process Saf Environ Prot 96:125–137. https://doi.org/10.1016/j.psep.2015.05.002

Mane VS, Babu PV (2011) Evaluation of performance of coagulation/flocculation method for the removal of dyes from aqueous solutions. In: International conference on current trends in technology,'NUiCONE—2011, pp 8–10

Mittal A, Kaur D, Malviya A, Mittal J, Gupta V (2009) Adsorption studies on the removal of coloring agent phenol red from wastewater using waste materials as adsorbents. J Colloid Interface Sci 337(2):345–354. https://doi.org/10.1016/j.jcis.2009.05.016

Moghaddam SS, Moghaddam MA, Arami M (2010) Coagulation/flocculation process for dye removal using sludge from water treatment plant: optimization through response surface methodology. J Hazard Mater 175(1–3):651–657. https://doi.org/10.1016/j.jhazmat.2009.10.058

Mohammadifar E, Shemirani F, Majidi B, Ezoddin M (2015) Application of modified nano-γ-alumina as an efficient adsorbent for removing malachite green (MG) from aqueous solution. Desalin Water Treat 54(3):758–768. https://doi.org/10.1080/19443994.2014.890549

Mollah MYA, Gomes JA, Das KK, Cocke DL (2010) Electrochemical treatment of Orange II dye solution—use of aluminum sacrificial electrodes and floc characterization. J Hazard Mater 174 (1–3):851–858. https://doi.org/10.1016/j.jhazmat.2009.09.131

Monika K (2012) Use of various technologies, methods and adsorbents for the removal of dye. J Environ Res Dev 6(3A):879–883

Monsalvo VM, Mohedano AF, Rodriguez JJ (2011) Activated carbons from sewage sludge: application to aqueous-phase adsorption of 4-chlorophenol. Desalination 277(1–3):377–382. https://doi.org/10.1016/j.desal.2011.04.059

Monsalvo VM, Mohedano AF, Rodriguez JJ (2012) Adsorption of 4-chlorophenol by inexpensive sewage sludge-based adsorbents. Chem Eng Res Des 90(11):1807–1814. https://doi.org/10.1016/j.cherd.2012.03.018

Moussas P, Tzoupanos N, Zouboulis A (2011) Advances in coagulation/flocculation field: Al-and Fe-based composite coagulation reagents. Desalin Water Treat 33(1–3):140–146. https://doi.org/10.5004/dwt.2011.2622

Moussavi G, Mahmoudi M (2009) Degradation and biodegradability improvement of the reactive red 198 azo dye using catalytic ozonation with MgO nanocrystals. Chem Eng J 152(1):1–7. https://doi.org/10.1016/j.cej.2009.03.014

Mukhlish MZB, Khan MR, Bhoumick MC, Paul S (2012) Papaya (Carica papaya L.) leaf powder: novel adsorbent for removal of methylene blue from aqueous solution. Water Air Soil Pollut 223 (8):4949–4958. https://doi.org/10.1007/s11270-012-1249-7

Nadafi K, Vosoughi M, Asadi A, Borna MO, Shirmardi M (2014) Reactive Red 120 dye removal from aqueous solution by adsorption on nano-alumina. J Water Chem Technol 36(3):125–133. https://doi.org/10.3103/S1063455X14030059

Nandi BK, Goswami A, Purkait MK (2009) Adsorption characteristics of brilliant green dye on kaolin. J Hazard Mater 161(1):387–395. https://doi.org/10.1016/j.jhazmat.2008.03.110

Nasuha N, Zurainan H, Maarof H, Zubir N, Amri N (2011) Effect of cationic and anionic dye adsorption from aqueous solution by using chemically modified papaya seed. In: International conference on environment science and engineering, pp 50–54

Nataraj S, Hosamani K, Aminabhavi T (2009) Nanofiltration and reverse osmosis thin film composite membrane module for the removal of dye and salts from the simulated mixtures. Desalination 249(1):12–17. https://doi.org/10.1016/j.desal.2009.06.008

Natarajan S, Bajaj HC, Tayade RJ (2018) Recent advances based on the synergetic effect of adsorption for removal of dyes from waste water using photocatalytic process. J Environ Sci (China) 65:201–222. https://doi.org/10.1016/j.jes.2017.03.011

Nazari S, Yari AR, Mahmodian MH, Tanhaye Reshvanloo M, Alizadeh Matboo S, Majidi G, Emamian M (2013) Application of H2O2 and H2O2/Fe0 in removal of acid red 18 dye from aqueous solutions %J archives of hygiene. Sciences 2(3):104–110

Ncibi M, Hamissa AB, Fathallah A, Kortas M, Baklouti T, Mahjoub B, Seffen M (2009) Biosorptive uptake of methylene blue using Mediterranean green alga Enteromorpha spp. J Hazard Mater 170(2–3):1050–1055. https://doi.org/10.1016/j.jhazmat.2009.05.075

Nešić AR, Veličković SJ, Antonović DG (2013) Modification of chitosan by zeolite A and adsorption of Bezactive Orange 16 from aqueous solution. Compos Part B 53:145–151. https://doi.org/10.1016/j.compositesb.2013.04.053

Nuithitikul K, Srikhun S, Hirunpraditkoon S (2010) Influences of pyrolysis condition and acid treatment on properties of durian peel-based activated carbon. Bioresour Technol 101 (1):426–429. https://doi.org/10.1016/j.biortech.2009.07.040

Obiora-Okafo I, Onukwuli O (2015) Optimization of coagulation-flocculation process for color removal from synthetic dye wastewater using natural organic polymers: response surface methodology applied. Inter J of Scientific & Eng Research 6(12):693–704

Obiora-Okafo I, Onukwuli O (2017) Optimization of coagulation-flocculation process for color removal from azo dye using natural polymers: response surface methodological approach. Niger J Technol 36(2):482–495. https://doi.org/10.4314/njt.v36i2.23

Oei BC, Ibrahim S, Wang S, Ang HM (2009) Surfactant modified barley straw for removal of acid and reactive dyes from aqueous solution. Bioresour Technol 100(18):4292–4295. https://doi.org/10.1016/j.biortech.2009.03.063

Ogugbue CJ, Sawidis T (2011) Bioremediation and detoxification of synthetic wastewater containing triarylmethane dyes by Aeromonas hydrophila isolated from industrial effluent. Biotechnol Res Int 2011. https://doi.org/10.4061/2011/967925

Ollis DF (1993) Comparative aspects of advanced oxidation processes, ACS symposium series. American Chemical Society, Washington, DC, pp 18–34. https://doi.org/10.1021/bk-1993-0518.ch002

Pachhade K, Sandhya S, Swaminathan K (2009) Ozonation of reactive dye, Procion red MX-5B catalyzed by metal ions. J Hazard Mater 167(1–3):313–318. https://doi.org/10.1016/j.jhazmat.2008.12.126

Parolin F, Nascimento UM, Azevedo EB (2013) Microwave-enhanced UV/H2O2 degradation of an azo dye (tartrazine): optimization, color removal, mineralization and ecotoxicity. Environ Technol 34(10):1247–1253. https://doi.org/10.1080/09593330.2012.744431

Parsa JB, Negahdar SH (2012) Treatment of wastewater containing Acid Blue 92 dye by advanced ozone-based oxidation methods. Sep Purif Technol 98:315–320. https://doi.org/10.1016/j.seppur.2012.06.041

Patel H, Vashi R (2012) Removal of Congo Red dye from its aqueous solution using natural coagulants. J Saudi Chem Soc 16(2):131–136. https://doi.org/10.1016/j.jscs.2010.12.003

Patra AS, Ghorai S, Ghosh S, Mandal B, Pal S (2016) Selective removal of toxic anionic dyes using a novel nanocomposite derived from cationically modified guar gum and silica nanoparticles. J Hazard Mater 301:127–136. https://doi.org/10.1016/j.jhazmat.2015.08.042

Paz DS, Baiotto A, Schwaab M, Mazutti MA, Bassaco MM, Bertuol DA, Foletto EL, Meili L (2013) Use of papaya seeds as a biosorbent of methylene blue from aqueous solution. Water Sci Technol 68(2):441–447. https://doi.org/10.2166/wst.2013.185

Paździor K, Klepacz-Smółka A, Ledakowicz S, Sójka-Ledakowicz J, Mrozińska Z, Żyłła R (2009) Integration of nanofiltration and biological degradation of textile wastewater containing azo dye. Chemosphere 75(2):250–255. https://doi.org/10.1016/j.chemosphere.2008.12.016

Peng N, Hu D, Zeng J, Li Y, Liang L, Chang C (2016) Superabsorbent cellulose–clay nanocomposite hydrogels for highly efficient removal of dye in water. ACS Sustain Chem Eng 4(12):7217–7224. https://doi.org/10.1021/acssuschemeng.6b02178

Pengthamkeerati P, Satapanajaru T, Chatsatapattayakul N, Chairattanamanokorn P, Sananwai N (2010) Alkaline treatment of biomass fly ash for reactive dye removal from aqueous solution. Desalination 261(1–2):34–40. https://doi.org/10.1016/j.desal.2010.05.050

Peralta-Hernández J, Méndez-Tovar M, Guerra-Sánchez R, Martínez-Huitle C, Nava J (2012) A brief review on environmental application of boron doped diamond electrodes as a new way for electrochemical incineration of synthetic dyes. https://doi.org/10.1155/2012/154316

Phalakornkule C, Polgumhang S, Tongdaung W, Karakat B, Nuyut T (2010) Electrocoagulation of blue reactive, red disperse and mixed dyes, and application in treating textile effluent. J Environ Manage 91(4):918–926. https://doi.org/10.1016/j.jenvman.2009.11.008

Ponraj M, Gokila K, VJIjoab Z (2011) Research. Bacterial decolorization of textile dye-Orange 3R 2(1):168–177

Poyatos JM, Muñio M, Almecija M, Torres J, Hontoria E, Osorio F (2010) Advanced oxidation processes for wastewater treatment: state of the art. Water Air Soil Pollut 205(1–4):187. https://doi.org/10.1007/s11270-009-0065-1

Prigione V, Zerlottin M, Refosco D, Tigini V, Anastasi A, Varese GC (2009) Chromium removal from a real tanning effluent by autochthonous and allochthonous fungi. Bioresour Technol 100 (11):2770–2776. https://doi.org/10.1016/j.biortech.2009.01.002

Racyte J, Rimeika M, Bruning HJEPE (2009) pH effect on decolorization of raw textile wastewater polluted with reactive dyes by advanced oxidation with UV/H2O2. 35 (3):167

Rafati L, Ehrampoush MH, Rafati AA, Mokhtari M, Mahvi AH (2016) Modeling of adsorption kinetic and equilibrium isotherms of naproxen onto functionalized nano-clay composite adsorbent. J Mol Liq 224:832–841. https://doi.org/10.1016/j.molliq.2016.10.059

Rafatullah M, Sulaiman O, Hashim R, Ahmad A (2010) Adsorption of methylene blue on low-cost adsorbents: a review. J Hazard Mater 177(1–3):70–80. https://doi.org/10.1016/j.jhazmat.2009.12.047

Raghu S, Lee CW, Chellammal S, Palanichamy S, Basha CA (2009) Evaluation of electrochemical oxidation techniques for degradation of dye effluents—a comparative approach. J Hazard Mater 171(1–3):748–754. https://doi.org/10.1016/j.jhazmat.2009.06.063

Rahman MA, Amin SR, Alam AS (2012) Removal of methylene blue from waste water using activated carbon prepared from rice husk. Dhaka Univ J Sci 60(2):185–189. https://doi.org/10.3329/dujs.v60i2.11491

Rahman A, Urabe T, Kishimoto N (2013) Color removal of reactive procion dyes by clay adsorbents. Procedia Environ Sci 17:270–278. https://doi.org/10.1016/j.proenv.2013.02.038

Rangabhashiyam S, Anu N, Selvaraju N (2013) Sequestration of dye from textile industry wastewater using agricultural waste products as adsorbents. J Environ Chem Eng 1(4):629–641. https://doi.org/10.1016/j.jece.2013.07.014

Rani B, Kumar V, Singh J, Bisht S, Teotia P, Sharma S, Kela R (2014) Bioremediation of dyes by fungi isolated from contaminated dye effluent sites for bio-usability. Braz J Microbiol 45 (3):1055–1063. https://doi.org/10.1590/S1517-83822014000300039

Ratnamala G, Shetty KV, Srinikethan G (2012) Removal of remazol brilliant blue dye from dye-contaminated water by adsorption using red mud: equilibrium, kinetic, and thermodynamic studies. Water Air Soil Pollut 223(9):6187–6199. https://doi.org/10.1007/s11270-012-1349-4

Rehman MSU, Munir M, Ashfaq M, Rashid N, Nazar MF, Danish M, Han J-I (2013) Adsorption of Brilliant Green dye from aqueous solution onto red clay. Chem Eng J 228:54–62. https://doi.org/10.1016/j.cej.2013.04.094

Renault F, Sancey B, Badot P-M, Crini G (2009) Chitosan for coagulation/flocculation processes–an eco-friendly approach. Eur Polym J 45(5):1337–1348. https://doi.org/10.1016/j.eurpolymj.2008.12.027

Rida K, Bouraoui S, Hadnine S (2013) Adsorption of methylene blue from aqueous solution by kaolin and zeolite. Appl Clay Sci 83:99–105. https://doi.org/10.1016/j.clay.2013.08.015

Riera-Torres M, Gutiérrez M-C (2010) Colour removal of three reactive dyes by UV light exposure after electrochemical treatment. Chemical Eng J 156(1):114–120. https://doi.org/10.1016/j.cej.2009.10.006

Robinson T, McMullan G, Marchant R, Nigam P (2001) Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. Bioresour Technol 77(3):247–255. https://doi.org/10.1016/S0960-8524(00)00080-8

Rodrigues CS, Madeira LM, Boaventura RA (2013) Treatment of textile dye wastewaters using ferrous sulphate in a chemical coagulation/flocculation process. Environ Technol 34 (6):719–729. https://doi.org/10.1080/09593330.2012.715679

Rodrigues CS, Madeira LM, Boaventura RA (2014) Synthetic textile dyeing wastewater treatment by integration of advanced oxidation and biological processes–Performance analysis with costs reduction. J Environ Chem Eng 2(2):1027–1039. https://doi.org/10.1016/j.jece.2014.03.019

Rodríguez A, García J, Ovejero G, Mestanza M (2009) Adsorption of anionic and cationic dyes on activated carbon from aqueous solutions: equilibrium and kinetics. J Hazard Mater 172 (2–3):1311–1320. https://doi.org/10.1016/j.jhazmat.2009.07.138

Rosenfeldt EJ, Chen PJ, Kullman S, Linden KG (2007) Destruction of estrogenic activity in water using UV advanced oxidation. Sci Total Environ 377(1):105–113. https://doi.org/10.1016/j.scitotenv.2007.01.096

Rubín E, Rodríguez P, Herrero R, Sastre de Vicente ME (2010) Adsorption of methylene blue on chemically modified algal biomass: equilibrium, dynamic, and surface data. J Chem Eng Data 55(12):5707–5714. https://doi.org/10.1021/je100666v

Ruppert G, Bauer R, Heisler G (1993) The photo-Fenton reaction—an effective photochemical wastewater treatment process. J Photochem Photobiol A Chem 73(1):75–78. https://doi.org/10.1016/1010-6030(93)80035-8

Rusu L, Harja M, Simion AI, Suteu D, Ciobanu G, Favier L (2014) Removal of Astrazone Blue from aqueous solutions onto brown peat. Equilibrium and kinetics studies. Korean J Chem Eng 31(6):1008–1015. https://doi.org/10.1007/s11814-014-0009-3

Safavi A, Momeni S (2012) Highly efficient degradation of azo dyes by palladium/hydroxyapatite/Fe_3O_4 nanocatalyst. J Hazard Mater 201:125–131. https://doi.org/10.1016/j.jhazmat.2011.11.048

Sahu MK, Sahu UK, Patel RK (2015) Adsorption of safranin-O dye on CO_2 neutralized activated red mud waste: process modelling, analysis and optimization using statistical design. RSC Adv 5(53):42294–42304. https://doi.org/10.1039/C5RA03777H

Saitoh T, Saitoh M, Hattori C, Hiraide M (2014) Rapid removal of cationic dyes from water by coprecipitation with aluminum hydroxide and sodium dodecyl sulfate. J Environ Chem Eng 2 (1):752–758. https://doi.org/10.1016/j.jece.2013.11.015

Salima A, Benaouda B, Noureddine B, Duclaux L (2013) Application of Ulva lactuca and Systoceira stricta algae-based activated carbons to hazardous cationic dyes removal from industrial effluents. Water Res 47(10):3375–3388. https://doi.org/10.1016/j.watres.2013.03.038

Salleh MAM, Mahmoud DK, Karim WAWA, Idris A (2011) Cationic and anionic dye adsorption by agricultural solid wastes: a comprehensive review. Desalination 280(1–3):1–13. https://doi.org/10.1016/j.desal.2011.07.019

San Keskin NO, Celebioglu A, Uyar T, Tekinay T (2015) Microalgae immobilized by nanofibrous web for removal of reactive dyes from wastewater. Ind Eng Chem Res 54(21):5802–5809. https://doi.org/10.1021/acs.iecr.5b01033

San NO, Celebioglu A, Tümtaş Y, Uyar T, Tekinay T (2014) Reusable bacteria immobilized electrospun nanofibrous webs for decolorization of methylene blue dye in wastewater treatment. RSC Adv 4(61):32249–32255. https://doi.org/10.1039/C4RA04250F

Santhi T, Manonmani S (2011) Malachite green removal from aqueous solution by the peel of Cucumis sativa fruit. Clean–Soil Air Water 39(2):162–170. https://doi.org/10.1002/clen.201000077

Santhi T, Manonmani S, Smitha T (2010) Removal of malachite green from aqueous solution by activated carbon prepared from the epicarp of Ricinus communis by adsorption. J Hazard Mater 179(1–3):178–186. https://doi.org/10.1016/j.jhazmat.2010.02.076

Santhi T, Manonmani S, Vasantha V, Chang Y (2016) A new alternative adsorbent for the removal of cationic dyes from aqueous solution. Arab J Chem 9:S466–S474. https://doi.org/10.1016/j.arabjc.2011.06.004

Sapawe N, Jalil A, Triwahyono S, Shah M, Jusoh R, Salleh N, Hameed B, Karim A (2013) Cost-effective microwave rapid synthesis of zeolite NaA for removal of methylene blue. Chem Eng J 229:388–398. https://doi.org/10.1016/j.cej.2013.06.005

Saratale R, Saratale G, Chang J-S, Govindwar S (2010) Decolorization and biodegradation of reactive dyes and dye wastewater by a developed bacterial consortium. Biodegradation 21 (6):999–1015. https://doi.org/10.1007/s10532-010-9360-1

Saranraj P, Sumathi V, Reetha D, Stella DJJoE (2010) Decolorization and Degradation of Dirct Azo Dyes and Biodegradation of Textile Dye Effluent by using Bacteria Isolated from Textile Dye Effluent

Saratale RG, Saratale GD, Chang J-S, Govindwar S (2011) Bacterial decolorization and degradation of azo dyes: a review. J Taiwan Inst Chem Eng 42(1):138–157. https://doi.org/10.1016/j.jtice.2010.06.006

Shakoor S, Nasar A (2017) Adsorptive treatment of hazardous methylene blue dye from artificially contaminated water using cucumis sativus peel waste as a low-cost adsorbent. Groundw Sustain Dev 5:152–159. https://doi.org/10.1016/j.gsd.2017.06.005

Shakoor S, Nasar A (2019) Utilization of Cucumis Sativus Peel as an eco-friendly biosorbent for the confiscation of crystal violet dye from artificially contaminated wastewater. Anal Chem Lett 9 (1):1–19. https://doi.org/10.1080/22297928.2019.1588162

Sharma Y (2009) Fast removal of malachite green by adsorption on rice husk activated carbon. Open Environ Pollut Toxicol J 1:1. https://doi.org/10.2174/1876397900901010074

Sharma YC, Upadhyay SN (2009) Removal of a cationic dye from wastewaters by adsorption on activated carbon developed from coconut coir. Energy Fuel 23(6):2983–2988. https://doi.org/10.1021/ef9001132

Sharma P, Kaur R, Baskar C, Chung W-J (2010) Removal of methylene blue from aqueous waste using rice husk and rice husk ash. Desalination 259(1–3):249–257. https://doi.org/10.1016/j.desal.2010.03.044

Shen Z, Wu D, Yang J, Yuan T, Wang W, Jia J (2006) Methods to improve electrochemical treatment effect of dye wastewater. J Hazard Mater 131(1–3):90–97. https://doi.org/10.1016/j.jhazmat.2005.09.010

Shirani M, Semnani A, Haddadi H, Habibollahi S (2014) Optimization of simultaneous removal of methylene blue, crystal violet, and fuchsine from aqueous solutions by magnetic NaY zeolite composite. Water Air Soil Pollut 225(8):2054. https://doi.org/10.1007/s11270-014-2054-2

Shirsath SR, Patil AP, Patil R, Naik JB, Gogate PR, Sonawane SH (2013) Removal of Brilliant Green from wastewater using conventional and ultrasonically prepared poly (acrylic acid) hydrogel loaded with kaolin clay: a comparative study. Ultrason Sonochem 20(3):914–923. https://doi.org/10.1016/j.ultsonch.2012.11.010

Shirzad-Siboni M, Jafari S-J, Farrokhi M, Yang JK (2013) Removal of phenol from aqueous solutions by activated red mud: equilibrium and kinetics studies. Environ Eng Res 18 (4):247–252. https://doi.org/10.4491/eer.2013.18.4.247

Shirzad-Siboni M, Jafari SJ, Giahi O, Kim I, Lee S-M, Yang J-K (2014) Removal of acid blue 113 and reactive black 5 dye from aqueous solutions by activated red mud. J Ind Eng Chem 20 (4):1432–1437. https://doi.org/10.1016/j.jiec.2013.07.028

Shu H-Y, Chang M-C (2005) Decolorization and mineralization of a phthalocyanine dye CI Direct Blue 199 using UV/H2O2 process. J Hazard Mater 125(1–3):96–101. https://doi.org/10.1016/j.jhazmat.2005.05.016

Shu H-Y, Huang C-R (1995) Degradation of commercial azo dyes in water using ozonation and UV enhanced ozonation process. Chemosphere 31(8):3813–3825. https://doi.org/10.1016/0045-6535(95)00255-7

Silva AC, Pic JS, Sant'Anna GL Jr, Dezotti M (2009) Ozonation of azo dyes (Orange II and Acid Red 27) in saline media. J Hazard Mater 169(1–3):965–971. https://doi.org/10.1016/j.jhazmat.2009.04.051

Silva MM, Oliveira MM, Avelino MC, Fonseca MG, Almeida RK, Silva Filho EC (2012) Adsorption of an industrial anionic dye by modified-KSF-montmorillonite: evaluation of the kinetic, thermodynamic and equilibrium data. Chem Eng J 203:259–268. https://doi.org/10.1016/j.cej.2012.07.009

Singh RP, Singh PK, Singh RL (2014) Bacterial decolorization of textile azo dye acid orange by Staphylococcus hominis RMLRT03. Toxicol Int 21(2):160. https://doi.org/10.4103/0971-6580.139797

Singh S, Srivastava VC, Mall IDJIJCR (2013) Electrochemical treatment of malachite green dye solution using iron electrode 5(2):592–596

Skoumal M, Cabot P-L, Centellas F, Arias C, Rodríguez RM, Garrido JA, Brillas E (2006) Mineralization of paracetamol by ozonation catalyzed with Fe^{2+}, Cu^{2+} and UVA light. Appl Catal B Environ 66(3–4):228–240. https://doi.org/10.1016/j.apcatb.2006.03.016

Smitha T, Santhi T, Prasad AL, Manonmani S (2017) Cucumis sativus used as adsorbent for the removal of dyes from aqueous solution. Arab J Chem 10:S244–S251. https://doi.org/10.1016/j.arabjc.2012.07.030

Sonawane G, Shrivastava V (2011) Orange-II removal from simulated wastewater by adsorption using Annona squamosa shell–a kinetic and equilibrium studies. Desalin Water Treat 36 (1–3):374–382. https://doi.org/10.5004/dwt.2011.2247

Srinivasan S, Rema T, Chitra K, Balakameswari KS, Suthanthararajan R, Maheswari BU, Ravindranath E, Rajamani S (2009) Decolorisation of leather dye by ozonation. Desalination 235(1–3):88–92. https://doi.org/10.1016/j.desal.2007.07.032

Sriram N, Reetha D, Saranraj P (2013) Biological degradation of Reactive dyes by using bacteria isolated from dye effluent contaminated soil. Middle East J Sci Res 17(12):1695–1700. https://doi.org/10.5829/idosi.mejsr.2013.17.12.81146

Srivastava V, Sillanpää M (2017) Synthesis of malachite@ clay nanocomposite for rapid scavenging of cationic and anionic dyes from synthetic wastewater. J Environ Sci 51:97–110. https://doi.org/10.1016/j.jes.2016.08.011

Sun D, Zhang X, Wu Y, Liu X (2010) Adsorption of anionic dyes from aqueous solution on fly ash. J Hazard Mater 181(1–3):335–342. https://doi.org/10.1016/j.jhazmat.2010.05.015

Szyguła A, Guibal E, Palacín MA, Ruiz M, Sastre AM (2009) Removal of an anionic dye (Acid Blue 92) by coagulation–flocculation using chitosan. J Environ Manag 90(10):2979–2986. https://doi.org/10.1016/j.jenvman.2009.04.002

Taha DN, Samaka IS, Mohammed LA (2013) Adsorptive removal of dye from industrial effluents using natural Iraqi palygorskite clay as low-cost adsorbent. J Asian Sci Res 3(9):945–955. https://doi.org/10.1109/NCES.2012.6740473

Tehrani-Bagha A, Mahmoodi N, Menger F (2010) Degradation of a persistent organic dye from colored textile wastewater by ozonation. Desalination 260(1–3):34–38. https://doi.org/10.1016/j.desal.2010.05.004

Thong Z, Gao J, Lim JXZ, Wang K-Y, Chung T-S (2018) Fabrication of loose outer-selective nanofiltration (NF) polyethersulfone (PES) hollow fibers via single-step spinning process for dye removal. Sep Purif Technol 192:483–490. https://doi.org/10.1016/j.seppur.2017.10.031

Toor M, Jin B (2012) Adsorption characteristics, isotherm, kinetics, and diffusion of modified natural bentonite for removing diazo dye. Chem Eng J 187:79–88. https://doi.org/10.1016/j.cej.2012.01.089

Tsai C-H, Chang W-C, Saikia D, Wu C-E, Kao H-M (2016) Functionalization of cubic mesoporous silica SBA-16 with carboxylic acid via one-pot synthesis route for effective removal of cationic dyes. J Hazard Mater 309:236–248. https://doi.org/10.1016/j.jhazmat.2015.08.051

Turhan K, Ozturkcan SA (2013) Decolorization and degradation of reactive dye in aqueous solution by ozonation in a semi-batch bubble column reactor. Water Air Soil Pollut 224(1):1353

Turhan K, Turgut Z (2009) Decolorization of direct dye in textile wastewater by ozonization in a semi-batch bubble column reactor. Desalination 242(1–3):256–263. https://doi.org/10.1007/s11270-012-1353-8

Unuabonah EI, Adie GU, Onah LO, Adeyemi OG (2009) Multistage optimization of the adsorption of methylene blue dye onto defatted Carica papaya seeds. Chem Eng J 155(3):567–579. https://doi.org/10.1016/j.cej.2009.07.012

Vaithanomsat P, Apiwatanapiwat W, Petchoy O, Chedchant J (2010) Production of ligninolytic enzymes by white-rot fungus Datronia sp. KAPI0039 and their application for reactive dye removal. Int J Chem Eng. https://doi.org/10.1155/2010/162504

Vanaamudan A, Pathan N, Pamidimukkala P (2014) Adsorption of Reactive Blue 21 from aqueous solutions onto clay, activated clay, and modified clay. Desalin Water Treat 52(7–9):1589–1599. https://doi.org/10.1080/19443994.2013.789405

Vasconcelos VM, Ribeiro FL, Migliorini FL, Alves SA, Steter JR, Baldan MR, Ferreira NG, Lanza MR (2015) Electrochemical removal of Reactive Black 5 azo dye using non-commercial boron-doped diamond film anodes. Electrochim Acta 178:484–493. https://doi.org/10.1016/j.electacta.2015.07.133

Verma V, Mishra A (2010) Kinetic and isotherm modeling of adsorption of dyes onto rice husk carbon. Global NEST J 12(2):190–196. https://doi.org/10.30955/gnj.000638

Verma AK, Dash RR, Bhunia P (2012) A review on chemical coagulation/flocculation technologies for removal of color from textile wastewaters. J Environ Manag 93(1):154–168. https://doi.org/10.1016/j.jenvman.2011.09.012

Vijayaraghavan K, Premkumar Y, Jegan J (2016) Malachite green and crystal violet biosorption onto coco-peat: characterization and removal studies. Desalin Water Treat 57(14):6423–6431. https://doi.org/10.1080/19443994.2015.1011709

Vikrant K, Giri BS, Raza N, Roy K, Kim K-H, Rai BN, Singh RS (2018) Recent advancements in bioremediation of dye: current status and challenges. Bioresour Technol 253:355–367. https://doi.org/10.1016/j.biortech.2018.01.029

Vilaseca M, López-Grimau V, Gutiérrez-Bouzán C (2014) Valorization of waste obtained from oil extraction in Moringa oleifera seeds: coagulation of reactive dyes in textile effluents. Materials 7 (9):6569–6584. https://doi.org/10.3390/ma7096569

Vimonses V, Jin B, Chow CW (2010) Insight into removal kinetic and mechanisms of anionic dye by calcined clay materials and lime. J Hazard Mater 177(1–3):420–427. https://doi.org/10.1016/j.jhazmat.2009.12.049

Visa M, Chelaru A-M (2014) Hydrothermally modified fly ash for heavy metals and dyes removal in advanced wastewater treatment. Appl Surf Sci 303:14–22. https://doi.org/10.1016/j.apsusc.2014.02.025

Visa M, Duta A (2013) Methyl-orange and cadmium simultaneous removal using fly ash and photo-Fenton systems. J Hazard Mater 244:773–779. https://doi.org/10.1016/j.jhazmat.2012.11.013

Visa M, Andronic L, Lucaci D, Duta A (2011) Concurrent dyes adsorption and photo-degradation on fly ash based substrates. Adsorption 17(1):101–108. https://doi.org/10.1007/s10450-010-9295-1

Walling C (1975) Fenton's reagent revisited. Acc Chem Res 8(4):125–131

Wang Q, Luan Z, Wei N, Li J, Liu C (2009) The color removal of dye wastewater by magnesium chloride/red mud (MRM) from aqueous solution. J Hazard Mater 170(2–3):690–698. https://doi.org/10.1016/j.jhazmat.2009.05.011

Wang Y, Ho S-H, Cheng C-L, Guo W-Q, Nagarajan D, Ren N-Q, Lee D-J, Chang J-S (2016) Perspectives on the feasibility of using microalgae for industrial wastewater treatment. Bioresour Technol 222:485–497. https://doi.org/10.1016/j.biortech.2016.09.106

Wang W, Yue Q, Li R, Song W, Gao B, Shen X (2017) Investigating coagulation behavior of chitosan with different Al species dual-coagulants in dye wastewater treatment. J Taiwan Inst Chem Eng 78:423–430. https://doi.org/10.1016/j.jtice.2017.06.052

Wang X, Ju X, Jia TZ, Xia QC, Guo JL, Wang C, Cui Z, Wang Y, Xing W, Sun SP (2018) New surface cross-linking method to fabricate positively charged nanofiltration membranes for dye removal. J Chem Technol Biotechnol 93(8):2281–2291. https://doi.org/10.1002/jctb.5571

Wawrzkiewicz M (2013) Removal of CI Basic Blue 3 dye by sorption onto cation exchange resin, functionalized and non-functionalized polymeric sorbents from aqueous solutions and wastewaters. Chem Eng J 217:414–425. https://doi.org/10.1016/j.cej.2012.11.119

Wawrzkiewicz M, Hubicki Z (2011) Remazol Black B removal from aqueous solutions and wastewater using weakly basic anion exchange resins. Open Chem 9(5):867–876. https://doi.org/10.2478/s11532-011-0072-0

Weber CT, Foletto EL, Meili L (2013) Removal of tannery dye from aqueous solution using papaya seed as an efficient natural biosorbent. Water Air Soil Pollut 224(2):1427. https://doi.org/10.1007/s11270-012-1427-7

Wei X-Z, Yang J, Xu Y-Y, Zhu B-K, Zhang G-L (2012) Preparation and characterization of low-pressure nanofiltration membranes and the application in the separation process of dye molecules. J Porous Mater 19(5):721–731. https://doi.org/10.1007/s10934-011-9524-3

Wesenberg D, Kyriakides I, Agathos SN (2003) White-rot fungi and their enzymes for the treatment of industrial dye effluents. Biotechnol Adv 22(1–2):161–187. https://doi.org/10.1016/j.biotechadv.2003.08.011

Wongkalasin P, Chavadej S, Sreethawong T (2011) Photocatalytic degradation of mixed azo dyes in aqueous wastewater using mesoporous-assembled TiO2 nanocrystal synthesized by a modified sol–gel process. Colloids Surf A Physicochem Eng Asp 384(1–3):519–528. https://doi.org/10.1016/j.colsurfa.2011.05.022

Wu Z-C, Zhang Y, Tao T-X, Zhang L, Fong H (2010) Silver nanoparticles on amidoxime fibers for photo-catalytic degradation of organic dyes in waste water. Appl Surf Sci 257(3):1092–1097. https://doi.org/10.1016/j.apsusc.2010.08.022

Xiang X, Chen X, Dai R, Luo Y, Ma P, Ni S, Ma C (2016) Anaerobic digestion of recalcitrant textile dyeing sludge with alternative pretreatment strategies. Bioresour Technol 222:252–260. https://doi.org/10.1016/j.biortech.2016.09.098

Xuan Nguyen H, Van der Bruggen B (2015) Nanofiltration of synthetic and industrial dye baths: influence of temperature on rejection and membrane fouling. J Membrane Sci Res 1(1):34–40. https://doi.org/10.22079/jmsr.2015.12304

Xue A, Zhou S, Zhao Y, Lu X, Han P (2010) Adsorption of reactive dyes from aqueous solution by silylated palygorskite. Appl Clay Sci 48(4):638–640. https://doi.org/10.1016/j.clay.2010.03.011

Yagub MT, Sen TK, Afroze S, Ang HM (2014) Dye and its removal from aqueous solution by adsorption: a review. Adv Colloid Interf Sci 209:172–184. https://doi.org/10.1016/j.cis.2014.04.002

Yang Q, Li C, Li H, Li Y, Yu N (2009) Degradation of synthetic reactive azo dyes and treatment of textile wastewater by a fungi consortium reactor. Biochem Eng J 43(3):225–230. https://doi.org/10.1016/j.bej.2008.10.002

Yao M, Zhang X, Lei L (2012) Removal of Reactive Blue 13 from dyeing wastewater by self-assembled organobentonite in a one-step process. J Chem Eng Data 57(7):1915–1922. https://doi.org/10.1021/je300216e

Yeap KL, Teng TT, Poh BT, Morad N, Lee KE (2014) Preparation and characterization of coagulation/flocculation behavior of a novel inorganic–organic hybrid polymer for reactive and disperse dyes removal. Chem Eng J 243:305–314. https://doi.org/10.1016/j.cej.2014.01.004

Yola ML, Eren T, Atar N, Wang S (2014) Adsorptive and photocatalytic removal of reactive dyes by silver nanoparticle-colemanite ore waste. Chem Eng J 242:333–340. https://doi.org/10.1016/j.cej.2013.12.086

Yousef RI, El-Eswed B, Ala'a H (2011) Adsorption characteristics of natural zeolites as solid adsorbents for phenol removal from aqueous solutions: kinetics, mechanism, and thermodynamics studies. Chem Eng J 171(3):1143–1149. https://doi.org/10.1016/j.cej.2011.05.012

Yu S, Chen Z, Cheng Q, Lü Z, Liu M, Gao C (2012) Application of thin-film composite hollow fiber membrane to submerged nanofiltration of anionic dye aqueous solutions. Sep Purif Technol 88:121–129. https://doi.org/10.1016/j.seppur.2011.12.024

Yu Y, Murthy BN, Shapter JG, Constantopoulos KT, Voelcker NH, Ellis AV (2013) Benzene carboxylic acid derivatized graphene oxide nanosheets on natural zeolites as effective adsorbents for cationic dye removal. J Hazard Mater 260:330–338. https://doi.org/10.1016/j.jhazmat.2013.05.041

Yu H-Y, Zhang D-Z, Lu F-F, Yao J (2016) New approach for single-step extraction of carboxylated cellulose nanocrystals for their use as adsorbents and flocculants. ACS Sustain Chem Eng 4(5):2632–2643. https://doi.org/10.1021/acssuschemeng.6b00126

Yue D, Jing Y, Ma J, Xia C, Yin X, Jia Y (2011) Removal of Neutral Red from aqueous solution by using modified hectorite. Desalination 267(1):9–15. https://doi.org/10.1016/j.desal.2010.08.038

Zaharia C, Suteu D, Muresan A, Muresan R, Popescu A (2009) Textile wastewater treatment by homogenous oxidation with hydrogen peroxide. Environ Eng Manage J 8(6):1359–1369. https://doi.org/10.30638/eemj.2009.199

Zaini MAA, Cher TY, Zakaria M, Kamaruddin MJ, Mohd Setapar SH, Che Yunus MA (2014) Palm oil mill effluent sludge ash as adsorbent for methylene blue dye removal. Desalin Water Treat 52 (19-21):3654–3662. https://doi.org/10.1080/19443994.2013.854041

Zazouli MA, Balarak D, Mahdavi Y, Barafrashtehpour M, Ebrahimi M (2013a) Adsorption of bisphenol from industrial wastewater by modified red mud. J Health Dev 2(1):1–11. https://doi.org/10.18869/acadpub.jhs.1.1.36

Zazouli MA, Balarak D, Mahdavi Y, Ebrahimi M (2013b) Adsorption rate of 198 reactive red dye from aqueous solutions by using activated red mud. Iran J Health Sci 1(1):36–43. https://doi.org/10.18869/acadpub.jhs.1.1.36

Zehra T, Priyantha N, Lim LB (2016) Removal of crystal violet dye from aqueous solution using yeast-treated peat as adsorbent: thermodynamics, kinetics, and equilibrium studies. Environ Earth Sci 75(4):357. https://doi.org/10.1007/s12665-016-5255-8

Zhan X, Wang J, Wen X, Qian YJ (2001) Indirect electrochemical treatment of saline dyestuff wastewater. Environ Technol 22(9):1105–1111. https://doi.org/10.1080/09593332208618222

Zhang H, Tang Y, Liu X, Ke Z, Su X, Cai D, Wang X, Liu Y, Huang Q, Yu Z (2011) Improved adsorptive capacity of pine wood decayed by fungi Poria cocos for removal of malachite green from aqueous solutions. Desalination 274(1–3):97–104. https://doi.org/10.1016/j.desal.2011.01.077

Zhang L, Zhang H, Guo W, Tian Y (2014) Removal of malachite green and crystal violet cationic dyes from aqueous solution using activated sintering process red mud. Appl Clay Sci 93:85–93. https://doi.org/10.1016/j.clay.2014.03.004

Zhao S, Song P, Wang Z, Zhu H (2018) The PEGylation of plant polyphenols/polypeptide-mediated loose nanofiltration membrane for textile wastewater treatment and antibacterial application. J Taiwan Inst Chem Eng 82:42–55. https://doi.org/10.1016/j.jtice.2017.11.005

Zheng Y, Yao G, Cheng Q, Yu S, Liu M, Gao C (2013) Positively charged thin-film composite hollow fiber nanofiltration membrane for the removal of cationic dyes through submerged filtration. Desalination 328:42–50. https://doi.org/10.1016/j.desal.2013.08.009

Zhong PS, Widjojo N, Chung T-S, Weber M, Maletzko C (2012) Positively charged nanofiltration (NF) membranes via UV grafting on sulfonated polyphenylenesulfone (sPPSU) for effective removal of textile dyes from wastewater. J Membr Sci 417:52–60. https://doi.org/10.1016/j.memsci.2012.06.013

Zhou Y, Chen L, Lu P, Tang X, Lu J (2011) Removal of bisphenol A from aqueous solution using modified fibric peat as a novel biosorbent. Sep Purif Technol 81(2):184–190. https://doi.org/10.1016/j.seppur.2011.07.026

Zhou Q, Gao Q, Luo W, Yan C, Ji Z, Duan P (2015) One-step synthesis of amino-functionalized attapulgite clay nanoparticles adsorbent by hydrothermal carbonization of chitosan for removal of methylene blue from wastewater. Colloids Surf A Physicochem Eng Asp 470:248–257. https://doi.org/10.1016/j.colsurfa.2015.01.092

Zhu J, Wang Y, Liu J, Zhang Y (2014) Facile one-pot synthesis of novel spherical zeolite–reduced graphene oxide composites for cationic dye adsorption. Ind Eng Chem Res 53 (35):13711–13717. https://doi.org/10.1021/ie502030w

Zidane F, Drogui P, Lekhlif B, Bensaid J, Blais J-F, Belcadi SJ (2008) Decolorization of dye-containing effluent using mineral coagulants produced by electrocoagulation. J Hazard Mater 155(1–2):153–163. https://doi.org/10.1016/j.jhazmat.2007.11.041

Zonoozi MH, Moghaddam M, Arami M (2009) Coagulation/flocculation of dye-containing solutions using polyaluminium chloride and alum. Water Sci Technol 59(7):1343–1351. https://doi.org/10.2166/wst.2009.128

Zuriaga-Agusti E, Iborra-Clar M, Mendoza-Roca J, Tancredi M, Alcaina-Miranda M, Iborra-Clar A (2010) Sequencing batch reactor technology coupled with nanofiltration for textile wastewater reclamation. Chem Eng J 161(1–2):122–128. https://doi.org/10.1016/j.cej.2010.04.044

Chapter 18
Nanomaterials for Textile Waste Treatment

Bilal Akram, Habib-ur-Rehman, and Javeed Akhtar

Contents

Abstract The blessings of modern civilization have created some adverse effects on the earth's ecosystem at micro- and macro-scale. Textile industries are an integral part of modern civilization which has helped to shape our modern lifestyle. Unfortunately, side products from these industries, such as affluent (liquid form) or those in gaseous forms, are being discharged constantly. This trend is more prominent in under-developing countries where carbon emission and toxic dye discharge in fresh water is growing at an alarming rate. Adsorption, ion exchange, ozonation, membrane filtration, crystallization, phytoremediation, flocculation, and photochemical degradation are some of the methods used to address the problems associated with

---

B. Akram
Department of Chemistry, Tsinghua University, Beijing, China
e-mail: bai-l16@mails.tsinghua.edu.cn

Habib-ur-Rehman · J. Akhtar (✉)
Materials Laboratory, Department of Chemistry, Mirpur University of Science and Technology (MUST), Mirpur, AJK, Pakistan

Inamuddin et al. (eds.), *Water Pollution and Remediation: Organic Pollutants*, Environmental Chemistry for a Sustainable World 54,
https://doi.org/10.1007/978-3-030-52395-4_18

dye wastes. Among the listed methods, adsorption and photochemical degradation are popular due to their economic, upscaling, and greener nature. Similarly, nanostructured materials have the potential to offer viable solutions to tackle such toxic effluents owing to their greater surface to volume ratio and enhanced chemical reactivity compared with their bulk form. Photochemical degradation of textile wastes using such nanostructured materials has received considerable interest in the last few decades. Extensive research has led to the design of smart and high-power adsorbents and photochemical degrading agents, such as composites, using large number of polymeric materials. This chapter highlights and discusses the role of important class of inorganic materials such as silica, carbon, and polymeric composite materials for effective adsorbents and photochemical degrading agents for a wide range of textile wastes. The chapter will give readers an overview of the work done in the literature and directions for designing tools and strategies to implement greener chemistry protocols for the protection of our environment.

Keywords Nanoparticles · Effluent · Textile waste · Chemical degradation · Silica nanoparticle · Sorbents · Photochemical degradation · Magnetic nanoparticles · ZnO

18.1 Introduction

Water is a vital source of life for all living beings in the universe. However, wastewater becomes a major threat for living beings worldwide. Sewage from the textile industry is the foremost contributor to water pollution. Different effluents from textile industries are enriched with auxiliary chemical species and dyes. The dyeing process of a cloth is very important as it gives beauty to the finished fabric, but at the same time, the dyes used in this process may cause environmental pollution (Varadarajan and Venkatachalam 2016). Various kinds of synthetic dyes are used in the textile industry, depending on the nature of fibers. During the process of dyeing, the major portion of the dye is exhausted in the fabric material, whereas some unexhausted portion is disposed off into the water and produces colored wastewater. In general, synthetic dyes used in textile industry can be categorized into three classes: anionic, cationic, and nonionic. Most of the anionic dyes have acidic nature and are reactive, whereas cationic dyes possess basic character due to the presence of the azo group. Because the cationic dyes are mostly composed of benzidine and/or other related aromatic compounds, they are generally regarded as carcinogenic. Due to their good solubility in water, such solutions cannot be treated through conventional methods. Likewise, organic dyes in effluents are rich in chemical compounds having high stability. Although their discharge in the water streams is not very much, it is highly visible due to the staining features.

Various treatment strategies have been employed to handle dye-based wastes from textile industries, such as adsorption, membrane filtration, ion exchange, ozonation, evaporation, electrochemical oxidation, phytoremediation, flocculation, photochemical degradation, and crystallization. However, the emergence of secondary pollutant in the water as a result of the treatment, as well as the limitations in both space and time, has limited their use for environmental remediation (Crini and Lichtfouse 2019). Therefore, effective and efficient methodologies to treat these wastewaters are still being developed.

During the last decades, micro and nanomaterials have been extensively investigated and found to possess great potential for environmental remediation owing to their remarkable chemical and physical characteristics, such as large surface area, superwetting, and photocatalytic behavior. For example, adsorbent materials (Madhura et al. 2019) constructed via modification of cost-effective, commercially available materials, such as inorganic nanomaterials (Crini et al. 2019), melamine and cellulose foam, polyurethane sponge, and several carbon-based materials, have been used for the removal of dyes and other organic solvents from wastewater(Jang et al. 2008; Wang et al. 2015; Zhu et al. 2015b; Zhu et al. 2015c). The use of several photocatalytically active materials are further extended for the treatment of wastewater for environmental remediation, for instance, few conventional semiconducting materials, such as TiO_2, ZnO, and CdS, can photodegrade synthetic dyes used in textile industries for coloring purpose and make the wastewater clean (Akram et al. 2018). Moreover, new novel multifunctional composite materials have also been designed to treat wastewater. Such composite materials with multifunctional properties can be prepared by combining different nanomaterials having distinct functions or immobilizing them on substrate materials. Such composites are established to have superior performance than individual material. Here, we aim to present an overview of the application of various nanomaterials either alone or in the composite form to treat textile effluents via adsorption or photodegradation.

18.2 Inorganic Nanomaterials as Sorbents

With the advancement in the field of nanotechnology during the last decades, a diverse range of inorganic nano- or micromaterials have been extensively used for environmental remediation. Such materials possess large specific surface areas and function as excellent sorbents and photocatalysts for wastewater treatment (Dsikowitzky and Schwarzbauer 2014). The higher surface to volume ratio of these materials can significantly enhance their adsorption capacities. Several inorganic nanomaterials with higher redox potential and photocatalytic performance can also be used to degrade wastewatercontaminants. Few representative examples of sorbent materials are discussed below.

18.2.1 Silica Nanoparticles

A material should have an ordered porous structure and large surface area in order to be a good absorbent. Accessible adsorption sites with excellent stability under adsorption and regeneration conditions endowed the material with good adsorption features. Porous silica has proven to be an excellent sorbent for wastewater treatment. Since their discovery in the early 1990s, their use is greatly extended for environmental remediation. Different kinds of silica nanoparticles having mesoporous nature, as shown in Fig. 18.1, have been synthesized and used in a variety of applications, such as catalysis, ion exchange, separation, filtration via molecular sieving, and adsorption (Slowing et al. 2010; Yang 2011). These silica nanostructures have attracted substantial interest in the treatment of polluted water owing to their intrinsic large specific surface area and porous nature having pores of

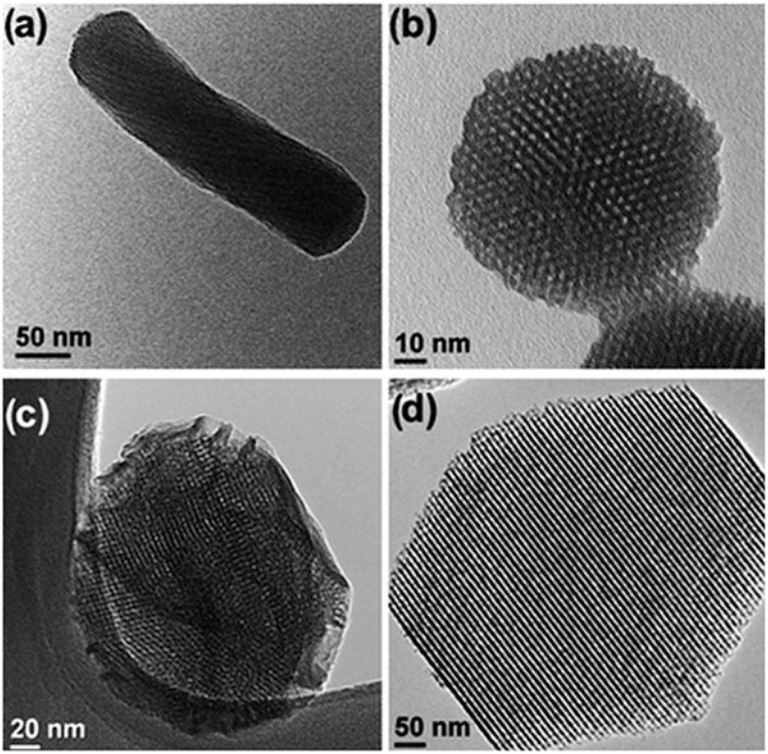


Fig. 18.1 Various nanostructures of mesoporous silica: (**a**) 1D rods having helicoidal pores with a size of about 3 nm (**b** and **c**); spherical structures having hexagonal and cuboidal pores with a width of 4 and 3 nm, respectively; and (**d**) hexagonal plates possessing hexagonal pores with a width of about 10 nm. Reprinted with permission of [Mesoporous silica nanoparticles: structural design and applications. Journal of Materials Chemistry, The Royal Society of Chemistry] from [Slowing et al. 2010]. (1D, one dimensional)

definite dimension and geometry. Porous silica nanostructures might be classified on the basis of the shape and size of their pores. Silica nanoparticles with pore sizes ranging from 2 to 5 nm are regarded as 2D hexagonal p6m (MCM-41), 3D cubic Ia3d (MCM-48), and lamellar p2 (MCM-50) (Fig. 18.1b and c). Silicas with larger pore sizes, i.e., in the range of 6 to 20 nm, are called SBA-15, and the shape specification of their pores is 2D-hexagonal-p6mm. Additional 3D cubic silicas with even larger pores are also known, such as IBN-2 (Fm3m) (Han and Ying 2005).

During the past few years, significant attention has been paid to the use of MCM-41 to trap some volatile organic moieties via physisorption or chemisorption after structural and compositional modifications. It has also been effectively employed to confiscate toxic heavy metals and dissolve dyes from polluted water (Yoshitake et al. 2003). Functionalization of silicas with organic functional groups, such as amino, malonamide, imidazole, carbonyl, carboxyl, humic acid, and dithiocarbamate, can lead to a material having a much improved capacity for the degradation of aqueous dyes. In comparison with MCM-41, SBA-15 possesses bigger pores with a tunable size that permits targeted pollutants to easily access the inner surface of the nanoparticles. This leads to swift kinetics and non-equilibrium adsorption, and SBA-15 exhibits improved ability of adsorption than MCM-41. Furthermore, the ultrathin (around 4 nm) pore walls provide remarkable mechanical stability. Even though such materials behave as promising adsorbents, as compared with other conventional absorbents, such as active carbon, the lack of surface functionalities greatly limits their adsorption utilizations, particularly in case of high adsorption selectivity and capacity. This limitation can be overcome simply by chemical modification of its surface. Surface modifications have been achieved by using dodecylamine, tetrakis(4-carboxyphenyl)porphyrin, 2-mercaptopyridine, and 3-aminopropyltrimethoxy silane. These surface-modified mesoporous silicas were than employed to eliminate dyes and toxic heavy metal species from wastewater (Benhamou et al. 2013; Davarpanah and Kiasat 2014; Pérez-Quintanilla et al. 2006).

18.2.2 Iron-Based Magnetic Materials

The ability of nanomaterials to recycle carbon coated Fe3O4 nanoparticles must be considered while choosing the best agent to treat wastewater from textile industries. Magnetism helps in water purification by effecting the physical characteristics of contaminants. Best adsorption ability along with easy magnetic separation has been widely employed in the treatment of wastewater and environmental remediation. During the past few years, magnetic iron oxide nanomaterials have been extensively investigated in large-scale treatment of wastewater owing to their enhanced adsorption capability, easy recyclability, and superior stability (Xu et al. 2012). The use of Fe_3O_4 materials in both lab scale and industrial scale has revealed that such magnetic responsive nanomaterials possess more improved ability to treat huge quantities of effluents discharged from a textile industry than carbon-based materials and atomic

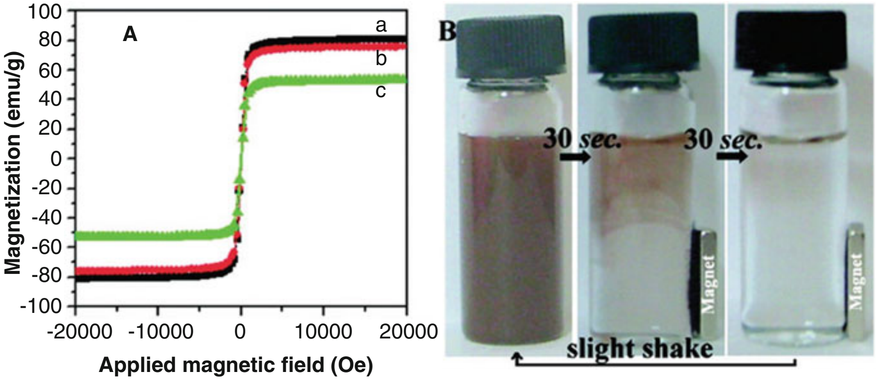


Fig. 18.2 (**a**) Magnetic hysteresis loops of Fe_3O_4particles (a), Fe_3O_4@nSiO_2 (b), and Fe_3O_4@nSiO_2@mSiO_2 (c) microspheres. (**b**) Separation redispersion process of Fe_3O_4@nSiO_2@mSiO_2 microspheres. (Reprinted with permission of [Superparamagnetic High-Magnetization Microspheres with an Fe_3O_4@SiO_2 Core and Perpendicularly Aligned Mesoporous SiO_2 Shell for Removal of Microcystins. Journal of the American Chemical Society] from Deng et al. 2008)

iron (Tang et al. 2013). The easy separation of such nanomaterials using an externally applied magnetic field further favors their use at an industrial scale. Contaminantsadsorption may occur via surface exchange reactions until full occupation of all surface functional sites. Pollutants may also diffuse into the magnetic adsorbent material through interactions with surface functionalities. Therefore, surface modification of magnetic nanomaterials with small organic functional groups results in enhanced adsorption capacity by binding through surface site, electrostatic interactions, magnetic selective adsorption, and tailored ligand blend. Additionally, surface modifications of Fe_3O_4nanoparticles with other inorganic materials stabilize the nanoparticles (NPs) and ultimately control their oxidation. This strategy also improves their adsorption capability owing to the larger specific surface area. For instance, carbon coated Fe_3O_4 nanoparticles have been synthesized to absorb multiring aromatic compounds from wastewater (Wang et al. 2013). The experimental findings demonstrated that their adsorption tendency is greatly improved than plain Fe_3O_4nanoparticles. Surface coating of Fe_3O_4nanoparticles with silica imparts enhanced surface area and magnetic sensitivity, which results in improved capacity for the removal of microcystins from aqueous solution. This material could be reused eight times with the same efficiency, and the recovery percentage of the adsorbent is higher than 90% (Deng et al. 2008).

To sum up, nanomaterials as sorbents have been extensively investigated for the treatment of aqueous industrial effluents due to having large adsorption tendency and easy recyclability (Fig. 18.2). However, large-scale applications of such nanomaterials are still restricted because of the obscurity in sorting out the pollutants from the adsorbent, which is not economic and cost-effective. Therefore, it is imperative to design materials that can be reused as sorbent directly without any treatment to separate them from contaminants. Moreover, the contaminants cannot be removed completely through adsorption, particularly when they are in low concentrations. Thus, an efficient strategy should be developed to handle the contaminants present in trace amount in order to reduce their accretion.

18.3 Concurrent Adsorption and Degradation

18.3.1 Photocatalytically Active Inorganic Nanomaterials

During the last few years, the semiconductor photoactive nanomaterial-catalyzed heterogeneous oxidation of organics has attained special interest due to its cost-effective, eco-friendly, and sustainable treatment technology for wastewater treatment. This strategy involves the degradation of aqueous contaminants at ambient conditions to more biodegradable and less-toxic components that may not be the cause of secondary pollution (García-Ripoll et al. 2007). The hydroxyl radicals ($^{\bullet}OH$) produced during this process are transferred into organic compounds. The ultraviolet–visible light is the driving force for the production of such an oxidant, depending on the nature of photocatalysts. Under light illumination, photons having energies higher than the semiconductor band gap energy (ΔE) can result in the excitation of electrons from the valence band, thus accelerating the reactions. In the case of absorbed photons with lesser energies (lesser than ΔE), the energy in the heat form dissipates. The absorption of sufficient energy by photocatalyst results in the formation of a positive hole (h^+) in the valance band and an electron (e^-) in the conduction band (Fig. 18.3). The generated h^+ can react with organic species or water to produce hydroxyl radicals ($^{\bullet}OH$), whereas the oxygen adsorbed on the catalyst is reduced by the electrons present in the conduction band.

The following steps demonstrate the ultraviolet–visible light-assisted activation of photocatalysts and the redox reaction of organic moieties.

Photoactivation:

$$\text{Photocatalyst} + \text{light illumination} \rightarrow e^- + h^+ \tag{18.1}$$

$$e^- + O_2 \rightarrow O_2^{-\cdot} \tag{18.2}$$

Oxidation:

$$h^+ + \text{Pollutant} \rightarrow CO_2 \tag{18.3}$$

$$h^+ + H_2O \rightarrow {}^{\cdot}OH + H^+ \tag{18.4}$$

Reductive reaction:

$${}^{\cdot}OH + \text{organics} \rightarrow CO_2 \tag{18.5}$$

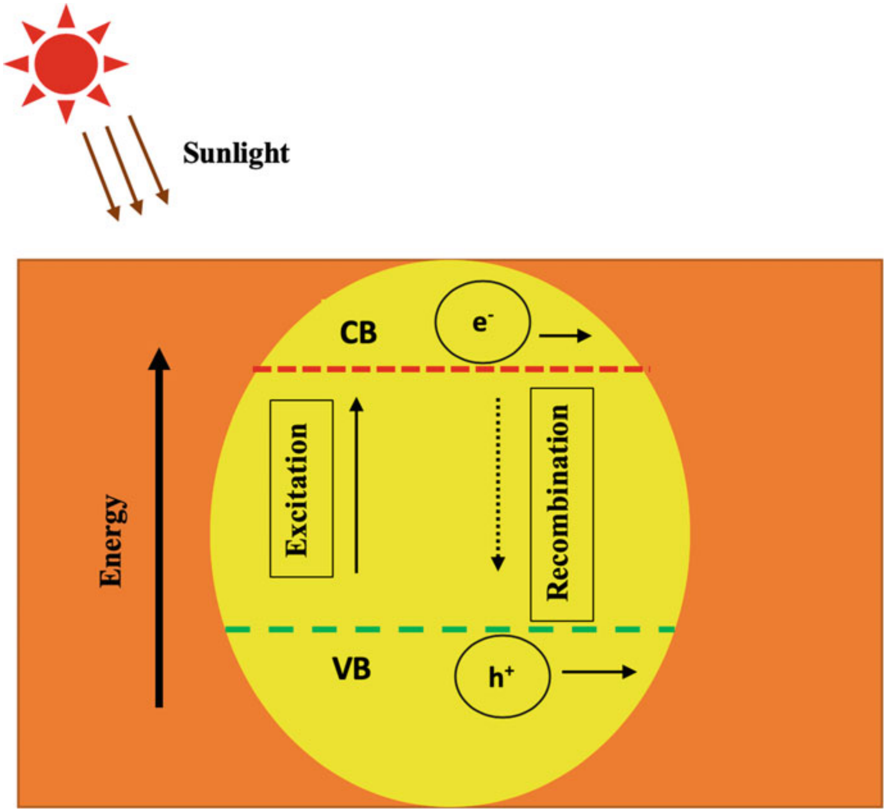


Fig. 18.3 Schematic illustration of the formation of holes and electrons under light irradiation during a photocatalytic reaction. (*VB* denotes valence band, *CB* denotes conduction band, e^- denotes electron, h^+ denotes hole)

During the last few years, a lot of semiconductor photocatalysts have been designed for the treatment of wastewater, such as metal oxides; ZnO, TiO_2, and Fe_2O_3 and metal sulfides; and CdS and SnS_2. Among these, TiO_2 has engrossed considerable interest for photocatalytic water treatment owing to its thermal and chemical stability and remarkable mechanical characteristics. The photocatalytic activity of TiO_2nanoparticles was first demonstrated by Fujishima and Honda (Fujishima and Honda 1972). Since then, the use of TiO_2 photocatalysts for the treatment of wastewater and degradation of several hazardous organic compounds has been broadly investigated. TiO_2 photocatalyst mostly works in the limited range of photon energy, i.e., from 300 nm to 390 nm. Moreover, electron–hole recombination in the absence of appropriate electron acceptors still confines its large-scale use since it leads to wastage of energy.

Although a number of electron acceptors, such as H_2O_2, $(NH_4)_2S_2O_8$), and $KBrO_3$, have been explored to trounce this limitation, mineralization photo efficiency is still lower. The modification of TiO_2 via doping or alloying has proven to be an effective approach to improve the photo efficiency. For instance, noble metal-decorated TiO_2 has been demonstrated to have enhanced photo efficiency. The electrons present in the conduction band can be excited and moved to the decorated metal having narrower band gap to shun the recombination of electrons and holes, resulting in the efficient separation of charges and high rates of photocatalytic reaction (Ni et al. 2007). The doping of transition-metal ions and rare-earth metal ions into TiO_2 lattice has also been shown to enhance its photocatalytic performance. The doping of non-metallic species, such as nitrogen, fluorine, carbon, and sulfur, has also been investigated to obtain improved photo efficiency in the full solar spectrum (Malato et al. 2009).

Another important photocatalytic material that is broadly investigated for the treatment of wastewater is ZnO. ZnO is non-toxic, cost-effective, and chemically stable. Although TiO_2 is regarded as the most active photodegradation catalyst, ZnO exhibits even better photocatalytic performance in certain situations (Khan et al. 2019a; Khan et al. 2019b; Yu and Yu 2008). Moreover, it can work in the broader solar window than TiO_2, so it is the most appropriate catalyst for the photodegradation of organics under sunlight illumination. There are many reports demonstrating ZnO as a photocatalyst for the degradation of organic pollutants and colored dyes, such as kraft black liquor, 2-phenylphenol fungicide, phenols, lignin, and many other azo dyes. Furthermore, photocatalytic degradation of few antibiotics, such as sulfamethoxazole, amoxicillin, ampicillin, cloxacillin, and lincomycin, has also been reported (Elmolla and Chaudhuri 2010; Farzadkia et al. 2014).

Owing to low band gap of 2.2 eV and *n*-type semiconducting nature of Fe_2O_3, it becomes an appropriate candidate for photocatalytic degradation of organic dyes and pollutants. Several Fe^{3+} species have been used for the treatment of organic dye-polluted water, such as α-Fe_2O_3, γ-Fe_2O_3, α-FeOOH, β-FeOOH, and γ-FeOOH. Highly efficient photocatalytic degradation of Congo red using iron oxide nanoparticles has been demonstrated (Khedr et al. 2009). Moreover, this type of photocatalyst is stable and found to have the best performance even after several cycles. The limitation of such nanomaterials is the fast electron–hole recombination. To surmount this issue, different noble metal particles can be deposited on their surface and may be used as a support. For instance, Au/Fe_2O_3 has been employed for the photodegradation of water-dispersed azo dye, i.e., blue 79. The Au nanoparticles here are regarded as electron accumulation sites, thus can assist their transfer from the surface. Better charge separation imparts improved photocatalytic performance.

Many metal chalcogenides and nitrides have also been designed as catalysts for the photodegradation of pollutant to treat wastewater. For example the 2.42 eV band gap of CdS allows the easy transfer of electrons from valance band to the conduction band by light having a wavelength of less than 495 nm (Yang et al. 2013). Recently, semiconductor CdS nanoparticles have attracted much attention as photocatalysts to treat wastewater polluted with organic dyes owing to their distinct chemical and physical characteristics (Zhu et al. 2009). Another important material, which is SnS_2, is oxidatively more stable as compared with CdS, and Li et al. have demonstrated that SnS_2 exhibits much improved photocatalytic performance than CdS under visible light (Li et al. 2012).

Most of the abovementioned metal-based semiconductor photocatalysts are either functional in limited light window or non-economic, which confines their long-term and commercial applications. A metal-free and economic photocatalyst, i.e., graphitic carbon nitride (g-C_3N_4), overcomes the above limitations associated with metal-based photocatalysts (Shi et al. 2018). In recent times, the use of graphitic carbon nitride,g-C_3N_4 has been extended to reduce CO_2. Photocatalytic degradation of organic pollutants, such as dyes and heavy metal ions, has revealed that graphitic carbon nitride is an emerging photocatalyst for environmental remediation. As mentioned above, inorganic nanoparticles have been extensively investigated as sorbents or catalysts for the treatment of wastewater. Individual inorganic nanoparticles still cannot fulfill all the unambiguous requirements needed for environmental remediation. These limitations can be overcome by functionalization of such inorganic nanoparticles with functional organic polymers by forming core–shell nanocomposite materials. Furthermore, such modifications can also prevent the aggregation of nanoparticles and enhance the adsorption properties by stabilizing their uniform dispersion (Shin and Jang 2007). The most significant benefit of inorganic nanoparticles is their high capacity of adsorption owing to their large surface area. However, selective adsorption of some pollutants cannot be achieved using these pure nanomaterials in practical applications. This issue not only decreases the efficiency of adsorption but also influences the recyclability of materials. Scientists have investigated that these issues can be handled via surface modification of nanomaterials with functional groups such as protonic acids or bases through van der Waals or electrostatic interactions. For example, the amino-functionalized nanomaterials demonstrate outstanding capacity for the removal of toxic metallic species from polluted water due to labile protonation in acidic environment. Likewise, nanomaterials modified with carboxylate moieties were extensively used to capture cationic pollutant via complexation (Fresnais et al. 2013). Another approach to achieve selective adsorption is to functionalize inorganic nanoparticles with molecular imprinted polymers. Molecular imprinted polymers have been employed for molecular recognition purpose in several fields, such as solid-phase extraction, membrane separation, chromatograph separation, drug delivery, sensors, and catalysis (Vallano and Remcho 2000). Surface-imprinted inorganic nanomaterials not only function as excellent selective adsorbent but also overcome few disadvantages, such as the comparatively less unit volume identification sites of the matrix-embedded polymer. Molecular imprinted polymer-modified silica and carbon-based materials have been used for the removal of toxic metallic species and synthetic dyes from wastewater (Liu et al. 2014). The nanocomposites of other unique properties having inorganic nanoparticles prove to be more practical. For instance, magnetic nanoparticles and molecular imprinted polymer composite can be magnetically separated after use. There are several advanced techniques used to control their structure and enlarge their specific surface area, consequently improving adsorption and photo efficiency capacity. However, the demands of practical application may not be met by using them, particularly for highly polluted wastewater, due to their non-selective adsorption and low binding efficiency. Contrarily, it is established that the process of adsorption follows a dynamic equilibrium state where surface-adsorbed moieties pervade into the absorbents until equilibrium is achieved. Therefore, it is hard to remove contaminants completely only through adsorption, particularly in the case of higher contaminant concentration. Uniting the benefits of adsorbent and photocatalyst, composite materials having synergetic effect might be able to overcome these issues. One of the best strategies is to develop polymer surface-functionalized inorganic core–shell composite nanostructure capable of accumulating higher concentrations of contaminants on their surface and accelerating the photocatalytic degradation process. A continuous process is developed by combining adsorption and photodegradation of contaminants accompanied by the following steps: (i) the contaminants would efficiently bind with the surface of absorptive polymer, and then surface-bound contaminants might pervade into the photocatalytic core; (ii) under light illumination, the excitation of encapsulated photocatalysts would occur, leading to photocatalytic degradation of absorbed contaminants; (iii) the lesser contents inside polymer might result in non-equilibrium states, and incessant adsorption occurs. Such a continuous process of adsorption and degradation may not only completely eliminate contaminants in limited time, but the composite photocatalysts may also be reused directly without any additional treatment. The practical applications of this strategy involve two major steps: first efficient adsorption of contaminants onto the polymer, leading to a decrease in contaminant concentration; then a continuous process of adsorption and degradation takes place until degradation completes. Although these functional polymer-encapsulated materials exhibited attractive selectivity and adsorption capability, their method of preparation is comparatively lengthy and complex, which may not be appropriate for upscaling. Therefore, some carbon-based materials and several commercially available foams with low density, outstanding stretchability and flexibility, excellent chemical stability, high surface area, and eco-friendliness are supposed to be the best alternatives for efficient treatment of wastewater.

18.3.2 Carbonaceous Composite Materials

Carbon-based composite nanomaterials designed by using different forms of carbon, such as graphite, graphene, and carbon nanotubes, have been extensively investigated to achieve enhanced adsorption and photocatalytic degradation under visible light. Carbon in its activated form can effectively adsorb the pollutants, but the recycling cost is comparatively higher. Therefore, activated carbon was used as a support to load photocatalytically active TiO_2 for the degradation of dyes (Fu et al. 2006). In this composite, the activated carbon would aid to supplement the confined contaminant contents of photocatalyst and consequently accelerate the process of transfer of contaminants. Furthermore, the combined influence of photodegradation and adsorption plays an important role for improved efficiency in this composite, as confirmed by Matos et al. (Matos et al. 2001). The improved degradation of phenol might be credited to its strapping adsorption ability on the activated carbon, leading to the transfer of pollutant to the photocatalytically active TiO_2. Based on the combined effect, fullerene functions as an important emerging candidate as a carbon-based support material owing to the increased charge transfer property between the fullerene and inorganic nanophotocatalysts such as TiO_2 via surface group acidification. Additionally, the energy sensitization of fullerene would also enhance its efficiency.

Carbon nanotubes, as compared with activated carbon, possess higher surface area and therefore may further improve the capability of adsorption and photodegradation. Moreover, carbon nanotube surface functionalities (like hydroxyl, carbonyl, and carboxyl moieties) can be tailored to achieve improved selective performance towards pollutant degradation (Carp et al. 2004; Sher Shah et al. 2012). In this context, carbon nanotubes are outstanding candidates, allowing a deeper insight into the interfacial interaction between semiconductor photocatalyst and carbon materials. Because of their unique photonic and electronic features, graphene is also composited with other inorganic materials to achieve the desired performance. Several graphene composites, such as graphene/TiO_2, graphene/AgX (where X = Cl, Br), graphene/Cu_2O, and graphene/SnO_2, have remarkable photocatalytic activity (Seema et al. 2012, Sher Shah et al. 2012). Such composites have a broad range of applications in wastewater treatment, such as photocatalytic degradation of dyes and reduction of toxic metal ions. Fan et al. reported the formation of three-dimensional (3D) composites made up of AgX (where X = Cl, Br) and graphene by using a deposition approach, in which AgX (where X = Cl, Br) nanoparticles are deposited on the surface of three-dimensional graphene via a facile approach (Fan et al. 2015). Methyl orange and Cr(VI) ions were used to investigate the photocatalytic degradation and reduction performance of the designed composite. The results revealed that the composite material exhibited better performance than pristine AgX (where X = Cl, Br) nanoparticles. The three-dimensional configuration of the composite allows its easy recyclability from the solution, which is very significant for large-scale practical uses. The photocatalytic degradation activity of the graphene/Cu_2O crystal with different exposed facets was demonstrated via methylene blue degradation under visible light, and best performance was achieved using O-Cu_2O/rGO composite. In contrast to these metal-based NP composites, several metal-free composite nanomaterials even exhibit comparable photodegradation performance. For example, Jiang et al. constructed a graphitic carbon nitride (g-C_3N_4) and graphene oxide composite through solvothermal co-assembly approach (Tong et al. 2015). Graphene oxide functions as a support for graphitic carbon nitride immobilization, which facilitates electron transfer, whereas the graphitic carbon nitride functions as photocatalyst for the degradation of methyl orange. Due to the synergetic effect of both components, the photodegradation efficiency reaches up to 92% in 4 h under sunlight, which is superior to sole graphitic carbon nitride (12%).

18.3.3 Polyurethane Composite Materials

Polyurethane-based composite materials manifest superior performance compared with simple polyurethane-based materials. Such a composite material can be designed by using different materials having the desired function for targeted adsorption and photodegradation of pollutants from wastewater. For instance, a composite of polyurethane and chitosan foams was prepared via the reaction of polyurethane prepolymer with chitosan in different ratios, as reported by Lee et al. (Lee et al. 2009). Chitosan has superior performance in the treatment of wastewater, as its surface possesses plenty of hydroxyl and amine functionalities, which endow it with improved adsorption capacity of synthetic dyes discharged from textile industries and toxic metallic species through electrostatic interaction or chelating groups. The shared effect of these types of materials in the composite foams exhibits higher performance for the adsorption of acid violet 48. The capability of adsorption improves with the increase in chitosan concentration and reaches a maximum adsorption of 30 mg/g with 20 weight percent chitosan. Moreover, chemisorption of acid violet 48 occurs via interaction between its sulfonic ions and protonated amino groups of chitosan; hence the higher adsorption capacity was observed in aqueous solution of low pH. A composite foam was developed by Lee et al. to remove Pb^{2+} ions from wastewater. The composite was designed by using immobilized hydroxyapatite, an inorganic species having higher capacity for the removal of toxic metallic species, on polyurethane structure (Liao et al. 2010). The results of the removal tendency of Pb^{2+} showed that the composite foams manifested remarkable performance for Pb^{2+} removal at pH 5, and a maximum adsorption capacity of 150 mg/g was achieved with the composite having 50 wt% hydroxyapatite. Imae et al. fabricated silica/titania composite immobilized polyurethane matrix for the photodegradation of acid black 1, and excellent performance was observed under ultraviolet light due to the attachment of a large number of titania nanoparticles on the polyurethane matrix surface (Mahesh et al. 2014). The developed composite material was found to be stable and exhibited the same performance until three consecutive duplicate operations. Liu et al. developed a polyurethane-based composite foam via copper films covering followed by oleophilic treatment in n-dodecanoic acid and silver nitrate alcoholic solution (Zhu et al. 2011). The fabricated foams having rough and hierarchical structure exhibited superhydrophobicity and oleophobicity due to the agglomeration of a large number of $Cu–C_{11}H_{23}$ COOAg nanoparticles on the polyurethane matrix. These features allow it to swiftly absorb selective organics from polluted water. Moreover, the vigorous and compressible characteristics lead to excellent reusability for the separation of oil and water via an easy mechanical squeezing approach. Another research group demonstrated the fabrication of magnetic polyurethane composite by using Fe_3O_4 via dip coating using fluoropolymer aqueous solution. The obtained foam possesses a hydrophobic surface and is superoleophilic, chemically stable, and magnetically responsive (Wu et al. 2015). The designed composite foams may be magnetically driven to adsorb organics from the surface of wastewater with higher selectivity. Furthermore, it also exhibited outstanding performance in the separation of oil and water when used as a membrane.

18.3.4 Melamine Foam Composite Materials

Melamine foam possesses an open structure having pores, functioning as an ideal candidate to be a part of composite nanomaterials for wastewater treatment. Normally, other one-dimensional or two-dimensional materials along with melamine foam are generally used to make composite in order to retain its porous nature. Yu et al. constructed a composite foam containing polymer sponge@Ag/AgCl which functions as a photoreactor for the photodegradation of wastewater pollutant via photocatalyst immobilization on the melamine foam backbone (Fig. 18.4a) (Ge et al. 2015). Scanning electron microscopy images revealed that Ag/AgCl nanowires completely covered the backbone (Fig. 18.4b). Figure 18.4c illustrates the schematic of foams which is employed as a reactor for the sunlight-assisted degradation of methyl orange. In contrast to two-dimensional films composed of laminar Ag/AgCl,

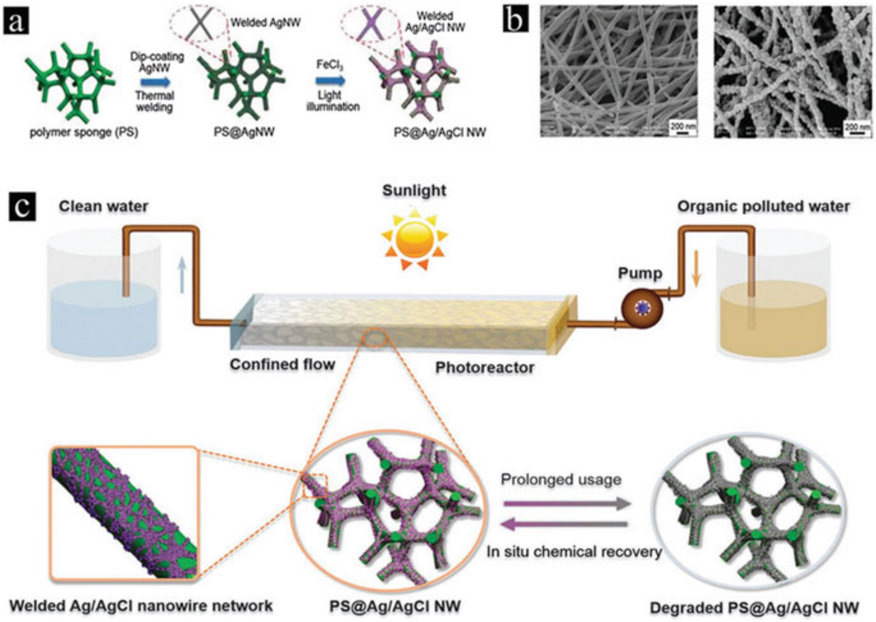


Fig. 18.4 (**a**) Schematic of fabrication strategy of the MF framed PS@Ag/AgCl composite. (**b**) Scanning electron microscopy images of melamine foam-coated Ag and Ag/AgCl nanowires. (**c**) Representation of the composite employed as a photoreactor for the photodegradation of textile effluents contained in wastewater. (Reprinted with permission of [Durable Ag/AgCl nanowires assembled in a sponge for continuous water purification under sunlight, Materials Horizons, The Royal Society of Chemistry] from Ge et al. 2015)

the one-dimensional nanowires of the same material contact better with polluted water during its flow in the photoreactor, consequently leading to much improved photodegradation efficiency. Significantly, the porous network structured photoreactor permits wastewater to flow quickly through it. The throughput can reach up to 9600 L/h/m^2, significantly better than other similar photoreactors containing microfluid.

Nguyen and co-workers reported the formation of melamine foam framed graphene composite foams through the simple dip-coating approach (Nguyen et al. 2012). The designed foams with stable matrix possess the superoleophilicity and superhydrophobicity of grapheme in addition to their well advantageous intrinsic porous structure. The designed composite foam has high capacity of adsorption, better selectivity, and remarkable reusability. Similarly, another research group fabricated the reduced grapheme oxide-functionalized foam via heat-assisted reduction of grapheme oxide on the backbone of melamine foam(Zhu et al. 2015a). Their design strategy is simple and economic, and the clean-up performance is much higher; therefore it functions as a model absorbent for wastewaterremediation.

18.3.5 Composite Materials Containing Cellulose

Cellulose is a biodegradable, non-toxic, environment-friendly, chemically stable, and inexhaustible material, which is generally employed as matrix to fabricate adsorbents for the treatment of wastewater via heavy metal and organic dye removal. For instance, Yao et al. constructed a composite adsorbent composed of cellulose and acrylamide or acrylic acid to remove Ni^{2+} ions from polluted water (Liao et al. 2016). Because of the presence of a large number of surface-exposed functional groups (such as hydroxyl, amino, carbonyl, and carboxyl groups), it manifests higher performance. Grishkewich and co-workers fabricated a composite of cellulose and alginate hydrogel to remove synthetic dyes from wastewater (Grishkewich et al. 2017). The alginate hydrogel being ionic in nature endows this composite with superior adsorption properties, as evidenced through the adsorption of methylene blue. Furthermore, the cellulose intrinsic features such as high surface area, porosity, and stability further improved the adsorption efficiency and reusability. It showed about 99% of methylene blue removal and can be reused with the same efficiency till five consecutive adsorption–desorption tests. Gupta and co-workers demonstrated superior photocatalytic activity of tin(IV)phosphate in degradation of methylene blue in aqueous solution under sunlight. (Gupta et al. 2015). Because of higher ion-exchange capability and improved photocatalytic performance of the tin (IV) phosphate component, the composite concurrently absorbed and degraded methylene blue dye in the presence of sunlight.

18.4 Destiny of Used Nanoparticles

Fabricated nanoparticles employed in wastewater treatment are generally regarded as consumables despite of their use in large amounts. Their fruitful lifecycle must be measured via the working time span through which a reasonable efficiency with regard to contaminant elimination and methodology price is assured. Because of their nanoscale dimensions, reactivity, stability, and mobility in the water system entail the chance of adverse effects to the living organisms; therefore used nanoparticles must be handled appropriately. Therefore, it is vital to investigate whether their revival, recovery, and safe discarding could be attained. Moreover, considering their loading with lethal contaminants, any degradation, leaching, or their conversion via chemical reactions in the ecosystem must additionally be checked while scheming a route to treat wastewater.

Over the last few years, several theoretical and experimental researchers have devoted their efforts to investigate the activities of inorganic nanoparticles in water or soil and the interaction of engineered nanoparticles with living beings as a cause of ecotoxicity (Moore 2006; Navarro et al. 2008). Likewise, an incessant attempt to build reproducible and consistent risk testing approaches and evaluation of living being exposure to engineered nanoparticles is still in progress. A collection of analytical tools has been introduced to examine the effect of nanoparticle size, shape, aggregation, and dissolution. A large number of reports demonstrate the nanoparticle cytotoxicity corresponding to human disclosure progressing the knowledge about their performance in living systems (Lewinski et al. 2008). However, the findings are contentious, and in majority of the reports, it is not clear which features are responsible for the uptake of cell and toxicity. Generally, Au nanoparticles seem to be the most stable and non-toxic when assessed with cells of freshwater algae and fish. Based on their surface, these nanoparticles might be easily absorbed in the cells of fish. The different adverse effects of titania nanoparticles on the mice have been investigated via in vivo studies. It has been found that these nanoparticles aggravate oxidative deoxyribose nucleic acid damage, inflammation, clastogenicity, and genotoxicity in mice (Trouiller et al. 2009). Another report demonstrated that the metabolism of pentachlorophenol in zebrafish larvae has been increased significantly in the presence of titania nanoparticles, so it can be concluded that these nanoparticles induce oxidative damage during the early stages of its development. Taking the above contents into account, several researchers have devoted their efforts to identifying the fate of nanoparticles used for the purification of wastewater. Schwab et al. have spiked titania, silver, and zinc oxide nanoparticles in five different samples of water, and they observed that although nanoparticles can be removed to high extent by using techniques, such as membrane filtration, the treated water was still found to possess noticeable metallic contents, which may present threats to the health of human being (Chalew Talia et al. 2013). The as-Synthesized ZnO nanoparticles may become toxic upon their dissolution and dissociation to Zn ions and active oxygen, whereas light-induced reactions may also take part in this course. The phytotoxicity and nanoparticle interactions with plants at seedling stage

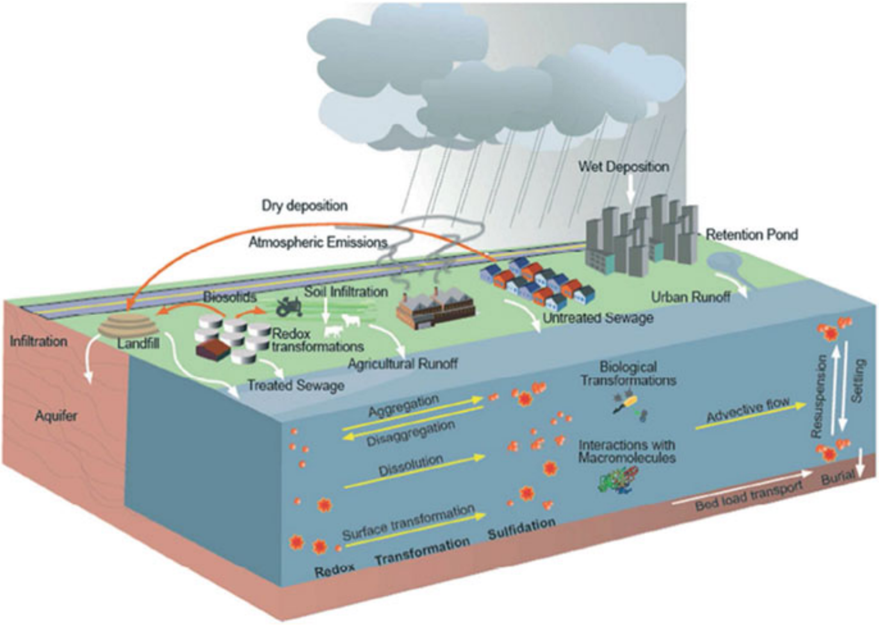


Fig. 18.5 Schematic representation of sources and flow of nanomaterials in the environment and the key processes determining the fate and behavior of nanomaterials in the aquatic environments. Reprinted with permission of [Modeling Nanomaterial Environmental Fate in Aquatic Systems. Environmental Science & Technology,The American chemical Society] from [(Dale et al. 2015)

is one more imperative issue for the adverse effects of nanoparticles (Lin and Xing 2007; Ma et al. 2010). The evaluation of risk factors after the use of zero-valent Fe and Fe_2O_3nanoparticles has also been demonstrated in many reports regarding their seed germination and phytotoxicity (Grieger et al. 2010). Surface oxidation of zero-valent Fe nanoparticles is a significant factor for the tendency of agglomeration and toxicity.

Investigation of the effect of released nanoparticles on various environmental species and their fate after being released to the environment is an active research direction (Fig. 18.5). Most of the strategies involve the theoretical modeling to explain the transport and transformations of used nanoparticles (Dale et al. 2015). A strong interaction between Au nanoparticles and natural organic matter was observed, which leads to swift aggregation of Au nanoparticles particularly under higher ionic strengths. However, the nanoparticle surface coating makes them stable and helps in their removal from aquatic environments, as indicated for silver nanoparticles. The environmental fate of titania nanoparticles in Rhine River was assessed through modeling, and results suggest that there is a possibility of an important downstream transport of nanoparticles. The suspended particulate matter helps in the downstream transport via the hetero-aggregation route (Praetorius et al. 2012).

Notably, the discharge of fabricated nanoparticles in polluted water might offer the appropriate substrate for self-conversion to green products. For example, silver nanoparticle sulfidation is a general approach in contaminated water that gives an insoluble and less toxic silver form (Levard et al. 2012). The unpredictable actions of nanoparticles in ecosystem forces the requirement of an effective approach to manage their potential risk. Few traditional approaches, such as the use of membranes or sorbents, have been developed for the exclusion of nanoparticles while treating wastewater. Nevertheless, an excellent approach to diminish potential risks of nanoparticle disposal is to reduce the amounts of solids employed in the remediation of wastewater. The complete recovery of nanoparticles enables their multiple use to validate the whole approach. There are many factors affecting the possibility of nanoparticle recycling. Among these various factors, the strategy to remove pollutants, such as adsorption, degradation, and photocatalysis, has the prime importance. For example, when the surface of nanoparticles is progressively sheltered by adsorbed species, a revival approach using appropriate chemical reagents, such as, NaOH must be accompanied. In this case, another issue that needs to be solved is the handling of the revival reagent that possesses a higher amount of the contaminant. When nanoparticles behave as catalysts of the reaction, the mild stimulation of surface characteristics at regular time intervals is sufficient to sustain a high process yield. There are also some routes in which nanoparticles do not attain saturation in the loading of pollutants after repeated operations. These kinds of systems must be designed in such a way that allows the recovery and constant reuse of nanoparticles to treat wastewater until saturation is reached.

Recovery of exhausted nanoparticles is a necessary step while investigating the use of nanoparticles in the field of water treatment. The inspiration behind the said strategy is to assure the lack of nanosized solid particles in the treated water as well as in the waste streams of the handling process. It is often very difficult to collect the dispersed nanoparticles due to their extremely small sizes. Moreover, in order to ensure the absolute separation of nanoparticles from purified water, a costly nanofiltration system should be designed.

Another relatively more “traditional” strategy to remove used nanoparticles from water is the process of coagulation. In this process, nanoparticles can be entangled via the coalesce floc as its sedimentation out of the water takes place. The stability of nanoparticles can be affected by the coagulating agents via the formation of charged hydrolytic moieties that help in the neutralization of nanoparticle surface charges. This approach creates a large aggregation of nanoparticles because of the alleviation of electrostatic repulsion. The effect of coagulant nature, amount of titania nanoparticles was explored on the removal of these nanoparticles through primary water treatment (Petersen et al. 2011). Contrarily, the way of aggregation of ZnO and titania nanoparticles in polluted water occurs and their hazardous effect on the oxygen uptake from sludge was investigated using high gradient external magnetic field. For the same reason, Fe(0) and Fe_2O_3nanoparticles are preferentially used either independently or as support to hold additional active materials. The separation of nanoparticles from water by using high-gradient magnetic fields is a broadly investigated field offering several chances of strategy design (Ditsch et al. 2005).

Nonetheless, upturn is not the ultimate intention of used nanoparticles. Saturated nanoparticles obtained after their use to treat wastewater are extremely toxic waste that demands safe disposal against prospect leakage of contaminants. Failure to overcome this issue implies a striking rise in the overall price of the route. Hence, it is important to explore the way of leaching out the entangled contaminants using the experimental approaches which classify wastes as non-reactive and non-toxic. The studies about the nature of ZnO, titania, and silver nanoparticles revealed that their influence on the processes of biological landfill is unimportant, whereas the leachate of metallic ionic species is principally related with other units. As the potency of adsorption of a contaminant is improved, nanoparticles look extremely stable against leaching. After this, saturated nanoparticles may be regarded and treated as non-reactive waste. Otherwise, different solutions should be investigated to make them inert. A model illustration is their use in building materials or ceramics as additives.

18.5 Conclusions

Environmental remediation is an ever-evolving field. The methods and techniques to address the challenges and rectify environmental threats are evolving with time. Textile wastewater is one of the major sources of water pollution worldwide. With the advent of nanotechnology, new and improved nanostructured sorbents and photocatalysts have been designed and used. They have shown promising results; however, still efforts are required to design more robust and efficient materials using earth's crust abundant elements.

Acknowledgments JA thanks higher education commission of Pakistan and MUST university for financial assistance.

References

Akram B, Ahmad K, Khan J, Khan BA, Akhtar J (2018) Low-temperature solution-phase route to sub-10 nm titanium oxide nanocrystals having super-enhanced photoreactivity. New J Chem 42:10947–10952

Benhamou A, Basly JP, Baudu M, Derriche Z, Hamacha R (2013) Amino-functionalized MCM-41 and MCM-48 for the removal of chromate and arsenate. J Colloid Interface Sci 404:135–139

Carp O, Huisman CL, Reller A (2004) Photoinduced reactivity of titanium dioxide. Prog Solid State Chem 32:33–177

Chalew Talia EA, Ajmani Gaurav S, Huang H, Schwab Kellogg J (2013) Evaluating nanoparticle breakthrough during drinking water treatment. Environ Health Perspect 121:1161–1166

Crini G, Lichtfouse E (2019) Advantages and disadvantages of techniques used for wastewater treatment. Environ Chem Lett 17:145–155

Crini G, Lichtfouse E, Wilson LD, Morin-Crini N (2019) Conventional and non-conventional adsorbents for wastewater treatment. Environ Chem Lett 17:195–213

Dale AL, Casman EA, Lowry GV, Lead JR, Viparelli E, Baalousha M (2015) Modeling nanomaterial environmental fate in aquatic systems. Environ Sci Technol 49:2587–2593

Davarpanah J, Kiasat AR (2014) Synthesis and characterization of SBA-polyperoxyacid: An efficient heterogeneous solid peroxyacid catalyst for epoxidation of alkenes. Catal Commun 46:75–80

Deng Y, Qi D, Deng C, Zhang X, Zhao D (2008) Superparamagnetic high-magnetization microspheres with an Fe3O4@SiO2 Core and perpendicularly aligned Mesoporous SiO2 Shell for removal of microcystins. J Am Chem Soc 130:28–29

Ditsch A, Lindenmann S, Laibinis PE, Wang DIC, Hatton TA (2005) High-gradient magnetic separation of magnetic Nanoclusters. Ind Eng Chem Res 44:6824–6836

Dsikowitzky L, Schwarzbauer J (2014) Industrial organic contaminants: identification, toxicity and fate in the environment. Environ Chem Lett 12:371–386

Elmolla ES, Chaudhuri M (2010) Degradation of amoxicillin, ampicillin and cloxacillin antibiotics in aqueous solution by the UV/ZnO photocatalytic process. J Hazard Mater 173:445–449

Fan Y, Ma W, Han D, Gan S, Dong X, Niu L (2015) Convenient recycling of 3D AgX/graphene aerogels (X = Br, cl) for efficient Photocatalytic degradation of water pollutants. Adv Mater 27:3767–3773

Farzadkia M, Rahmani K, Gholami M, Esrafili A, Rahmani A, Rahmani H (2014) Investigation of photocatalytic degradation of clindamycin antibiotic by using nano-ZnO catalysts. Korean J Chem Eng 31:2014–2019

Fresnais J, Yan M, Courtois J, Bostelmann T, Bée A, Berret JF (2013) Poly(acrylic acid)-coated iron oxide nanoparticles: quantitative evaluation of the coating properties and applications for the removal of a pollutant dye. J Colloid Interface Sci 395:24–30

Fu P-F, Luan Y, Dai X-G (2006) Interposition fixing structure of TiO2 film deposited on activated carbon fibers. Trans Nonferrous Metals Soc China 16:965–969

Fujishima A, Honda K (1972) Electrochemical photolysis of water at a semiconductor electrode. Nature 238:37–38

García-Ripoll A, Amat AM, Arques A, Vicente R, López MF, Oller I, Maldonado MI, Gernjak W (2007) Increased biodegradability of UltracidTM in aqueous solutions with solar TiO2 photocatalysis. Chemosphere 68:293–300

Ge J, Wang X, Yao H-B, Zhu H-W, Peng Y-C, Yu S-H (2015) Durable ag/AgCl nanowires assembled in a sponge for continuous water purification under sunlight. Materials Horizons 2:509–513

Grieger KD, Fjordbøge A, Hartmann NB, Eriksson E, Bjerg PL, Baun A (2010) Environmental benefits and risks of zero-valent iron nanoparticles (nZVI) for in situ remediation: risk mitigation or trade-off? J Contam Hydrol 118:165–183

Grishkewich N, Mohammed N, Tang J, Tam KC (2017) Recent advances in the application of cellulose nanocrystals. Curr Opin Colloid Interface Sci 29:32–45

Gupta VK, Saleh TA, Pathania D, Rathore BS, Sharma GJI (2015) A cellulose acetate based nanocomposite for photocatalytic degradation of methylene blue dye under solar light. Ionics 21:1787–1793

Han Y, Ying JY (2005) Generalized fluorocarbon-surfactant-mediated synthesis of nanoparticles with various Mesoporous structures. Angew Chem Int Ed 44:288–292

Jang SH, Min BG, Jeong YG, Lyoo WS, Lee SC (2008) Removal of lead ions in aqueous solution by hydroxyapatite/polyurethane composite foams. J Hazard Mater 152:1285–1292

Khan HR, Aamir M, Malik MA, Tahir AA, Akram B, Murtaza G, Choudhary MA, Akhtar J (2019a) Chemically vaporized cobalt incorporated wurtzite as photoanodes for efficient photoelectrochemical water splitting. Mater Sci Semicond Process 101:223–229

Khan HR, Akram B, Aamir M, Malik MA, Tahir AA, Choudhary MA, Akhtar J (2019b) Fabrication of Ni2+ incorporated ZnO photoanode for efficient overall water splitting. Appl Surf Sci 490:302–308

Khedr MH, Abdel Halim KS, Soliman NK (2009) Synthesis and photocatalytic activity of nano-sized iron oxides. Mater Lett 63:598–601

Lee HC, Jeong YG, Min BG, Lyoo WS, Lee SCJF, Polymers (2009): Preparation and acid dye adsorption behavior of polyurethane/chitosan composite foams. Fibers and Polymers 10, 636–642

Levard C, Hotze EM, Lowry GV, Brown GE (2012) Environmental transformations of silver nanoparticles: impact on stability and toxicity. Environ Sci Technol 46:6900–6914

Lewinski N, Colvin V, Drezek R (2008) Cytotoxicity of nanoparticles. Small 4:26–49

Li X, Zhu J, Li H (2012) Comparative study on the mechanism in photocatalytic degradation of different-type organic dyes on SnS2 and CdS. Appl Catal B Environ 123-124:174–181

Liao D, Zheng W, Li X, Yang Q, Yue X, Guo L, Zeng G (2010) Removal of lead(II) from aqueous solutions using carbonate hydroxyapatite extracted from eggshell waste. J Hazard Mater 177:126–130

Liao Q, Su X, Zhu W, Hua W, Qian Z, Liu L, Yao J (2016) Flexible and durable cellulose aerogels for highly effective oil/water separation. RSC Adv 6:63773–63781

Lin D, Xing B (2007) Phytotoxicity of nanoparticles: inhibition of seed germination and root growth. Environ Pollut 150:243–250

Liu X, Lv P, Yao G, Ma C, Tang Y, Wu Y, Huo P, Pan J, Shi W, Yan Y (2014) Selective degradation of ciprofloxacin with modified NaCl/TiO2 photocatalyst by surface molecular imprinted technology. Colloids Surf A Physicochem Eng Asp 441:420–426

Ma X, Geiser-Lee J, Deng Y, Kolmakov A (2010) Interactions between engineered nanoparticles (ENPs) and plants: Phytotoxicity, uptake and accumulation. Sci Total Environ 408:3053–3061

Madhura L, Singh S, Kanchi S, Sabela M, Bisetty K (2019) Nanotechnology-based water quality management for wastewater treatment. Environ Chem Lett 17:65–121

Mahesh KPO, Kuo D-H, Huang B-R, Ujihara M, Imae T (2014) Chemically modified polyurethane-SiO2/TiO2 hybrid composite film and its reusability for photocatalytic degradation of acid black 1 (AB 1) under UV light. Appl Catal A Gen 475:235–241

Malato S, Fernández-Ibáñez P, Maldonado MI, Blanco J, Gernjak W (2009) Decontamination and disinfection of water by solar photocatalysis: recent overview and trends. Catal Today 147:1–59

Matos J, Laine J, Herrmann JM (2001) Effect of the type of activated carbons on the Photocatalytic degradation of aqueous organic pollutants by UV-irradiated Titania. J Catal 200:10–20

Moore MN (2006) Do nanoparticles present ecotoxicological risks for the health of the aquatic environment? Environ Int 32:967–976

Navarro E, Baun A, Behra R, Hartmann NB, Filser J, Miao A-J, Quigg A, Santschi PH, Sigg LJE (2008) Environmental behavior and ecotoxicity of engineered nanoparticles to algae, plants, and fungi. Ecotoxicology 17:372–386

Nguyen DD, Tai N-H, Lee S-B, Kuo W-S (2012) Superhydrophobic and superoleophilic properties of graphene-based sponges fabricated using a facile dip coating method. Energy Environ Sci 5:7908–7912

Ni M, Leung MKH, Leung DYC, Sumathy K (2007) A review and recent developments in photocatalytic water-splitting using TiO2 for hydrogen production. Renew Sust Energ Rev 11:401–425

Pérez-Quintanilla D, del Hierro I, Fajardo M, Sierra I (2006) Mesoporous silica functionalized with 2-mercaptopyridine: synthesis, characterization and employment for hg(II) adsorption. Microporous Mesoporous Mater 89:58–68

Petersen EJ, Zhang L, Mattison NT, O'Carroll DM, Whelton AJ, Uddin N, Nguyen T, Huang Q, Henry TB, Holbrook RD, Chen KL (2011) Potential release pathways, environmental fate, and ecological risks of carbon nanotubes. Environ Sci Technol 45:9837–9856

Praetorius A, Scheringer M, Hungerbühler K (2012) Development of environmental fate models for engineered nanoparticles—a case study of TiO2 nanoparticles in the Rhine River. Environ Sci Technol 46:6705–6713

Seema H, Christian Kemp K, Chandra V, Kim KS (2012) Graphene–SnO2composites for highly efficient photocatalytic degradation of methylene blue under sunlight. Nanotechnology 23:355705

Sher Shah MSA, Park AR, Zhang K, Park JH, Yoo PJ (2012) Green synthesis of biphasic TiO2–reduced graphene oxide Nanocomposites with highly enhanced Photocatalytic activity. ACS Appl Mater Interfaces 4:3893–3901

Shi Y, Huang J, Zeng G, Cheng W, Yu H, Gu Y, Shi L, Yi K (2018) Stable, metal-free, visible-light-driven photocatalyst for efficient removal of pollutants: mechanism of action. J Colloid Interface Sci 531:433–443

Shin S, Jang J (2007) Thiol containing polymer encapsulated magnetic nanoparticles as reusable and efficiently separable adsorbent for heavy metal ions. Chem Commun:4230–4232

Slowing II, Vivero-Escoto JL, Trewyn BG, Lin VSY (2010) Mesoporous silica nanoparticles: structural design and applications. J Mater Chem 20:7924–7937

Tang Y, Liang S, Wang J, Yu S, Wang Y (2013) Amino-functionalized core-shell magnetic mesoporous composite microspheres for Pb(II) and cd(II) removal. J Environ Sci 25:830–837

Tong Z, Yang D, Shi J, Nan Y, Sun Y, Jiang Z (2015) Three-dimensional porous aerogel constructed by g-C3N4 and graphene oxide Nanosheets with excellent visible-light Photocatalytic performance. ACS Appl Mater Interfaces 7:25693–25701

Trouiller B, Reliene R, Westbrook A, Solaimani P, Schiestl RH (2009) Titanium dioxide nanoparticles induce DNA damage and genetic instability in vivo in mice. Cancer Res 69:8784–8789

Vallano PT, Remcho VT (2000) Highly selective separations by capillary electrochromatography: molecular imprint polymer sorbents. J Chromatogr A 887:125–135

Varadarajan G, Venkatachalam P (2016) Sustainable textile dyeing processes. Environ Chem Lett 14:113–122

Wang Y, Wang S, Niu H, Ma Y, Zeng T, Cai Y, Meng Z (2013) Preparation of polydopamine coated Fe3O4 nanoparticles and their application for enrichment of polycyclic aromatic hydrocarbons from environmental water samples. J Chromatogr A 1283:20–26

Wang G, He Y, Wang H, Zhang L, Yu Q, Peng S, Wu X, Ren T, Zeng Z, Xue Q (2015) A cellulose sponge with robust superhydrophilicity and under-water superoleophobicity for highly effective oil/water separation. Green Chem 17:3093–3099

Wu L, Li L, Li B, Zhang J, Wang A (2015) Magnetic, durable, and Superhydrophobic polyurethane@Fe3O4@SiO2@fluoropolymer sponges for selective oil absorption and oil/water separation. ACS Appl Mater Interfaces 7:4936–4946

Xu P, Zeng GM, Huang DL, Feng CL, Hu S, Zhao MH, Lai C, Wei Z, Huang C, Xie GX, Liu ZF (2012) Use of iron oxide nanomaterials in wastewater treatment: a review. Sci Total Environ 424:1–10

Yang Y-W (2011) Towards biocompatible nanovalves based on mesoporous silica nanoparticles. MedChemComm 2:1033–1049

Yang X, Yan Z, Jiang L, Wang X, Zheng K, Wang Y, Li Q, Wang J (2013) Synthesis and Photocatalysis of AL doped CdS Templated by non-surfactant Hypocrellins. Procedia Environ Sci 18:572–578

Yoshitake H, Yokoi T, Tatsumi T (2003) Adsorption behavior of arsenate at transition metal Cations captured by amino-functionalized Mesoporous Silicas. Chem Mater 15:1713–1721

Yu J, Yu X (2008) Hydrothermal synthesis and Photocatalytic activity of zinc oxide hollow spheres. Environ Sci Technol 42:4902–4907

Zhu H, Jiang R, Xiao L, Chang Y, Guan Y, Li X, Zeng G (2009) Photocatalytic decolorization and degradation of Congo red on innovative crosslinked chitosan/nano-CdS composite catalyst under visible light irradiation. J Hazard Mater 169:933–940

Zhu Q, Pan Q, Liu F (2011) Facile removal and collection of oils from water surfaces through Superhydrophobic and Superoleophilic sponges. J Phys Chem C 115:17464–17470

Zhu H, Chen D, An W, Li N, Xu Q, Li H, He J, Lu J (2015a) A robust and cost-effective Superhydrophobic graphene foam for efficient oil and organic solvent recovery. Small 11:5222–5229

Zhu H, Chen D, Li N, Xu Q, Li H, He J, Lu J (2015b) Graphene foam with switchable oil wettability for oil and organic solvents recovery. Adv Funct Mater 25:597–605

Zhu L, Fu Tan C, Gao M, Ho GW (2015c) Design of a Metal Oxide–Organic Framework (MoOF) foam microreactor: solar-induced direct pollutant degradation and hydrogen generation. Adv Mater 27:7713–7719

Index

Inamuddin et al. (eds.), *Water Pollution and Remediation: Organic Pollutants*, Environmental Chemistry for a Sustainable World 54,
https://doi.org/10.1007/978-3-030-52395-4