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Persistent Pollutants in Water and Advanced Treatment Technology

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Persistent Pollutants in Water and Advanced Treatment Technology

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Preface

Persistent pollutants are the compounds which are highly resistant to environmental degradation through natural processes and remain for a long time in nature. They remain untreated in conventional treatment processes. They are toxic, mutagenic, carcinogenic chemicals and adversely affect the aquatic environment as well as human health. Their easy transportation and long half-lives can affect people and wildlife farther away from the source from where they are used and released.

The International Society for Energy, Environment and Sustainability (ISEES) was founded at the Indian Institute of Technology Kanpur (IIT Kanpur), India, in January 2014 to spread knowledge/awareness and catalyse research activities in the fields of energy, environment, sustainability, and combustion. Society's goal is to contribute to the development of clean, affordable, and secure energy resources and a sustainable environment for society and spread knowledge in the areas mentioned above, and create awareness about the environmental challenges the world is facing today. The unique way adopted by ISEES was to break the conventional silos of specialisations (engineering, science, environment, agriculture, biotechnology, materials, fuels, etc.) to tackle the problems related to energy, environment, and sustainability in a holistic manner. This is quite evident in the participation of experts from all fields to resolve these issues. The ISEES is involved in various activities, such as conducting workshops, seminars, and conferences, in the domains of its interests. The society also recognises the outstanding works of young scientists, professionals, and engineers for their contributions in these fields by conferring them awards under various categories.

Sixth International Conference on 'Sustainable Energy and Environmental Challenges' (VI-SEEC) was organised under the auspices of ISEES from 27–29 December 2021, in hybrid mode due to restrictions on travel because of the ongoing COVID-19 pandemic situation. This conference provided a platform for discussions between eminent scientists and engineers from various countries, including India, Spain, Austria, Australia, South Korea, Brazil, Mexico, USA, Malaysia, Japan, Hong Kong, China, the UK, Netherlands, Poland, Finland, Italy, Israel, Kenya, Turkey, and Saudi Arabia. At this conference, eminent international speakers presented their views on energy, combustion, emissions, and alternative energy resources for sustainable development and a cleaner environment. The conference presented two high-voltage plenary talks by Prof. Ashutosh Sharma, Secretary, DST and Dr. V. K. Saraswat, Honourable Member, NITI Ayog.

The conference included 12 technical panel discussions on energy and environmental sustainability topics. Each session had 6–7 eminent scientists who shared their opinion and discussed the trends for the future. The technical sessions at the conference included Fuels for Sustainable Transport, Challenges for Desalination and Wastewater. Treatment and Possible Solutions, Engine Combustion Modelling, Simulation and Sprays, Bioenergy/biofuels, Coal Biomass Combustion for Power Generation, Microbial Processes and Products, Future of IC Engine Technology and Roadmap, Air Pollution and Climate Change: Sustainable Approaches, Sustainable Energy from Carbon Neutral Sources, Biological Waste Treatment, Combustion: Emerging Paradigm and Thermochemical Processes for Biomass. 500+ participants and speakers from around the world attended this three-day conference.

This conference laid out the roadmap for technology development, opportunities, and challenges in energy, environment, and sustainability domains. All these topics are very relevant for the country and the world in the present context. We acknowledge the support from various agencies and organisations for conducting the sixth ISEES conference (VI-SEEC) where these books germinated. We want to acknowledge our publishing partner Springer (special thanks to Ms Swati Mehershi).

The editors would like to express their sincere gratitude to many authors worldwide for submitting their high-quality work on time and revising it appropriately at short notice. We want to express our special gratitude to our prolific set of reviewers, Dr. Subrata Hait, Dr. Amritanshu Srivastava, Dr. Bhaskar Singh, Dr. Chiranjeeb kumar, Dr. Asif Qureshi, Dr. Abhay Kr. Singh, Prof. S. K. Patidar, Dr. K. D. Singh, Dr. Vipin Kumar, and Dr. Sheeja Jagadevan who reviewed various chapters of this monograph and provided their valuable suggestions to improve the manuscripts.

This book defines the current status of the occurrences, fate, and transport of persistent pollutants in water and wastewater. This book compiles the state of the art of emerging technologies, such as nanotechnology, advanced oxidation process, membrane processes, and sorption, for the clean-up of persistent pollutants in water, including heavy metals, pharmaceuticals, phenolic compounds, PFAs, phthalates as well as micoplastics and their by-products. The book will provide a single platform for the environmental researchers to build strategies to deal with the persistent pollutant. This book also discusses the principal aspects of degradation mechanism of the pollutants, toxic by-products, and effectiveness of the emerging technologies. Regulatory authorities are making effluent disposal standards more stringent, and there is a dire need of near-zero liquid discharge (NZLD) system to meet the effluent standards for disposal. This book discusses the application of recently developed membranes and modifications which can improve the efficiency and applicability of membrane-based ZLD systems. Chapters include recent results and focus on current trends in emerging contaminants in water environment, their fate and transport in natural environment, their adverse impacts on the environmental components, and the advanced treatment methods. We hope the book will greatly interest the professionals and post-graduate students involved in research in the field of emerging contaminants and their fate and recent treatment technologies.

Dhanbad, India	Alok Sinha
Mumbai, India	Swatantra P. Singh
Jaipur, India	A. B. Gupta

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Editors and Contributors

About the Editors

Prof. Dr. Alok Sinha is currently serving as Professor in the Department of Environmental Science and Engineering and Dean (Infrastructure) at Indian Institute of Technology (ISM), Dhanbad, India. He has also been granted a patent on "Novel system for regenerating and reusing nZVI/ZVI particles in wastewater treatment". He has more than 60 publications in peer reviewed journal and is Guest Editor for *Frontiers in Environmental Science*. He has been awarded Best Paper Award by BITS Pilani. He has received Certificate of Excellence for Knimbus "Young Innovator Award" for the year 2013–14. He is a Fellow Member of The Institution of Engineers (India). He has guided 13 Ph.D. thesis and more than 30 M.Tech. thesis and has completed many R&D and Consultancy proposals.

Dr. Swatantra P. Singh is an environmental engineer with experience in membrane fabrication, environmental nanotechnology, fate, and transport of pollutants and emerging contaminants in the environment. Currently, he is an associate professor in the Environmental science and Engineering Department (ESED) at IIT Bombay. He has developed a key technology to fabricate the membranes for water purification and print graphene in-situ in a single step. He has multiple US patents and Indian patents (filed) on membrane and laser-based graphene fabrication techniques. He has authored 31 journal articles, 5 book, and 23 book chapters. He has recently won INAE Young Engineer Award (2020), ISEES Young Scientists Award (2020), and IIT Bombay Early Research Award 2021.

Prof. Dr. A. B. Gupta holds B.E. (Civil) from MREC Jaipur; M.Tech. and Ph.D. (Environmental Science and Engineering) degrees from CESE, IIT Bombay. He joined MNIT as a lecturer of Civil Engineering in 1984 and is serving as a Professor since 1996. His administrative assignments at MNIT include HOD (Civil), Dean R&D, Dean (Faculty Affairs) and Director. He has published/presented over 480 papers in various international/national journals/conferences, guided Fifteen PhDs and over 100 Masters' theses, taken up several prestigious research/consultation projects funded by national/international agencies, and received many academic/research awards. He has been a non official member of RPCB and Environment and Health Board of Rajasthan and several important committees of DST(GOI), BIS, IRC etc. His major research contributions are in the areas of biological waste treatment; and Environment and health linkages; that have benefitted large segments of the society. Besides a distinguished category lecture at Iowa State University, he has delivered several invited talks, keynote addresses, memorial lectures at national and international institutions and conferences across the world. He is fellow of IE(I), IAEM and life member of many reputed organizations. He has been a member of many selection committees of IITs, NEERI, NITs and other universities.

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Part I
General

Chapter 1
Introduction to Persistent Pollutants in Water and Advanced Treatment Technology

Alok Sinha, Swatantra P. Singh, and A. B. Gupta

Abstract Persistent pollutants are extremely undesirable in the current scenario due to their stubborn, mutagenic, and bio-accumulative nature in the environment and food chain. Their easy exposure, long-distance transport, and mild concentration in the environment are other grave causes of concern. Moreover, the main difficulty with persistent pollutants is that they remain untreated during conventional treatment methods. This book primarily discusses the occurrence and fate of persistent pollutants and their transport in the environment, to understand their harmful impacts on living organisms. The chapters cover many emerging pollutants such as polychlorinated biphenyls (PCBs), per- and polyfluoroalkyl substances (PFASs), pharmaceuticals, phenolic compounds, persistent metals, quinolone, microplastics, and their by-products in water and wastewater medium. In addition, the book also covers the available conventional treatment technologies along with the in-depth discussion and suggestions on the newly developed treatment methods, such as advanced oxidation processes, membrane technologies, microbial techniques, nanotechnologies, and biosorption techniques, for the treatment of persistent pollutants from water and wastewater.

Keywords Advanced oxidation techniques · Membrane-based technologies · Wastewater treatment · Persistent pollutants · Emerging contaminants · Nano-zero valent iron (nZVI) · Heavy metals · Microplastics · Biosorption

Persistent pollutants are extremely stubborn in the environment, can easily bio-accumulate through the food chain, and show their adverse effects on the living

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beings and the environment. Most of them are highly toxic, carcinogenic, and mutagenic in nature. These pollutants can travel far away from their source of origin hence the fate and transport of these pollutants deserve a lot of attention. Further as these pollutants are not being eliminated during the conventional treatment technologies, which are practiced worldwide, trace concentrations of these toxic compounds are being detected in surface as well as groundwater. This book discusses the current status of some of the persistent pollutants, their occurrence, fate, and transport in water and wastewater and the new emerging technologies which are being developed for treating these recalcitrant compounds in water systems. In order to eliminate these pollutants, several conventional and emerging treatment technologies of wastewater have been summarized such as advanced oxidation processes, membrane-related technology, nanotechnologies, sorption/biosorption processes, electrochemical/bio-electrochemical process as well as the combination of these methods or hybrid methods. These treatment approaches are specifically related to the abolition of persistent pollutants such as persistent metals, PCBs, per- and polyfluoroalkyl substances (PFASs), pharmaceuticals, phenolic compounds, and quinolone, microplastics and their by-products from water and wastewater.

Second section of the book is dedicated to the understanding of emerging contaminants (like plastic, marine microplastic, plasticizers, phthalates, per- and polyfluoroalkyl substances (PFASs)), their availability in water and wastewater, and also their source of origin and related toxicity to the environment. Microplastic has been identified as a dangerous emerging contaminant generated via plastic fabrication and manufacturing industries. Microplastics act as a sink and source of plastic-associated anthropogenic pollutants and likely affect their fate, bioaccumulation, and toxic potency. This book provides information about the present status of the oceanic microplastics, contaminants-microorganisms interactions, and their effects on marine ecosystems. A comprehensive review is presented on the global generation profile of per- and polyfluoroalkyl substances (PFASs) from the related industries and their existing and probable treatment technologies from wastewater with a special recommendation of constructed wetland-microbial fuel cell (CW-MFC) technology. The roles of wetland plants, substrates, and electro-active bacteria (EAB) in the removal of PFASs in the CW-MFC system are also discussed with different mechanisms. Furthermore, this section discusses an overview of plasticizers and plastic monomers, their occurrence, transformations, and fate in wastewater. Phthalates are the most used plasticizers, and many previous studies have reported their endocrine-disrupting properties and carcinogenicity. Plasticizers and plastic monomers enter the environmental waters and wastewater, mainly through human activities and leaching from the plastic materials. Plasticizers and plastic monomers are ubiquitously found in all the environmental waters and wastewater ranging in the concentration from ng/L to μg/L. Most plasticizers and monomers undergo biological or non-biological transformations, and these transformed products are frequently detected in wastewater.

Third section of this book emphasizes on the utilization of advanced treatment technologies for the treatment of persistent pollutants. Since the conventional and existing treatment techniques are not effective for the complete removal of emerging persistent pollutants or persistent organic pollutants (POPs) such as polychlorinated biphenyls (PCBs), phenols and polyphenols, personal care products, phthalates, per- and polyfluoroalkyl substances (PFASs), microplastics, and quinoline from the wastewater, due to their recalcitrant nature, hence in order to achieve complete removal or mineralization of persistent organic compounds from wastewater several advanced oxidation practices are being employed or are in their developmental phase. Furthermore, the surge in cancer incidence and chemotherapy treatment have enhanced the application of anticancer drugs (ACDs) which contribute to the existing problem of pharmaceutical pollution. ACDs being one of the major emerging contaminants are frequently detected in surface water, municipal wastewater, and pharmaceutical effluent which substantially cause genotoxic and mutagenic effects on the aquatic environment. Several remediation techniques are available on the removal of pharmaceutical compounds such as anti-inflammatory, analgesic, and endocrine disruptors; however, very few studies document the degradation mechanism of anticancer drugs. This section is critically reviews the novel and advanced treatment (oxidation) methods, their mechanisms, and their possible modified versions, in order to accomplish high removal efficiency and cost-effective process. For the treatment by electrochemical methods, this section documents various key process parameters, reaction mechanisms, reactor designs, different types of electrode materials and their preparation, electro-catalysts, catalytic particle electrodes (CPEs), electrolytes, and their involvement in the reaction system. Moreover, the existing challenges and the limitations in the field of electrochemical and other advanced oxidation processes are also summarized.

Fourth section of this book deals with the persistent and toxic heavy metals in the water environment. The elimination or transformation of persistent metals (or heavy metals) from the aqueous medium includes the conversion of toxic metals to less-toxic metals or transfer from water medium to other medium. This section summarizes advanced treatment and metal recovery methods which are recently been recognized and are in their progressive phases such as selective biosorption, bio-electrochemical processes, and nanotechnology. This section focuses on the strategies which can be used to enhance the sorption capacity and selective nature of the bio-sorbents. A brief review of the processes, approaches, mechanisms, and mathematical models is also presented accompanied by a future course of further research in the field of bio-sorbents. Moreover, in the past few decades, the field of the bio-electrochemical system has flourished and successfully demonstrated the potential to treat a variety of contaminants along with the production of green energy, courtesy to the electrogenic microbes. This section also explores the advances in bio-electrochemical systems for the removal of metallic ions from different water media, with special reference to the mechanisms involved in the process as well as the persisting challenges for making the system more economical and sustainable. Iron-based nanomaterial and modified nanocomposites, for the effective treatment of persistent metals from soil and groundwater, are also discussed in this section with a special emphasis on its use in the treatment of deadly hexavalent chromium. This section also discusses the current status of chromium, its fate, transportation, and longevity in the water environment.

Fifth section of this book talks about the treatment of urea and ammonia from wastewater through various traditional and novel methods such as physicochemical, electrochemical, as well as non-electrochemical methods. Non-electrochemical methods for urea removal are hydrolysis, enzymatic decomposition, biological degradation, decomposition by strong oxidizing agents, and degradation by catalysts. Air stripping, struvite precipitation, and ion exchange are very common methods for ammonia removal, whereas microwave radiation and ozone micro-bubbles are relatively new and costly. The subsequent chapters in this section are focused on the application of the membrane-related technologies which exhibit higher efficiency, low footprint, reduced chemical use, and superior quality treatment of persistent pollutants from wastewater. Membrane technology has grown significantly due to its application in the industrial separation processes, as well as for desalination and wastewater treatment. However, these membrane systems encounter a major challenge of fouling which comprises bio-fouling, colloidal fouling, organic fouling, inorganic fouling, etc. Out of them, bio-fouling can impose a number of negative impacts on the membrane systems because of the undesirable deposition and microbial growth on the surfaces, which can hamper the efficiency of water and wastewater treatment plants. Section also provides insights on the possible approaches employed to control membrane bio-fouling, focusing on the physical, chemical, and biological methods. Recent advances in the development of bio-fouling mitigation techniques to improve treatment performance are also highlighted. Biomimetic membranes have emerged as a possible solution for membrane-based water purification and removal of emerging pollutants from water systems in recent years. This section discusses different membrane-based separation technologies and its advancements for future development, mainly focusing on biomimetic membranes. The ceramic membrane has made rapid progress in industrial/municipal wastewater as well as drinking water treatment owing to its advantageous properties over the conventional polymeric membrane, in the recent decades. This section also highlights the research and progress in fabrication methods for synthesizing ceramic membranes. Application of ceramic membranes in wastewater treatment, including oily wastewater treatment, heavy metal ion removal, industrial wastewater treatment, bacteria and viruses removal, and removal of emerging contaminants from wastewater is also discussed. Finally, future scope and challenges for improvements and development of low-cost ceramic membranes are also emphasized. In the end, an important insight is presented on the application of membrane technology in achieving zero liquid discharge (ZLD) systems and making it economically feasible. It is worth to mention that application of the recently developed membranes and modifications can improve the efficiency and applicability of membrane-based ZLD systems.

This monograph presents the source, occurrence, fate, transport, and advanced treatment technologies for the emerging contaminants in the water systems. Specific topics covered in the monograph include:

- Marine microplastics: abundance, ecotoxic consequences of associated anthropogenic contaminants, and interactions with microorganisms

- World profile of foreseeable strategies for the removal of per- and polyfluoroalkyl substances (PFASs) from water
- Plastic chemical constituents in wastewater, surface water, and drinking water
- Occurrence of phthalates in the environment, their toxicity, and treatment technologies
- Application of electrochemical technologies for the efficacious removal of persistent organic pollutants from wastewater
- Recent progress in electrochemical oxidation technology: its applicability in highly efficient treatment of persistent organic pollutants from industrial wastewater
- Advanced treatment methods for the emerging contaminants: an insight into the removal of anticancer drugs
- Occurrence of quinoline in the environment and its advanced treatment technologies
- Strategies to enhance selective biosorption-based remediation and recovery of persistent metal pollutants
- Bioelectrochemical systems for advanced treatment and recovery of persistent metals in the water system: mechanism, opportunities, and challenges
- Fate and transport of chromium contaminant in environment
- Iron-based modified nanomaterials for the efficacious treatment of Cr(VI) containing wastewater: a review
- Removal of urea and ammonia from wastewater
- Biofouling mitigation strategies in membrane systems for wastewater treatment
- Biomimetic membranes for effective desalination and emerging contaminants (ECs) removal
- Synthesis of ceramic membranes and their application in wastewater treatment and emerging contaminants removal
- Near zero liquid discharge (NZLD) for wastewater through membrane technology.

The topics are organized into five different sections: (i) General, (ii) Emerging persistent pollutants, (iii) Advanced oxidation processes for the removal of persistent pollutants, (iv) Removal of persistent metals from water systems, (v) Membrane technologies for remediation of persistent pollutants.

Part II
Emerging Persistent Pollutants

Chapter 2
Marine Microplastics: Abundance, Ecotoxic Consequences of Associated Anthropogenic Contaminants and Interactions with Microorganisms

Abhrajyoti Tarafdar, Dana Fahad M. S. Mohamed, and Jung-Hwan Kwon

Abstract The industrial fabrication of plastics has experienced outstanding growth in recent decades. At the current speed of advancement, this production has been estimated to be doubled and plastic waste spilling into the sea can raise up to threefold in the next twenty years. Presently, plastics are the most persistent components of the oceanic trash and the most accounted materials experienced by marine flora and fauna. Microplastics have been accounted for functioning as vectors by sorbing contaminants and leach various harmful plastic additives. In this way, microplastics can act as a sink and source of these plastic-associated anthropogenic pollutants and likely affecting their fate, bioaccumulation and toxic potency. Oceanic microplastics are readily invaded by aquatic microbes, forming "plastisphere" biofilms. Abundance of antibiotic resistance genes and potential pathogenic bacteria are frequently reported in plastisphere. Interactions between microplastics and their probable first-hand consumers, the lower trophic level microbes, are also topic of interest nowadays, with a particular focus on the effects of microplastics in these microbes. The current book chapter expects to highlight the present status of information on the oceanic microplastics affair, related contaminants microorganisms and effects on marine ecosystems.

Keywords Marine microplastic · POPs · Plastic additives · ARGs · Plastisphere · Pathogens

Abbreviations

ARGs	Antibiotic resistance genes,
BBP	Benzyl butyl phthalate,
BHT	Butylated hydroxytoluene,
BUVs	Benzotriazole UV stabilizers,

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DBP	Di-*n*-butyl phthalate,
DEHP	Di(2-ethylhexyl) phthalate,
DEP	Diethyl phthalate,
DNOP	Di-*n*-octyl phthalate,
EPS	Extracellular polymeric substances,
HDPE	High-density polyethylene,
HGT	Horizontal gene transfer,
LDPE	Low-density polyethylene,
MPs	Microplastics,
PA	Polyamide,
PAIs	Plastics-related pathogenicity islands,
PC	Polycarbonate,
PCL	Polycaprolactone,
PE	Polyethylene,
PES	Polysulfone,
PET	Polyethylene terephthalate,
PHA	Polyhydroxyalkanoate,
PHB	Poly-3-hydroxybutyrate,
PLA	Polylactic acid,
PMMA	Poly(methyl methacrylate),
POM	Polyoxymethylene,
POPs	Persistent organic pollutants,
PP	Polypropylene,
PS	Polystyrene,
PTFE	Polytetrafluoroethylene,
PU	Polyurethane,
PVA	Polyvinyl acetate,
PVC	Polyvinyl chloride,
QS	Quorum sensing.

2.1 Introduction

Plastics are widely used in our daily life due to its feasibility, lightweight and durability. They are commonly used in a variety of sectors such as building, construction, industrial purposes and packaging (Nikiema and Asiedu 2022). According to a report by European Association of Plastics Recycling & Recovery (2021), global plastic production reached 367 million tonnes in 2020 (Tarafdar et al. 2022). As a large portion of plastic products are for single-use purposes, they produce a lot of waste which is distributed in the environment due to mismanagement. There is a rising concern about the plastic debris present in the marine environment as they break down to microplastics through mechanical, photolytic and biological degradation (Alfaro-Núñez et al. 2021).

Plastics can be categorized according to their size. Macroplastics are plastic debris larger than 2.5 cm, mesoplastics are 5 mm–2.5 cm, microplastics size is within the range of 0.1 μm–5 mm, and nanoplastics are less than 100 nm (Huerta Lwanga et al. 2017; Jeyasanta et al. 2020). Plastic debris has been found along the coastal lines (Mohan et al. 2022; Purwiyanto et al. 2022), seabed (Cheang et al. 2018) and sea surfaces (Cincinelli et al. 2019; Pan et al. 2022; Russell and Webster 2021). As microplastics and nanoplastics are small in size, high specific surface area increases their reactivity and small size allows transport through organelles and cell membranes (Prata et al. 2020). Plastics also carry plastic additives and may act as vectors for chemical contaminants, possibly causing adverse effects on the organisms that consume them (Cormier et al. 2021). Some instances of the adverse effects due to the exposure to microplastics include: the impairment of the digestive system in mussels (Wang et al. 2020a), their effect on gametogenesis in oysters (Gardon et al. 2018) and increase in the levels of reactive oxygen species in marine copepod (Choi et al. 2020).

On the other hand, there are some instances where organisms thrive off microplastics. Since plastics are distributed in the marine environment, both prokaryotic and eukaryotic microorganisms can form a distinct microbial biofilm, known as “plastisphere” (Kirstein et al. 2018). Therefore, the complex structure of polymers in microplastics provides a home for microorganisms and adsorbed pollutants, which eventually alters the toxic impacts of microplastics (Fig. 2.1). Hence, in this chapter, current knowledge on the issues of microplastics pollution, marine microplastics abundance, the toxic potency of plastic-associated contaminants, the plastisphere, as well as the abundance of antibiotic resistance genes and potential pathogenic bacteria will be discussed.

2.2 Marine Microplastics Abundance

Microplastics can be classified based on its pristine production size, form, thickness and composition substances. Microplastics are characterized as materials made of anthropogenic plastics with a typical size of under 5 mm. The fracture of bigger plastics in the environment is brought about by chemical (e.g. photolysis, hydrolysis and heat), mechanical (e.g. abrasion) and bio-organic (e.g. microscopic organisms) degradation. Microplastics are classified into primary and secondary microplastics. Primary microplastics are derived from microplastics created in miniature estimated particles and consumer products that include microbeads, as well as industrial abrasives. They are initially fabricated as microplastics that are normally applied in cosmetics, drugs and technological or industry applications. On the other hand, secondary microplastics are initially made as macroplastics that are decayed and divided into more modest pieces by complex weathering processes, such as mechanical abrasion by sand or water, biodegradation, thermal processes and photodegradation. In view of the morphotypes, microplastics comprise fibres, fragments, films, pellets, globules and foam. Microplastics abundance in a water section relies upon

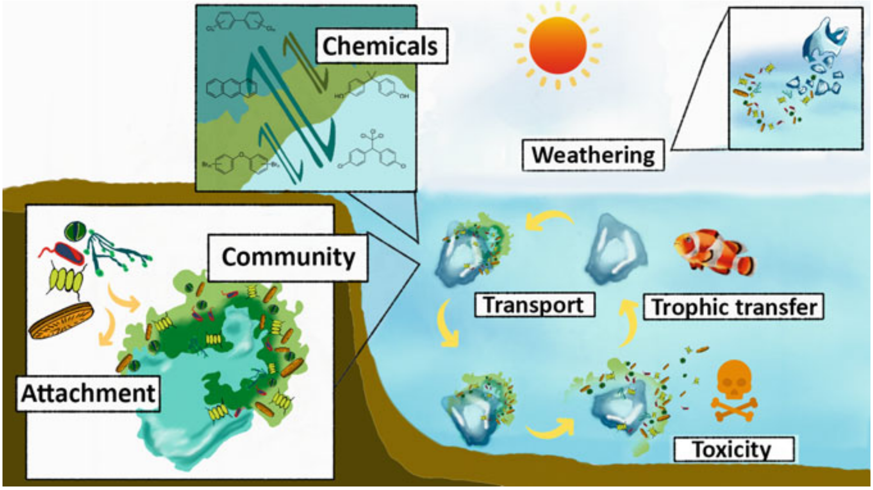

Fig. 2.1 Environmental fate and marine biological impacts of microplastics. The effects are frequently controlled by weathering of microplastics, development of plastisphere biofilms and adsorption of hazardous contaminants on microplastics surfaces. Adapted from Rummel et al. (2017)

its density. We can see, low molecular weight microplastics, for example, PE and PP, tend to float in the water, while high molecular weight microplastics will in general sink.

The presence of these perilous plastic particles in the environment (earthly and oceanic) is mainly caused by different human activities, which incorporate homegrown, modern manufacturing and seaboard exercises. Alongside maritime activities, the introduction of a large portion of microplastics in the marine environment is foremost because of the homegrown spill over which contain microbeads and microplastics particles (inside personal care and cosmetics) and furthermore from the fracture of the huge plastic wastes. Likewise, the seaside and beachfront exercises which incorporate fishing, water tourism and other aquatic industries are the origin of microplastics contamination in the aquatic environment nonpolar and lipophilic. (Sharma and Chatterjee 2017). Thus, microplastics can enter oceanic conditions through various complex pathways (Fig. 2.2). Recent studies show that the drifting air microplastics got from earthbound regions can be considered as a nonnegligible source of microplastics contamination in ocean (Huang et al. 2021a).

The microplastics abundance in the five oceans has been explored and summed up. Besides, subtleties of the sampling strategies embraced as well as the amount and sorts of microplastics analysed have been outfitted in Table 2.1 and visualized in Fig. 2.3.

When contributed to the oceanic conditions, microplastics can get dispersed in various waterbodies (e.g. surface water, water column and bottom sediment) due to the polymer properties (e.g. molecular weight, particle shapes, etc.), biofilm development on surface and circumstances of the flow of the waterbody. This occurrence

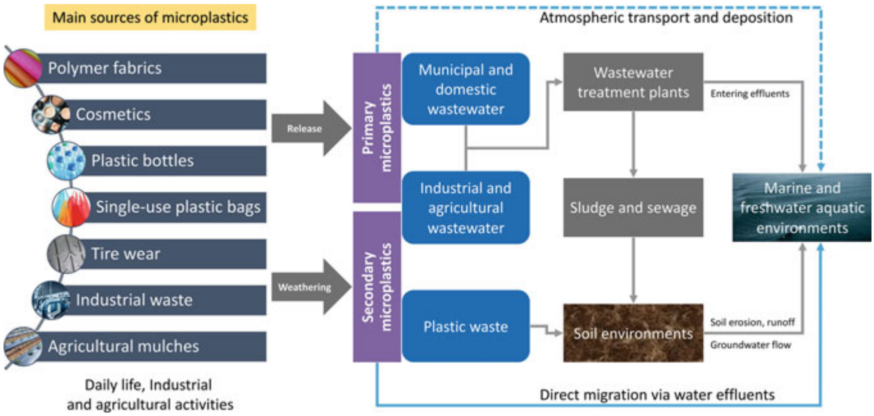

Fig. 2.2 Fundamental sources of plastic contaminations and migration of microplastics into the oceanic ecosystem. Marine environment is a significant sink for microplastics. Adapted from Huang et al. (2021b)

ultimately ends up influencing the availability of microplastics and toxicity to aquatic biota (Huang et al. 2021a).

2.3 Microplastics-Associated Contaminants

Microplastics tend to coexist with other environmental contaminants. They are suspected to act as vectors of these contaminants from the soil and water to the terrestrial and aquatic organisms. This hypothesis is based on strong sorption of organic pollutants to microplastics, resulting their enrichment in microplastics. The interaction between contaminants and microplastics can be categorized into two groups. One group is the plastic additives that are already present in the microplastics to enhance their desired property. The second group is the chemicals adsorbed from the surrounding media (Arienzo et al. 2021; Kwon et al. 2017).

Persistent organic pollutants (POPs) are a group of ubiquitous chemical compounds fit for lasting long in the ecosystem, travelling through the air, water, soil and sediment and accumulating at levels that can hurt flora and fauna. These contaminants might be generated from natural disaster or human activities and have typical physical and chemical properties making them environmentally persistent and impervious to photolytic, chemical and biodegradation (Tarafdar and Sinha 2017; Tarafdar et al. 2018a, 2019, 2020). Owing to the hydrophobicity of POPs, they strongly sorb on particulates including natural organic matter and microplastics. Some of POPs are added as plastic additives (Wagner and Schlummer 2020). For example, several polybrominated compounds used as flame retardants and photostabilizers (UV-328; 2-(2H-benzotriazol-2-yl)-4,6-bis(2-methyl-2-butanyl)phenol) are

Table 2.1 Microplastics abundance in oceans worldwide

Ocean	Study location	Sampling method	Detection method	Dominant polymer types	Dominant form	Dominant size	References
Pacific Ocean	Tropical Eastern Pacific and Galápagos	Plankton nets (500 μm pore size)	Light microscope, visual detection	Undetected	Fibres	150–500 μm	Alfaro-Núñez et al. (2021)
	Mid-west Pacific Ocean	Manta trawl (333 μm mesh)	dissecting microscope and μ-Raman spectroscopy	PP (39.1%), PMMA (16.2%), PET (14.2%) and PE (14.1%)	Fibre/filament (57.4%), fragment (18.3%) and film (17.6%)	1–2.5 mm (35.1%), 0.5–1 mm (28.5%)	Wang et al. (2020b)
	Western Pacific Ocean	Sediment sampling	Optical microscope and μ -FTIR	Poly(propylene-ethylene) copolymer (40.0%) and PET (27.5%)	Fibrous (52.5%)	100–500 μm (77.5%)	Zhang et al. (2020)
	Eastern North Pacific Ocean	Neuston net trawls (500 μm)	Visible identification	PE (69%) and PP (23%)	Particles	0.05–0.15 cm	Egger et al. (2020)
	West Pacific Ocean and the East Indian Ocean	Plankton pump (60 μm screen)	Visual counting in stereomicroscope and μ-FTIR	PET, PTFE, PMMA, PP and PVC (72% of total microplastics)	Fragments (61%) and fibres (25%)	30.12–6330 μm	Li et al. (2020)
	Mid-North Pacific Ocean	Manta trawl (330 μm mesh)	Light microscope and micro-Raman spectroscopy	PES, PS, PET, PE, PP, PC and PE (18–100% of total microplastics)	Films (18%), fibres (18%), lines (16%) and pellets (9%)	1–2.5 mm (38%)	Pan et al. (2022)

(continued)

Table 2.1 (continued)

Ocean	Study location	Sampling method	Detection method	Dominant polymer types	Dominant form	Dominant size	References
	South China Sea and the western Pacific Ocean	Centrifugal Teflon pump (44 µm mesh)	Optical microscope and µ -FTIR	PES (23.9%) and rayon (21.9%)	Granules (69.8%)	< 1000 µm	Cui et al. (2022)
	Northwestern Pacific Ocean	manta trawl (330 µm mesh)	Light microscope and Raman microscope	PE (58%), PP (36%)	Granules (39.7%), sheets (26.7%), films (24.7%)	0.5–1.0 mm (50%)	Pan et al. (2019)
Atlantic Ocean	North Atlantic Ocean	propeller gearbox-driven band of silk (270-µm mesh)	Stereo and FTIR spectroscopy	Microplastics paint flakes	Flake	180 µm	Turner et al. (2022)
	Surface layer of the Atlantic Ocean	Pump system and Manta net (500 µm mesh)	Stereoscopic Binocular microscope and FTIR	PP, PA, PVC, alkyd	Fragments (56%) and fibres (36%)	< 2.5 mm (70%)	Silvestrova and Stepanova (2021)
	Tropical Atlantic Ocean, Nigeria	Sediment sampling (3 mm and 1 mm sieves)	Stereo microscopy and FTIR spectroscopy	PE, PP, PS	Hard fragments and foam fragments	1–5 mm	Fred-Ahmadu et al. (2020)
	Latitudinal gradient in the Atlantic Ocean	Pump system (250 µm mesh)	FTIR spectroscopy	Polyesters (49%) and blends of polyamide or acrylic/polyester (43%)	Fibres (94%)	Not mentioned	Kanhai et al. (2017)

(continued)

Table 2.1 (continued)

Ocean	Study location	Sampling method	Detection method	Dominant polymer types	Dominant form	Dominant size	References
	Deep subtropical Northeast Atlantic	Sediment traps	Raman microscopy	PE, PVC, PS, PP	Particles	< 100 µm	Reineccius and Waniek (2022)
	Eastern North Atlantic Subtropical Gyre, Canary Islands, Spain	Water columns up to 1150 m depth	Stereomicroscope	Not mentioned	Fibres in winter, fragments in fall	> 500 µm	Vega-Moreno et al. (2021)
	Macaronesian region, NE Atlantic	manta net (200 µm mesh)	Visual inspection under a binocular stereomicroscope	Not mentioned	Fragments (47.5–57.3%), fibres (27.4–30%)	0.2–1 mm (50.6%)	Herrera et al. (2020)
Indian Ocean	Tropical Indian Ocean	Microplastics Fractionator, submersed pump (2 sets, $d > 300$ µm and 10 µm $\leq d \leq 300$ µm)	Visual inspection, ATR-FTIR spectroscopy	Acrylates/PU/varnish (49%), PET (26%)	Particles & fibres	20–50 µm (75%)	Hildebrandt et al. (2022)
	Eastern Indian Ocean	Sediment sampling (330 µm mesh)	µ-FTIR	Rayon (62.2%) and polyester (25.7%)	Fragments (47.5%) and fibres (45.6%)	200–500 µm (41.7%)	Qi et al. (2022)
	Eastern Indian Ocean	Manta trawl (330 µm mesh)	Stereo microscopy and µ-FTIR spectroscopy	PP (51.11%) and PE (20.07%)	Particles (68.36%)	< 2 mm comprises more than 70%	Li et al. (2021)

(continued)

Table 2.1 (continued)

Ocean	Study location	Sampling method	Detection method	Dominant polymer types	Dominant form	Dominant size	References
	Maldives, Indian Ocean	Sediment sample from coral reef	Stereo Zoom Microscope	Undetected	Filamentous (49%) and fragmented (51%)	< 0.4 mm	Patti et al. (2020)
	Western Indian Ocean	Sediment sampling at intertidal zone	Stereo dissecting microscope	Undetected	Fibres (90%)	(500–4999 µm)	Kerubo et al. (2021)
Antarctic Ocean	Southern Ocean	Neuston Net (200 µm mesh)	µFTIR	PE (61%), PP (29%)	Particles	0.68–21.5 mm	Suaria et al. (2020)
	Ross Sea, Dumont d'Urville Sea, Davis Sea and Prydz Bay	Surface trawl and rotor pump (330-µm mesh)	Dissecting microscope and µFTIR	Surface: PET (87.3%) Subsurface: PP (33.1%), PET (28.7%), PE (22.8%)	Line/fibre (Surface: 98.9% and subsurface: 46.3%)	Surface: 2.0–2.5 mm (16.0%) Subsurface: 0.5–1.0 mm (26.5%)	Zhang et al. (2022a)
	Casey station, east Antarctic Sea	Sea ice core sampling	µFTIR	PE (34%), PP (15%), PA (14%), varnish (11%)	Particles	$\leq$ 100 µm (90%)	Kelly et al. 2020)
	Southern Ocean	Neuston net (0.35 mm)	Stereoscopic microscope and µFTIR	Polyethylene, polypropylene (65.9%)	Fragments	Not mentioned	Isobe et al. (2017)
Arctic Ocean	Arctic Ocean basin	Neuston Net (330 µm mesh)	Visual inspection, FTIR spectroscopy	PE (52.6%), PP (36.8%)	Fragments (82%)	0.333–5 mm	Zhdanov et al. (2022)

(continued)

Table 2.1 (continued)

Ocean	Study location	Sampling method	Detection method	Dominant polymer types	Dominant form	Dominant size	References
	Near-surface waters from East Asian Seas to Arctic Central Basin	Water pump (0.3-mm stainless-steel mesh)	Stereoscopic microscope and µFTIR	PET (71.3%)	Fibres (83.8%)	< 2 mm (81.9%)	Huang et al. (2022)
	Eurasian Arctic—including Kara, Laptev and East-Siberian Seas	Neuston net (200 µm)	Dissecting microscope and FTIR	PE (36.6%), PU (17.1%), PVC (14.6%), polyester (14.6%)	Fibres Fragments and films	2.5 ± 1.5 mm	Yakushev et al. (2021)
	Svalbard, Arctic	Surface sediments	Stereozoom microscope and ATR-FTIR	Polyethylene (36.79%–48.45%), polypropylene (27.32%–27.36%)	Fibres (91.59% -97.10%)	0.3–1 mm (26.67%–55.50%)	Choudhary et al. (2022)
	Arctic Central Basin	Deep sediments sampling using piston corer	FTIR spectroscopy	Polyester, polystyrene	Particles and fibres	< 5 mm	Kanhai et al. (2019)

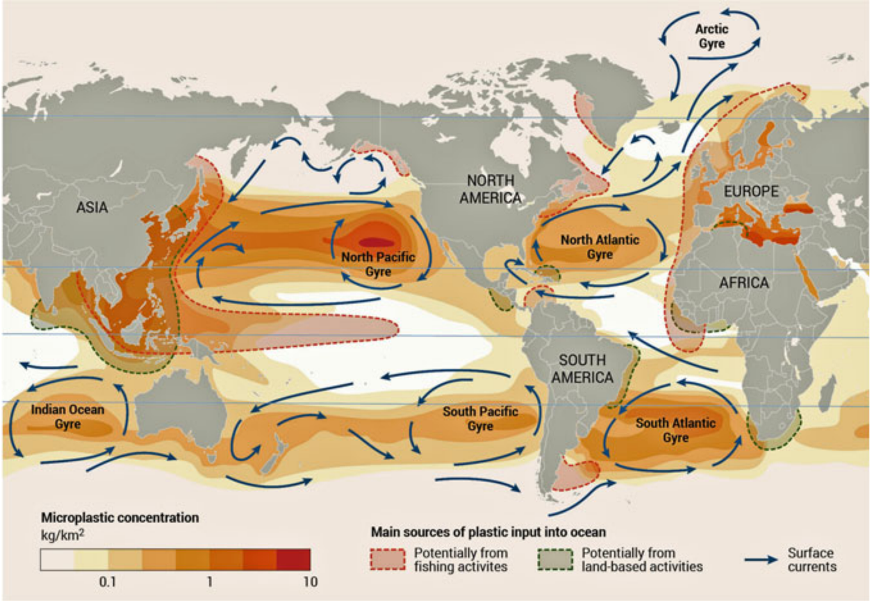

Fig. 2.3 Global marine concentration of microplastics (Cartography by Riccardo Pravettoni and Philippe Rekacewicz 2019)

listed or under review in the Stockholm Convention on POPs (http://www.pops.int/). Leaching of plastic additives and related environmental consequences are further discussed in the following chapter.

Hydrophobic domain of synthetic polymers is a good reservoir for POPs from environmental matrices. Polyethylene and other synthetic polymers have long been used as passive sampling materials for POPs and other hydrophobic organic chemicals (Wania and Shunthirasingham 2020; Adams et al. 2007). Many studies have been conducted in the last decade and proved that microplastics of many different origins have strong sorptive capacities for those environmental contaminants. In addition, polymer characteristics, such as glass transition temperature, degree of cross-linking and crystallinity, are important in explaining sorption processes. Rubbery polymers like polyethylene and polypropylene tend to have greater distribution constant between microplastics (MPs) and water (K_{pw}) than glassy polymers like PET and PVC (Rochman et al. 2013). Crystalline regions of polymers are densely packed and the free space between chains are lower than the amorphous regions. Amorphous plastic has more prominent free volume because of interspace among polymeric chains which permits chemicals to diffuse on the polymer. In addition to polymer properties, environmental conditions also affect the equilibrium distribution and desorption kinetics. For example, lower pH and elevated temperature in the digestive systems may increase the desorption rates (Bakir et al. 2014) and elevated salinity can increase K_{pw} via salting-out effects (Velzeboer et al. 2014).

However, the strong sorption capacity of MPs towards POPs does not necessarily mean that intake of MPs sorbing POPs meaningfully increase the rate of POPs intake by organisms. POPs are already widespread and found in diverse environmental media. The driving force of passive chemical transfer is difference in fugacity (Kwon et al. 2017). Although the concentration of POPs in MPs could be higher than water and soils, it is usual that fugacity of POPs in MPs is lower than those in water, soil and sediment. Due to this reason, MPs are mostly acting as sinks for POPs (Reineccius and Waniek 2022; Burns and Boxall 2018; Lohmann 2017; Lee et al. 2017; Koelmans et al. 2016). In addition, MP ingestion does not meaningfully increase chemical uptake flux because abundance of MPs is still much lower than other important sorbing phases such as dissolved and suspended organic matter both in modelling (Lee et al. 2019; Bang et al. 2021; Gouin et al. 2011) and in vitro or in vivo studies (Norland et al. 2021; Mohamed Nor and Koelmans 2019). Although several laboratory studies showed that microplastic bound ingestion of POPs affects their bioaccumulation and related toxic effects (PAHs (Sharma et al. 2020; Sørensen et al. 2020; Chen et al. 2020; Sun et al. 2021); PCBs (Wu et al. 2021; Rios-Fuster et al. 2021; Fred-Ahmadu et al. 2022); DDTs (Fred-Ahmadu et al. 2022; Santana-Viera et al. 2021; Herrera et al. 2022); BPA (Han et al. 2022; Tang et al. 2022; López-Vázquez et al. 2022); PBDEs (Turner 2022; Sun and Zeng 2022; Palacio-Cortés et al. 2022), etc.), they were conducted at highly elevated levels of POPs in MPs, but no studies showed observable effects at ecological relevant exposure conditions and evidence is weak to support the roles of MPs to meaningfully enhance bioaccumulation of POPs (Ziccardi et al. 2016).

2.4 Leaching of Plastic Additives

Properties of plastics are enhanced by adding various plastic additives (Fig. 2.4) (Hahladakis et al. 2018). Most plastic additives are not covalently bound to plastic polymers, which as a consequence, allows them to be released into the environment (Chen et al. 2021). The formation of oxidation products and fragmentation by weathering processes may accelerate the leaching of plastic additives (Khaled et al. 2018). The interaction between MPs and environmental contaminants can be influenced by the generated oxygen-containing groups (carboxylic, carbonyl, ketone and hydroxyl groups) which increase the hydrophilicity and charges on the surface of the MPs (Changfu et al. 2022; Shih et al. 2021). This has been a concern as additives (such as brominated flame retardants, phthalates and UV stabilizers) released from weathering processes of MPs can cause adverse effects including disruption of metabolism pathways, hindrance in signalling of neurotransmitter, adverse effect on reproduction, immunosuppression, hepato- and neurotoxicity in various aquatic organisms (Liu et al. 2020). Several studies have been conducted on the leaching of plastic additives from microplastics in environment (plasticizers (Cao et al. 2022; Deng et al. 2021); antioxidants (Wang et al. 2021; Nurlatifah and Nakata 2021); UV stabilizers (Ngoc Do et al. 2022a; Rani et al. 2015)); flame retardants (Camacho et al.

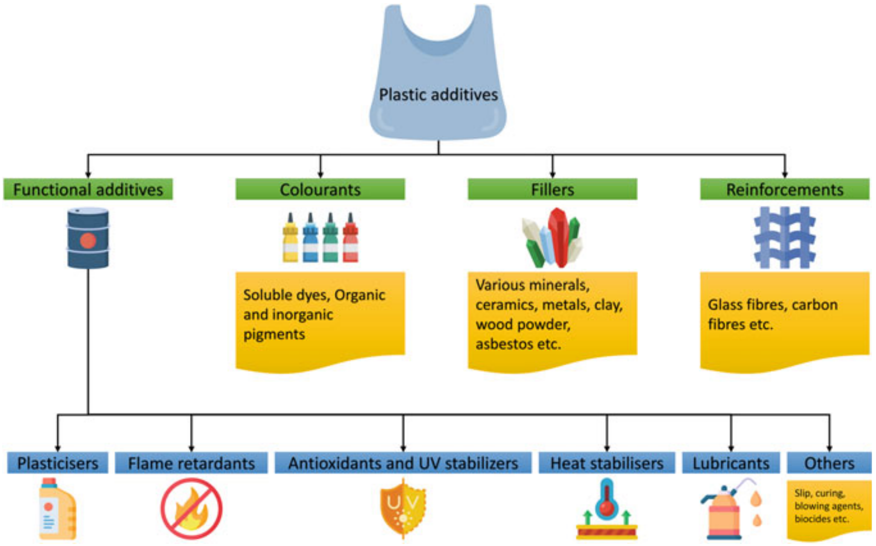

Fig. 2.4 An outline of chemical additives present in commercial plastics

2019; Sun et al. 2019), etc.). Antimicrobial agents are also added to polymer materials to prevent microbial settlement on the surface of plastic and these substances can promote microbial resistance which makes it another emerging contaminant (Meyer and Cookson 2010).

The most common plastic additives found in the environment include plasticizers, photostabilizers, antioxidants, dyes and pigments and flame retardants (Table 2.2).

2.4.1 Plasticizers

Plasticizers are small organic molecules used as additives to create more semi-rigid or flexible plastic products. Almost 90% of all plasticizers produced worldwide are used in the production of poly(vinyl chloride) (PVC) (Jamarani et al. 2018). Phthalic acid esters are a family of plasticizers mainly used in PVC production, and they include benzyl butyl phthalate (BBP), di-*n*-butyl phthalate (DBP), di(2-ethylexyl) phthalate (DEHP), di-*n*-octyl phthalate (DNOP) and diethyl phthalate (DEP).

The widespread release of phthalates during the manufacture, use and disposal of PVC products, as well as their use as additives in various other open-ended applications, has led to their ubiquitous distribution and abundance in the global environment. Humans can be exposed not only to background pollution in air, food and water but also through direct contact with soft PVC products, particularly those intended as high-contact products such as children's toys and toothpaste (Kim et al. 2020).

Table 2.2 Overview of major groups of plastic additives

Types of additives	Purpose	Substances	Health effects	References
Plasticizers	Used to the chemical and physical properties of the material and can take up 10–70% of the material weight. Widely used for the production of flexible poly(vinyl chloride) (PVC) which is a material that comprises around 80% of the global use of plasticizers	Phthalates, terephthalates, epoxies, aliphatics, trimellitates and citrates	Endocrine disruptors, asthma inducer and carcinogens	Wright et al. (2020a)
Antioxidants	Delay oxidation and prevent ageing of plastics. It preserves the structure of the plastic and provides thermal stability	Bisphenol A, Octylphenol, Nonylphenol, Irganox®	Endocrine disruptors, Mimics estrogen	Hermabessiere et al. (2017)

(continued)

Table 2.2 (continued)

Types of additives	Purpose	Substances	Health effects	References
UV stabilizers	Added to plastics for the prevention photochemical destruction processes induced by UV radiation (within the range of 300–400 nm). It increases the stability of polymers	UV320 2-(2H-benzotriazol-2-yl)-4,6-bis(2-methyl-2-propanyl)phenol, UV326 2-(5-chlor-2H-benzotriazol-2-yl)-4-methyl-6-(2-methyl-2-propanyl)phenol, UV327 2,4-di-tert-butyl-6-(5-chlorobenzotriazol-2-yl)phenol	Endocrine-disrupting effects, reproductive toxicity and genotoxicity	Hong et al. (2018), Tang et al. (2018)
Flame retardants	Used as an additive in combustible products in order to decrease their combustibility and increase their resistance to fire	Brominated flame retardants, Chlorinated flame retardants, Organophosphorus flame retardants	Endocrine and thyroid disrupting effects, reduced fertility and reduced IQ in children	Babrauskas et al. (2014)

Recent studies have connected phthalates to brain developmental issues like cognitive behaviour and poor IQ (Loftus et al. 2021), alteration in thyroid level (Yang et al. 2022), breast cancer (Zuccarello et al. 2018), obesity and type II diabetes (Zhang et al. 2022b), coronary heart disease, blood pressure problems (Yao et al. 2020), respiratory problems like allergic symptoms and asthma (Zhu et al. 2022; Babadi et al. 2022), acute liver toxicity (Cai et al. 2021; Yu et al. 2021), reproduction problems like pregnancy complications (Stevens et al. 2022; Fruh et al. 2022), sperm damage and testosterone imbalance (https://www.theguardian.com/lifeandstyle/2015/feb/10/phthalates-plastics-chemicals-research-analysis; Pacyga et al. 2021). Therefore, there are concerns about phthalates due to their potential toxicity, exposure scenario and their ability to leach out of plastic products. A study by Cao et al. (2022) revealed that microplastics can release up to 16 tonnes of phthalate esters into marine environments annually. As per this report, di-*n*-butyl phthalate (DBP) leached out of PA, PP and PET is the highest contributor, closely followed by diethyl phthalate (DEP) from PVC and rubbery microplastics. Among all plastic types, PVC microplastics were the highest releasers of phthalate esters, followed by PA and rubbery microplastics particles.

2.4.2 Antioxidants

Antioxidants are used as additives in many synthetic polymers, including polyolefins (such as PE and PP), which account for 60% of global demand for these additives (Hermabessiere et al. 2017). They are substances which include both natural and chemical compounds that scavenge free radicals and inhibit the oxidation process. Extreme temperatures are used to manufacture plastic products. It consists of raw polymers that are exposed to thermal oxidation. To maintain the stability of the polymer during this process, antioxidants must be introduced. They also function to prevent plastics from ageing and delay oxidation. They can leach from plastic and migrate from plastic packaging into food and pose a food safety hazard (Hermabessiere et al. 2017). Butylated hydroxytoluene (BHT) is among the most used antioxidants in plastics (Wang et al. 2021). BHT is harmful for higher trophic organisms like fish, and with respect to the green algae, its poisonous potential is even higher (Wang et al. 2019).

2.4.3 UV Stabilizers

Plastics tend to undergo photooxidation under harsh conditions (sunlight for long duration) in the presence of oxygen. Too much exposure to UV light can lead to discoloration, changes of mechanical and physical properties and even cause cracks in plastic products. Therefore, it is important to prevent this by adding certain plastic additives during the manufacturing process. This will help the product last longer as it ensures that the material can withstand harsh UV exposure and inhibit photodegradation processes (El-Hiti et al. 2022). Ultraviolet (UV) light stabilizers are widely used as an additive in plastic materials for outdoor applications.

Benzophenone and benzotriazole UV stabilizers (BUVs) are a type of plastic additives used in acrylonitrile butadiene styrene, polypropylene and polyethylene products (Rani et al. 2015). BUVs tend to persist in the environment, and they are toxic, bioaccumulative, endocrine disrupting and mutagenic (Ngoc Do et al. 2022b). Benzotriazole UV stabilizers like UV-234 and UV-320 have been reported to affect mitochondrial bioenergetics along with the expression of transcripts associated with oxidative stress in the embryos of zebrafish (Liang et al. 2019). UV-P, UV-PS, UV-090, UV-329, UV-320 and UV-328 have been reported to exhibit partial estrogenic activity prompting the endocrine disruption effects via human estrogen and androgen receptors (Feng et al. 2020; Sakuragi et al. 2021; Kubota et al. 2022). Some UV stabilizers such as UV-320, UV-350 are prohibited from import, production and usage in certain countries due to their toxicity in livers and other tissues in laboratory animals (European Commission 2013).

2.4.4 Flame Retardants

Although plastics are widely used, they have inherent flammability properties which come from their chemical composition and structure. This may limit their application in various industrial areas. After all, plastics are carbon-based materials that consist of chains of carbons. As a result, plastics pyrolyze/decompose and carbon bonds are broken when exposed to high heat (250–450 °C). Volatile gases are then released as a result, mixing with the air to create an ignitable mixture. When heated to a high temperature, the mixture either self-ignites or ignites with the aid of a spark, flame, etc. The pyrolysis process is sustained by the substance's constant exposure to the flame's heat flux until the material burns out and the flame goes out. Toxic gases are released into the environment as a result of the combustion process which is harmful to the environment and organisms living in it (Mensah et al. 2022).

Flame retardants are a type of additive used in plastic products to reduce the flammability of the product. They are widely used in a variety of consumer products, from electronic devices to insulating foams. When an ignition source is present, flame retardants become active and work in a variety of physical and chemical ways to stop or delay the spread of ignition. They can be included into the polymer during the polymerization process as a copolymer, or later on during the moulding or extrusion process, or (especially for textiles) as a topical finish. Brominated flame retardants, chlorinated flame retardants and organophosphorus flame retardants are widely used in the plastics industry.

2.5 Plastisphere: Microbe-Microplastic Interactions

The term “plastisphere” was coined by Zettler et al. (2013) to describe a specific microorganismic community which is associated with plastic surface and is mostly differentiable from its surrounding microbial ecosystem. Comparable with other biofilms, the plastisphere usually includes attachment of microbes, discharge of extracellular polymeric substances (EPS) and proliferation of microbes. After a microplastic particle is discharged into ocean (or freshwater), microorganisms promptly (in a timespan of few minutes to hours) colonize the marine plastic trash, and the individuals from these biofilm networks can incorporate pathogens, toxic and plastic biodegrading microbial communities (Oberbeckmann et al. 2016). Though microplastics can be conquered by primary invaders in a short time, it can take up to months to develop a stable biofilm (Fig. 2.5a). In the first place, colonizer microbes possess the plastic surface by reversible attachment, framing the principal layer of the primary biofilm. With the settlement of these microbes, the surface hydrophobicity of the microplastics diminishes over the long run (Tu et al. 2020). Additionally, the exopolysaccharides secreted by these primary colonizers can elevate the adhesivity of the surface of microplastics, which eventually helps to attach more microbes on the surface (Ganesh Kumar et al. 2020). Consequently, a secondary enduring microbial formation gets developed onto the primary microbial layer by the use of pili/fimbriae, adhesion proteins and secreting EPS, making more adherence regions on the microplastics surface (Dussud et al. 2018a). In the marine ecosystem, a temporal succession of microbial communities takes place. Early colonizers of microplastic surfaces are reported to be dominated by *Gammaproteobacteria* (genera *Aeromonas*, *Pseudomonas*, *Marinobacter*, *Thalassolituus*, *Acinetobacter, Alteromonas,* etc.) and *Alphaproteobacteria* (genera *Loktanella, Methylobacterium, Rhodobacter, Pelagibacter,* etc.), with a rising pattern in Bacteroidetes as secondary colonizers over the time (Stabnikova et al. 2021a; Quero and Luna, 2017; Sooriyakumar et al. 2022). Studies of aquatic biofilms showed that *Gammaproteobacteria* are usually among the early colonizers of any kind of inert surfaces (Lawes et al. 2016; Tender et al. 2017). As copiotrophs, *Gammaproteobacteria* might have the option to rapidly counter the elevated accessibility of the organic substances, for example, proteins and polysaccharides that adsorb to drenched MP surfaces (Kesy et al. 2019).

Abundance of Bacillariophyceae (especially pennate diatoms) and Cyanobacteria were repeatedly reported on the early days of biofilm formation (Schlundt et al. 2020). This abundance of photosynthetic cells is reported to decrease while the biofilm enters its maturation phase (Zhao et al. 2021a). The trend for the quantity of Bacteroidetes (particularly *Flavobacteriaceae*) to get high with time is mainly because of their wide circulation, adaptability and capacity to use the EPS by primary invaders. Subsequently, these Bacteroidetes are followed by *Planctomycetes* and *Firmicutes* (Zhang et al. 2022c). The primary formation of biofilm generally requires several weeks, while secondary biofilm requires months to take shape (Wright et al. 2020b). As for the difference in plastisphere biofilms components from that of other biofilms that

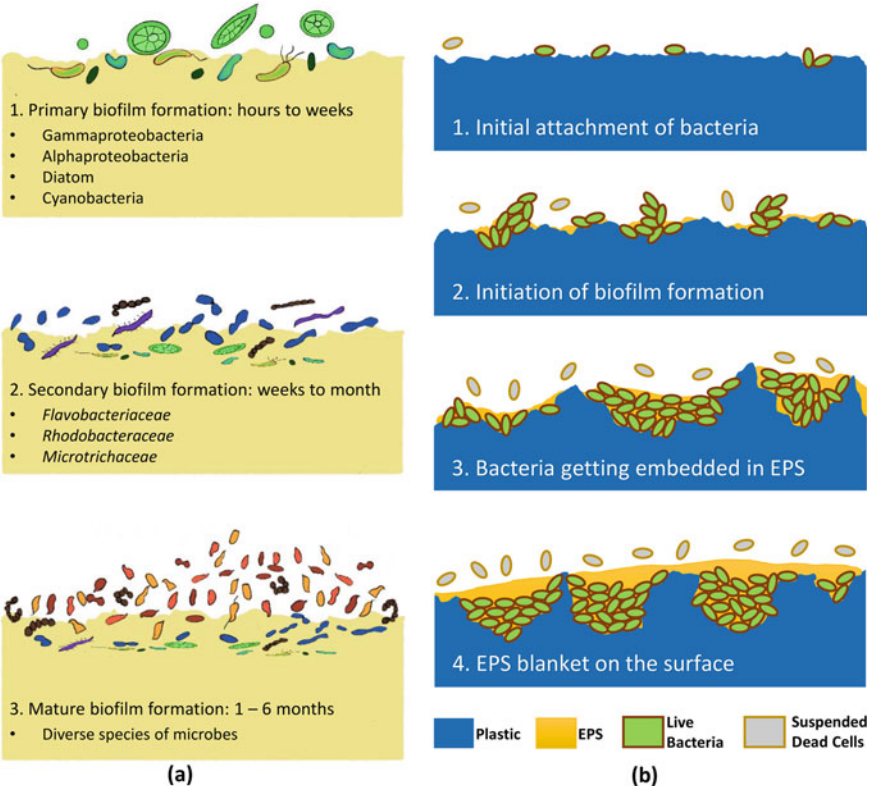

Fig. 2.5 **a** Steps for plastisphere formation on microplastics surface, **b** developmental stages of plastic-degrading primary biofilm on microplastics surface (Tarafdar et al. 2021)

develop over natural particles, Zhao et al. (2021b) reported lower volume proportions of photosynthetic cells on plastic surfaces over glass substrate after 8 weeks of in-situ study. Shen et al. (2021) found smaller diversities of species in plastisphere compared to the biofilms on wood and cobblestones. Pathogens, along with plastic-degrading bacteria, were found to be more abundant on plastic surfaces rather than natural substances (Stabnikova et al. 2021b; Song et al. 2022).

To observe the primary adherence of plastic-degrading microbes onto microplastics surface and evolution of the biofilm, a step-by-step 3D morphological study (Fig. 2.5b) was conducted by Tarafdar et al. (2021). Primarily, attachment of bacterial cells elevated the roughness of the surface of microplastics while forming biofilm. This observation is similar to some earlier studies on biofilm development on non-plastic material surfaces (Chatterjee et al. 2014; Tarafdar et al. 2018b). A slight decrement in surface roughness was observed during the course of time, probably because of the metabolic discharges, (i.e. microorganisms got "embedded in EPS") (Rummel et al. 2017). Eventually, the deposited EPS forms a blanket on the surface, submerging microbes inside it, hence creating visual obstructions for distinct microbial bodies. As hydrophobic metabolic discharges (EPS) from biofilm tend to settle down onto the surface, this growth model can be common for most of the plastisphere.

The transport of environmental contaminants between MPs and water can be affected by biofilms due to its sorptive properties. Whether the kinetic and thermodynamic processes are influenced by biofilm formation which is still being studied. This is in question as biofilms provide a superficial organic phase consisting of water, lipids and proteins as a barrier for diffusive uptake and also a potential sorptive phase (Rummel et al. 2017). Extracellular polymeric substances (EPS) provide a rich biological matrix containing various proteins, polysaccharides, lipids and other biopolymers that contribute to the sorptive capacity of MP surfaces coated with biofilms. The release of additives from microplastics is suspected to even promote microbial growth by acting as a nutrient source (Wang et al. 2022). Various types of bacteria and fungi are capable of degrading various environmental contaminants, which is why they can be used for bioremediation and in engineered bioreactors. Therefore, biofilms are highly relevant in the removal of plastic-associated chemicals due to their metabolization, and this can affect the bioavailability of consumers who can ingest the microplastics.

The sorption of environmental contaminants may accelerate the release of chemicals due to the higher surface-to-volume ratios of weathered microplastics. Weathered microplastics provide a favourable environment for biofilms due to their corroded and elevated surface area. When biofilm forms on the surface of microplastics, it can influence the uptake and release of contaminants into and from the EPS. Studying the active microbial interface needs to be considered in order to have a realistic estimate on how much contaminants in the environment organisms are actually being exposed to Rummel et al. (2017).

2.6 Abundance of Potential Pathogenic Bacteria and Antibiotic Resistance Genes

Recent reports show that the pathogens can populate and grow biofilms on oceanic microplastic debris (Kaur et al. 2022). *Vibrio* spp. is a notable variety of microorganisms containing pathogenic strains to people (cholera-causing bacteria). Plastic particles can perform as a support for cradle and proliferation of non-native microbial species into new environments (Audrézet et al. 2021). The special concern is recent rise in academic reports about pathogenic microbial content of plastisphere (Table 2.3). This, integrated with the significant spreading capability of floating microplastics, brings up the consequential issue, whether the rising measure of microplastics debris in worldwide marine systems is providing more noteworthy open doors to vibrios and various other pathogens to be shipped and circulated towards possible hosts, prompting expanded infectious outbreaks (Bowley et al. 2021). The contribution of microplastic contamination as a transporter for pathogenic microscopic organisms is considered in their impact on microbial community. It was observed that microplastics can specifically enrich pathogenic microbes along with antibiotic resistance genes (ARGs) (Shi et al. 2021; Parthasarathy et al. 2019), which can ease the foundation of plastics-related pathogenicity islands (PAIs). Considerable surge of ARGs like sul1, tetC, tetX and ermE on polyethylene microplastic particles in marine environment, along with appearance of new ARGs like sulA/folP-01 and tetA was found earlier (Wang et al. 2020c). Relative abundance of ARGs like sul1, erm(B), intI1 and intI2 were observed to be elevated on microplastic biofilms compared to the surrounding freshwater ecosystems (Wang et al. 2020d; Mughini-Gras et al. 2021). Arias-Andres et al. (2018) researched on the plasmid transfer and gene exchange in microplastics contaminated oceanic biological systems and concluded that biofilms on plastic surface can furnish unconventional hotspot areas for outspreading and proliferation of antibiotic resistance genes by horizontal gene transfer (HGT) in usual marine environments.

Development of biofilms on plastic surface in aqueous ecosystem is supervised by the quorum sensing (QS) genes expressed because of attaining a critical cell density and is likewise engaged with additional adhesion among cells, development and dispersal of biofilms. These QS additionally govern the virulence factors, for example, in *Vibrio harveyi*, production of type III excretion framework, a significant virulence factor is investigated to be managed by QS genes AphA and LuxR consecutively under lower and elevated cell densities (Lami 2019). Eventually, plastics might boost the affluence of pathogenic microscopic organisms and improve their endurance capacity, subsequently causing ecological and health hazards (Meng et al. 2021). Despite that substantial exploration on abundance of pathogens on microplastics, ARGs and HGT on microplastics are going on; there are some deficits of studies on the effects of microplastics-associated chemicals (adsorbed or leached out) on plastisphere biofilms, particularly, regarding determination and transfer of ARGs on plastic surfaces in marine ecosystem.

2.7 Conclusions

The current book chapter covers several aspects of marine microplastics pollution. Discussion started with the sources and latest data on oceanic microplastics abundance. Further, we tried to look into the microplastics-associated and adsorbed chemicals and their health effects. Toxicology of the leached-out plastic additives was also taken into concern. Recent opinions on the developmental stages of plastisphere biofilms were explored. We noticed special attention of researchers on microplastic-associated pathogenic microbes and abundance of antimicrobial-resistant genes on microplastic biofilms. Each of the study sectors needs extensive detailed research before attaining final conclusions. Succeeding studies should focus on,

Table 2.3 Pathogens found on microplastics in aqueous environment

Pathogens	Study location	Microbial characterization	Microplastic type	Microplastic detection	Citation
Vibrio parahaemolyticus	North and Baltic Sea	MALDI-TOF MS	PE, PP, PS	ATR FTIR	Kirstein et al. (2016)
Sphingorhabdus, Sphingomonas, Rhodobacter, Aquabacterium, Acidovorax	Lentic Italian ecosystem	16S rRNA gene high-throughput sequencing and FISH-CLSM	PE, PP	FTIR, SEM	Pippo et al. (2020)
Pseudomonas aeruginosa, Escherichia coli, Acinetobacter baumannii, Afipia broomeae, Acinetobacter lwoffii, Ochrobactrum anthropi	Shanghai, China	16S rRNA gene sequencing	PS	Spiked microplastics	Shi et al. (2021)
Raoultella ornithinolytica and Stenotrophomonas maltophilia	WWTP, northern New Jersey, USA	16S rRNA sequence reads using QIIME2 pipeline	PE and PS	Spiked microplastics	Pham et al. (2021)
Pseudomonas monteilii, Pseudomonas mendocina, Pseudomonas syringae	Haihe River, China	16S rRNA gene sequencing and Shotgun metagenomics	PVC	Spiked microplastics	Wu et al. (2019)
Aeromonas salmonicida	Slovenian coast of the North Adriatic Sea	16S RNA PCR amplification	PE, PP, PA	ATR FTIR microscopy	Viršek et al. (2017)
Vibrio splendidus, Pseudoalteromonas spp.	Bay of Brest, Brittany, France	16S amplicon high-throughput sequencing	PE, PP, PS	Raman spectroscopy	Frère et al. (2018)
Sphingobium, Aquabacterium, Flavobacterium	Coastal Bay, Stockholm, Sweden	Illumina sequencing of 16S rRNA gene libraries	PE, PS, PP	Spiked microplastics	Ogonowski et al. (2018)

(continued)

Table 2.3 (continued)

Pathogens	Study location	Microbial characterization	Microplastic type	Microplastic detection	Citation
Pseudomonas, Acinetobacter, Arcobacter	Dutch portion of Rhine, Netherlands	16S rRNA-sequencing and qPCR	PA, PVC	LDIR	Mughini-Gras et al. (2021)
E. coli and *Vibrio* spp.	Forth Estuary, Scotland	Selective media	Undetected	Undetected	Rodrigues et al. (2019)
Escherichia coli, Enterococcus faecalis, Acinetobacter baumannii	Süreyyabey, Turkey	MALDI-TOF	PET, PVC, PS, PE, PP	FTIR and Raman	Tavşanoğlu et al. (2020)
Pseudomonadaceae, Moraxellaceae, Bacillus sp.	Haihe Estuary, Bohai Bay, China	Amplicon sequencing of V4 variable region of 16S rRNA gene	PE, PP, PS, PET, PUR,	ATR-FTIR	Wu et al. (2020)
Arcobacter, Vibrio and Pseudomonas	Singapore coastline	High-throughput amplicon sequencing of V3-V4 (515F-806R) hypervariable region of 16S rRNA gene	EPS foam	Visual detection	Curren and Leong (2019)

(continued)

Table 2.3 (continued)

Pathogens	Study location	Microbial characterization	Microplastic type	Microplastic detection	Citation
Escherichia coli, *Vibrio cholerae*, *Vibrio vulnificus*, *Vibrio mimicus*, *Vibrio parahaemolyticus*	Guanabara Bay, Brazil	PCR, 16s rRNA	PE, PP, PET	ATR-FTIR	Silva et al. (2019)
V. anguillarum, *V. harveyi*, *V. pectenicida*, *V. xiamenensis*, *Tenacibaculum* sp., *Phormidium* sp., *Leptolyngbya* sp.	Western Mediterranean Sea	Next-generation sequencing of 16S rRNA genes	PE, PP, PS	FTIR	Dussud et al. (2018b)

1. The probable effects of integrated impacts and trophic transfer of plastic particles and related pollutants on marine creatures. Especially, the health risk analysis on transfer of microplastics, related pollutants through food chain and their involvement in wellbeing of human.
2. Sources of microplastics (primary or secondary) based on human exercises and linking them to abundant oceanic microplastics—a cradle-to-grave fate analysis of plastics.
3. Investigate the effects of nano/microplastics and related pollutants on human health based on environmentally sound uptake level. A microbial risk assessment on plastic-associated pathogens and ARGs is also necessary.
4. Bioaccumulation and biomagnification effects of microplastics should be taken into account for further research. Special concern should be given to biomagnification effects of microplastics-associated chemicals from marine organism to higher trophic level creatures (i.e. humans).
5. Toxicity study and environmental effects of degradation byproducts of plastic additives and leached-out chemicals should be conducted.

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Chapter 3
World Profile of Foreseeable Strategies for the Removal of Per- and Polyfluoroalkyl Substances (PFASs) from Water

Bin Ji and Yaqian Zhao

Abstract Per- and polyfluoroalkyl substances (PFASs) have been used in wide range of industries and daily life and therefore released into the aqueous environment. Due to their unique properties, such as environmental persistence, bioaccumulation, and toxicity, PFASs have drawn increasing concern in recent years. PFASs-contaminated water has adverse effects on water microorganisms and aquatic life as well as human life. So far, tremendous efforts have been made on PFASs pollution and their treatment, yet most of the efforts have been spent on laboratory experiments. Their feasibility, cost-effectiveness, and field applicability are questionable. This review examined studies on existing while updated treatment technologies, with the goal of providing an outlook on these technologies and more importantly, proposing the most likely technique. As such, a constructed wetland-microbial fuel cell (CW-MFC) technology was recommended, which is a newly emerged technology by integrating physical, chemical, and enhanced biological processes plus the wetland plants' functions with strong eco-friendly features for the comprehensive removal of PFASs. The roles of wetland plants, substrates, and electroactive bacteria (EAB) in the removal of PFASs in the CW-MFC system were discussed with focus on highlighting the different mechanisms. It is expected that the review can strengthen our understanding of PFASs' research and thus can help select reasonable technical means of aqueous PFASs control.

Keywords Per- and polyfluoroalkyl substances · Water treatment · Degradation technologies · Construct wetlands · Microbial fuel cell

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3.1 Introduction

Per- and polyfluoroalkyl substances (PFASs) are a group of synthetic chemicals comprising more than 9000 chemicals (Cordner et al. 2021). Due to their unique hydrophobic/lipophobic physicochemical properties, they have a wide range of industrial and consumer applications such as packaging materials, waterproof material, electronics, polishes, and aqueous film-forming foams (AFFFs) (Naidu et al. 2020). PFASs have been developed for more than seven decades with the different types of fluoropolymers over 230,000 tons/year worldwide for the moment (Zhang et al. 2022). PFASs are released into the environment as a result of their widespread manufacture and application both purposefully and unintentionally. Due to persistent (P), bioaccumulative (B), and toxic (T) properties, as well as long-range transport potential (LRTP), PFASs have been detected in different environments (such as water, soil, and aerosols), which have caused great concern among the scientific community and the public. Previous studies have reported that PFASs have been linked to a slew of negative health effects in both animal and human (Naidu et al. 2020; Silva et al. 2021; Teymourian et al. 2021). Therefore, when PFASs enter the environment, they are labeled as "contaminants of emergent concerns (CECs)."

Water environment is regarded as a significant sink and source for PFASs. Many researchers have conducted a series of studies on the content level, distribution characteristics, influencing factors, and environmental behavior of PFASs in aqueous environment in recent years (Macorps et al. 2022; Pistocchi and Loos 2009; Szabo et al. 2018). In order to control and reduce the environmental risk of PFASs, some remediation technologies and methods have been tested, such as coagulation, adsorption, membrane separation, photodegradation, and hydrothermal as well as microbial degradation (Hao et al. 2022; Oyetade et al. 2018; Zhuo et al. 2020). It should be noted that these approaches have both advantages and disadvantages in foreseeable applications. When it comes to controlling or removing PFASs from water, integrated technologies are thought to be more effective than solo techniques.

Constructed wetlands (CWs) are widely applied across the world due to their cost-effectiveness and satisfactory treatment effects. CWs use plants, substrates (soil, sand, and gravel), microbial and interaction processes to remove contaminants in wastewater with minimal dependence on mechanical elements. So far, CW system has been proven effectively to removal CECs and persistent organic pollutants (POPs) in the aqueous environment (Li et al. 2014; Matamoros et al. 2008; Vymazal and Březinová 2015). In recent years, a novel technique of introducing microbial fuel cell (MFC) into CW to form CW-MFC has been studied. Compared with conventional CW, CW-MFC system is more powerful in removing several hard- or non-degradable contaminants (Wang et al. 2019a; Zhang et al. 2018). To the best of our knowledge, rare information exists on foreseeable strategies for the removal of PFASs from water in CW-MFC system.

This review covers the state of the art and understanding of treatment strategies for PFASs from water environment after briefly describing their characteristics, hazards, and challenges. Moreover, this review focuses on the potential of employing CW-MFC system for PFASs removal. The knowledge provided in this review is hoped to improve our understanding of PFASs research and aid in the selection of suitable technological ways of aqueous PFASs control.

3.2 Overview of PFASs in Water Environment

3.2.1 Properties

PFASs are organofluorine compounds with alkyl chain as the skeleton and hydrogen atom partially or completely replaced by fluorine atom, which can vary in chain length and linear or branched isomers (Buck et al. 2011). The general chemical formula of PFASs is F(CF2)n-R, where R is hydrophilic functional group. Recently, according to the Organization for Economic Cooperation and Development, "*PFASs are defined as fluorinated substances that contain at least one fully fluorinated methyl or methylene carbon atom (without any H/Cl/Br/I atom attached to it), i.e., with a few noted exceptions, any chemical with at least a perfluorinated methyl group* ($-CF_3$) *or a perfluorinated methylene group* ($-CF_2-$) *is a PFAS*" (Wang et al. 2021). All the PFASs have the structure of a C–F bond, which is extremely polar, strong, and stable, giving PFASs exceptional chemical properties such as extremely high thermal and chemical stability. Perfluoroalkyl acids (PFAAs) are the most important and basic PFASs molecule, which are divided into two groups: perfluoroalkyl sulfonic acids (PFSAs) and perfluoroalkyl carboxylic acids (PFCAs). The most frequently detected PFSAs and PFCAs in the water environment are perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS), respectively (Podder et al. 2021).

Regarding the carbon chain length of PFASs, PFASs can further divide into two main categories, the long-chain PFASs (the carbon number ≥ 8 with PFCAs, and ≥ 7 with PFSAs) and the short-chain PFASs (Fig. 3.1). With different chain length and hydrophilic functional group, PFASs have unique properties. As explained, for example, the short-chain PFASs, such as perfluorobutanoic acid (PFBA), are highly soluble with lower sorption tendency in soil, which leads to greater mobility and bioaccumulation than that of the long-chain PFASs in the environment (Teymourian et al. 2021; Macorps et al. 2022).

Concerns about the potential environmental issues and human hazard impact of PFASs have been investigated. Researchers have well-documented that the toxicities of PFASs involve muscle, liver, reproduction and development, neurotoxicity and potential carcinogenicity (Sunderland et al. 2019), while the arithmetic and geometric mean half-lives of serum elimination are 5.4 years for PFOS, and 3.8 years for PFOA, respectively (Olsen et al. 2007). The main exposure pathways for human may include drinking contaminated water, eating contaminated foods, and inhalation of some neutral volatile PFASs, such as fluorotelomer alcohols (FTOHs). In terms of environmental risk assessment, there has been a rise in ecological toxicity studies

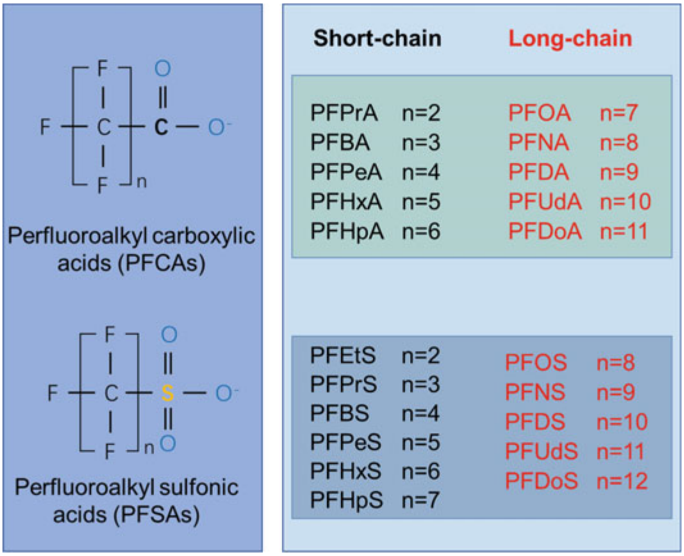

Fig. 3.1 Typical classification of PFASs

as researchers attempt to understand the impacts of PFASs on various ecosystems (Zhang et al. 2022; Cai et al. 2019). However, evaluating the toxicity of PFASs involves a number of obstacles, not the least of which being the diversity of PFASs compounds, as well as variances in their mechanisms of action in different animals. According to Sinclair et al. (2020) who reviewed the PFASs toxicity data in invertebrates, fish, and amphibians, the concentrations that induced mortality in 50% (LC_{50}) of the studied population of PFASs are unlikely to occur in the outside environment. To move forward, scientists must bridge the data gap between laboratory exposures and the actual environmental concentration.

3.2.2 *Occurrence of PFASs in Water Environment*

Monitoring the occurrence of PFASs in the water environment has recently become a major concern in the world. PFASs have been widely detected in wastewater, surface water, and groundwater, and even drinkable bottle water (Table 3.1).

The domestic and industrial wastewater and landfill leachate are the major sources of PFASs in water environment. As shown in Table 3.1, the high total concentrations of PFASs (0.2–6000 μg/L) were found in the wastewater from the chrome plating industry (Qu et al. 2020). Moreover, more than 800 μg/L of PFASs was detected in the effluent of electroplating wastewater treatment plant (WWTP) although this electroplating WWTP had ultrafiltration (UF) and reverse osmosis (RO) processes (Qu et al. 2020). On the other hand, landfill leachate is a significant source of high

Table 3.1 Detection and investigation of PFASs in water environment

Water environment	Main compounds	PFASs analyte count	Total concentration (ng/L)	Reference
Municipal wastewater treatment plant (WWTP)	PFOS, 6:2 Cl-PFAES	4	1610–153,000	Qu et al. (2020)
Municipal WWTP	PFOA, PFOS	3–17	1030–3360	Masoner et al. (2020)
Municipal WWTP	PFOA, PFBA	21	9.3–520	Coggan et al. (2019)
Municipal WWTP	PFBA, PFHxA	27	16–1400	Lu et al. (2021)
Landfill leachate	PFHxA	21–31	19,800–48,700	Masoner et al. (2020)
Landfill leachate	PFBS	7	0.1–17,000	Harrad et al. (2019)
Industrial wastewater	6:2 Cl-PFESA, 8:2 Cl-PFESA	17	2100–4200	Liu et al. (2022)
Industry wastewater	PFOS, 6:2 Cl-PFAES	7	200–6,000,000	Qu et al. (2020)
Seawater	PFOA	21	0.98–2.64	Xiao et al. (2021)
Seawater	PFBA, PFOA	20	0.125–1015	Wang et al. (2019b)
River	PFOS, 6:2 Cl-PFAES, 6:2 FTS, PFOA	4	400–2300	Qu et al. (2020)
River	PFOA, PFOS, PFHxA	14	0.04–31.3	Cai et al. (2022)
River	PFOA, PFBA	15	11.8–281	Li et al. (2022)
River	PFOA	13	0.8–274.6	Dong et al. (2020)
Lake	PFPeA, PFHxA	16	17.7–467.0	Lee et al. (2020)
Lake	PFHxS	13	30.45–1563	An et al. (2021)
Groundwater	PFOS	3	1.9–2.4	Qu et al. (2020)
Groundwater	PFOS, PFBA	24	31.4–15,656.0	Gao et al. (2019)
Drinking Water	PFOA, PFOS	9	1.36–20.2	Jiang et al. (2021)
Drinking water	PFBA, PFHxA	6	11.8–59.7	Gao et al. (2019)
Drinking water	PFBA, PFOA	17	9.29–266.68	Chen et al. (2019a)
Bottle water	PFPrA, PFCA	32	0.17–18.87	Chow et al. (2021)

PFASs concentrations. In a study, more than 20 types of PFASs were found in landfill leachate with a total concentration of 93,100 ng/L, which was an order of magnitude greater than the influent and effluent of the WWTP receiving this landfill leachate (Masoner et al. 2020). Compared with industrial wastewater and landfill leachate, the concentrations of PFASs in domestic wastewater are generally lower. Many home products, such as fast food containers/wraps, cleaning products, and non-stick cookware, contain PFASs and release them into wastewater after usage. Coggan et al. (2019) investigated the PFASs in the influent and effluent of nineteen Australian WWTPs with varied sizes, capacities, localities, and treatment types. The results demonstrated that the range of PFASs concentrations in WWTPs influent and effluent was 9.3–520 ng/L, and there were no significant PFASs removals after WWTPs.

It is worth noting that most conventional WWTPs were not capable to remove PFASs. Thus, a considerable amount of PFASs-containing wastewater is discharged into natural water bodies, resulting in surface water and groundwater pollution. In the Asan Lake of South Korea, the 19 PFASs were detected with the total average concentration of 17.7–467.0 ng/L, the wastewater from the nearby industrial parks may be a major source of PFASs in the lake (Lee et al. 2020). Similarly, the average concentrations of PFASs in Tai Lake in China in 2018 and 2019 were 205.6 ng/L and 171.9 ng/L, respectively, while the study also suggested that the local industry was the main source of PFASs (An et al. 2021). Furthermore, the vertical transfer in soil and water bodies contaminated by PFASs leads to groundwater contamination. One study found that the total concentrations of PFAAs range from 31.4 to 15,656.0 ng/L in groundwater sample, with short-chain PFAAs being the most frequent (Gao et al. 2019). This study also found that the concentration of PFASs in groundwater decreased with increasing distance from the manufactory.

The presence of PFAS in drinking and bottled water seems inevitable due to the ubiquitous occurrence of PFASs in surface and groundwater, especially because present technologies of drinking water treatment plants (DWTPs) are incapable to completely remove PFASs. Research in Ireland found that PFOS, PFOA, PFBS, and PFHxS were all discovered in tap water from homes and offices (Harrad et al. 2019). Chen et al. (2019a) further investigated the occurrence and transport behaviors of PFASs in drinking water distribution systems (DWDS), they detected 17 kinds of PFAAs in the tap water with the average concentrations ranging from 9.29 to 266.68 ng/L. The results also found that the fate and migration of PFASs in the DWDS were influenced by their physicochemical characteristics and the sediments in the system. According to the results of PFASs in bottle water research done in the USA (Chow et al. 2021), the total PFASs concentration in 39 examined samples was 0.17–18.87 ng/L while 97% of samples were below 5 ng/L.

Overall, these studies suggest that PFASs are already widespread in a wide range of water environment. The government should take necessary and immediate action to set up relevant regulation for PFAS removal/control.

3.2.3 *Protocols of PFASs in Drinking Water*

PFASs are widespread in aquatic environments and have been associated with human and animal health. They are difficult to degrade in nature. As a result, some countries and local/state governments have enacted legislation/protocol to limit the concentration of PFASs in drinking water. Table 3.2 lists the updated information.

The US Environmental Protection Agency (EPA) proposed PFASs drinking water restrictions in 2016 with maximum contamination levels (MCLs) of 70 ng/L for either PFOS, PFOA, or their total. Some states in the USA also have strict or loose regulations of PFAS in drinking water (Table 3.2). National regulations

Table 3.2 Global protocol for limiting the amount of PFASs in drinking water

Country/state	PFOA (ng/L)	PFOS (ng/L)	Year of action
US EPA (https://www.epa.gov/sdwa/drinking-water-health-advisories-pfoa-and-pfos)	70	70	2016
California (https://www.jdsupra.com/legalnews/pfas-update-state-by-state-regulation-4639985/)	5.1	6.5	2021
Minnesota (https://www.jdsupra.com/legalnews/pfas-update-state-by-state-regulation-4639985/)	–	15	2019
New York (https://www.jdsupra.com/legalnews/pfas-update-state-by-state-regulation-4639985/)	10	10	2020
Massachusetts (https://www.jdsupra.com/legalnews/pfas-update-state-by-state-regulation-4639985/)	20	20	2018
Canada (https://www.canada.ca/en/health-canada/programs/consultation-perfluorooctanoic-acid-pfoa-in-drinking-water/document.html)	200	600	2018
Denmark (https://www2.mst.dk/Udgiv/publications/2015/04/978-87-93283-01-5.pdf)	300	100	2015
Germany (https://www2.mst.dk/Udgiv/publications/2015/04/978-87-93283-01-5.pdf)	300	300	2006
Sweden (https://www2.mst.dk/Udgiv/publications/2015/04/978-87-93283-01-5.pdf)	90	90	2014
Netherlands (Kurwadkar et al. 2022)	390	200	2020
United Kingdom (https://www.dwi.gov.uk/en/private-water-supplies/pws-installations/guidance-on-the-water-supply-water-quality-regulations-2016-specific-to-pfos-perfluorooctane-sulphonate-and-pfoa-perfluorooctanoic-acid-concentrations-in-drinking-water/)	10	10	2021
Australia (https://www.pfas.gov.au/government-action/pfas-food-water)	560	70	2017
China (https://openstd.samr.gov.cn/bzgk/gb/newGbInfo?hcno=99E9C17E3547A3C0CE2FD1FFD9F2F7BE)	80	40	2022

on PFASs in drinking water vary greatly throughout the world. The MCLs for PFOA and PFOS in Canadian drinking water are 200 and 600 ng/L, respectively (https://www.canada.ca/en/health-canada/programs/consultation-perfluorooctanoic-acid-pfoa-in-drinking-water/document.html), but the MCLs for these two compounds in the UK are only 10 ng/L (https://www2.mst.dk/Udgiv/publications/2015/04/978-87-93283-01-5.pdf). Most recently, the Chinese government announces a new "Standard for drinking water quality (GB 5749-2022)," which limits the values of PFOA and PFOS in drinking water of 80 ng/L and 40 ng/L, respectively (https://openstd.samr.gov.cn/bzgk/gb/newGbInfo?hcno=99E9C17E3547A3C0CE2FD1FFD9F2F7BE). Although PFAS concentration in drinking water has been subjected to a variety of regulatory laws and standards up to this point, it is important to keep in mind that PFASs are consistently harmful to humans. It is critical to implement corresponding regulations in some developing nations and regions to limit PFASs contamination in drinking water, as well as more comprehensive national collaboration.

3.3 Treatment Technologies for PFASs in Water

As "forever chemical," the treatment technologies for PFASs in water environment can be divided into separation technologies and destruction/degradation technologies. The main separation technologies include adsorption and membrane filtration, while thermal treatment, advanced oxidation/reduction, hydrothermal, and biological technologies are potential to the destruction of PFASs.

3.3.1 Adsorption

Adsorption is the most frequently investigated and employed treatment technology. It has been used for both ex-situ and in-situ water treatment applications. Various adsorbent materials have been tested regarding the removal performance of PFASs from water (Zhang et al. 2019a). Granular activated carbon (GAC) is considered as efficient and more economic sorbent with good performance (normally > 90%) in controlling aqueous PFASs. For example, the average removal efficiency of 15 PFASs in a full-scale DWTP with GAC as filter was from 92 to 100% (Belkouteb et al. 2020). A review of the PFASs adsorption performance of commercial carbon materials found that GAC has an adsorption capacity in the tens to hundreds of mg/g range (Pauletto and Bandosz 2022). Although powdered activated carbon (PAC) has a better adsorption capacity for PFASs than that of GAC (Zhang et al. 2019a), it has intrinsic disadvantages such as regeneration and reutilization. The impact of sorption, on the other hand, differs depending on the type of PFASs. For different PFASs, GAC/PAC has a variable adsorption capability and breakthrough time. Because the sulfonate group is more readily adsorbed onto oxide surfaces than the carboxylate group, PFSAs tend to adsorb more strongly than PFCAs with equal chain length (Du et al. 2014; Wang et al. 2012), whereas the adsorption of branched isomers is smaller than linear (McCleaf et al. 2017).

Other adsorbents, such as resins (McCleaf et al. 2017), cyclodextrin polymers (Ching et al. 2022), biochar (Sørmo et al. 2021; Xiao et al. 2017), and metal-organic frameworks (MOFs) (Pauletto and Bandosz 2022) have been tested in recent years to remove PFASs from water. It is worth noted that the properties of adsorbents and the kind of PFASs, as well as the environmental factors (i.e., solution pH, surface charge, dissolved organic matter, inorganic ions) can significantly affect the adsorption process (Oliver et al. 2019; Qi et al. 2022). When hydrophobic interaction is the primary mechanism in adsorption, short C–F chain PFASs have a more hydrophilic character as well as a smaller molecular size, resulting in a quick breakthrough time and low removal efficiency (Li et al. 2019a).

Electrocoagulation (EC) is another adsorption reaction-based technique for PFASs removal. The main mechanism of EC is adsorption of contaminants with metal hydroxide flocs which are formed by the soluble metal anode (e.g., Fe, Al, Zn) under the action of an applied electric field. At high influent concentrations (0.25 mM), a study using an air cathode in an electrocoagulation reactor demonstrated excellent PFOA removal efficiency (approximately 100%), whereas PFOS removal at low concentrations (0.1 μM) was superior than PFOA removal (Mu et al. 2021). In addition, the anode metal materials are the key to the electrocoagulation process. Liu et al. (2018) investigated the EC technique using Al-Zn electrodes for the removal of PFOA. The results achieved over 99% removal under 1 mg/L influent concentration.

Although adsorption appears to be a well-established method for PFASs removal, there are certain disadvantages to adsorption investigations to date. The majority of research has focused on the removal of a particular kind of legacy PFASs (i.e., PFOA and PFOS), despite the fact that the aquatic environment contains a variety of emerging PFASs with various functional groups and chain lengths (Oyetade et al. 2018; Zhang et al. 2019a, 2021). Furthermore, the effects of various organic matter components, inorganic ions, and microbials in water or wastewater must be investigated further. Adsorbents utilized to remove PFASs, on the other hand, should be carefully evaluated for disposal or regeneration after saturation. Information on the long-term stable adsorption of aqueous PFASs at full scale is particularly needed from an engineering standpoint.

3.3.2 Membrane Filtration

The membrane filtration, such as the reverse osmosis (RO) and nanofiltration (NF), achieves remarkable removal of aqueous PFASs (Wang et al. 2018). NF membranes have been used to remove various types of PFASs from water in several studies. They have been found to be particularly effective in removing PFASs regardless of chain length or functional group (Wang et al. 2018; Léniz-Pizarro et al. 2022;

Mastropietro et al. 2021; Xiong et al. 2021). PFOS and perfluorobutane sulfonate (PFBS) through NF (piperazine amide) membrane showed high retention rate with about 90% (Wang et al. 2018). RO is effective in the removal of mainly organic and inorganic contaminants from water and has been employed in industrial water treatment around the world. Regarding PFOS removal in water, RO membrane is better than NF (Tang et al. 2007). However, the ionic strength and solution pH significantly affected retention rate of membrane filtration process. In addition, the pretreatment processes (such as coagulation/flocculation–precipitation, adsorption) are important to avoid fouling with RO and NF to remove PFASs. Furthermore, high-pressure pumps are required to give transmembrane power to RO and NF, which subsequently hold fluid with high concentrations of PFASs. Another key question is how to manage and dispose of this hazardous liquid. The treatment train consisted of RO or NF filtration separation and degradative/destructive technologies have been recommended. This combination of several removal procedures improves removal efficiency while lowering costs and reducing hazardous by-product (Lu et al. 2020).

3.3.3 Destructive Techniques

3.3.3.1 Advanced Oxidation and Reduction

Advanced oxidation processes (AOPs) can form highly oxidizing species, like ozone (O_3), hydroxyl radicals ($HO^\bullet$), persulfate ($S_2O_8{}^{2-}$), sulfate radical anions ($SO_4{}^\bullet$), hydroperoxide ($HO_2{}^\bullet$), and superoxide ($O_2{}^\bullet$) ions, though oxidant activation with solar radiation, heat, and catalysts. However, because $HO^\bullet$ and O_3 do not destroy the C–F bond, they are unable to fully breakdown PFOA/PFOS (Qi et al. 2022). Sulfate or/and persulfate generated can successfully breakdown PFOA under a range of circumstances, according to several lab-scale research (Wu et al. 2018; Zhang et al. 2019b). Several shorter-chain PFAAs, such as perfluoroheptanoic acid (PFHpA) and PFBA, were generated by the loss of CF_2 units from PFOA with persulfate reaction (Bai et al. 2022). Although other studies have shown that ultrasonic treatment (Lei et al. 2020), persulfate photolysis (Li et al. 2019a), photocatalysis (Jin et al. 2014; Qian et al. 2021), sonochemical (Cao et al. 2020; Rodriguez-Freire et al. 2015), and Fenton (Santos et al. 2016) can be used to destroy PFASs, these studies mostly require strict operating conditions. This suggested that, in the field application, generating highly oxidizing species to remove PFASs might be difficult due to unreasonably high costs and sluggish reaction rates.

Several studies reported that zero-valent metals can be employed to eliminate PFASs by chemical reduction (Arvaniti et al. 2015; Chen et al. 2020; Hori et al. 2008). Hori et al. (2008) used subcritical water and zero-valent iron (ZVI) to breakdown PFASs at high pressure (20 MPa) and temperature (350 °C). The results revealed that the ZVI powder accelerated the breakdown of PFOS into F ions. Following that, other investigations revealed that PFOS and PFOA were destroyed at 380 °C, with yields of 9.2% fluorine and 21.9% sulfate, respectively. The ZVI surface area was shown to be linked with PFASs degradation rates, indicating that the reaction is surface catalyzed. This technique, like AOPs, needs more energy and appropriate reaction circumstances. Recently, Chen et al. (2019b, 2020) discovered that hydrated electrons can quickly destroy PFOA and PFOS under UV irradiation with surfactants. They suggest that hydrated electrons generated by photo-irradiation can attack C–F bonds under ambient environments, enabling defluorination and mineralization of PFASs in actual wastewater. However, there is currently a lack of long-term and field-scale application for this technique.

Several chemical redox technologies have also been shown to reduce PFASs contamination in laboratories. There are several considerations in a full-scale application. To begin with it, the factional group (carboxylic or sulfonic) of PFASs is more susceptible to redox transition than the C–F bond, resulting in the parent compound's partial transformation (Anumol et al. 2016). It will produce various intermediates, such as short-chain PFAAs, as well as potentially more mobile or hazardous substrates. Secondly, typical co-contaminants in wastewater would have an influence on the removal of PFASs and the generation of by-products (Mu et al. 2021). Furthermore, oxidizing species are more susceptible to readily oxidized other pollutants as well as self-quenching (Lenka et al. 2021; Ross et al. 2018).

3.3.3.2 Thermal Treatment

Incineration is usually used to destroy organic compounds, especially hazardous contaminants. Due to high stability of C–F bond, the PFASs have been used to produce aqueous film-forming foam (AFFF) and non-stick cookware. Incineration process to handle PFASs, therefore, must be capable of destruction of the C–F bond. To convert PFASs into HF and non-fluorinated compounds, thermal treatment is required at high temperatures (> 700 °C) for an extended length of time (Khan et al. 2020). Moreover, the greenhouse gases (GHGs), such as hexafluoroethane and tetrafluoromethane, may be formed during the incineration treatment of PFOS (Ahmed et al. 2020). High-temperature thermal treatment, on the other hand, consumes a range of fossil energy. Therefore, lowering the temperature of PFAS thermal treatment is a potential way. Wu et al. (2019) promised a novel thermal treatment technology for achieving rapid and complete destruction of PFOS via alkaline hydrothermal reaction under temperature with 200–350 °C and pressures with 2–16.5 MPa. They found that complete conversion of C–F bonds to F^- within 40 min for the hydrothermal reaction with 1 M NaOH. However, the intermediates and by-products may lead to secondly environmental risk. Generally, the thermal processes have yet to be proven at scale, where inefficiencies might impair performance. In addition, the incompletely destroyed of PFASs may form a potential source of air pollution.

3.3.3.3 Electrochemical Reaction

Electrochemical oxidation is the electrochemical approaches that have been proven to be effective in PFASs removal from water (Zhuo et al. 2020; Gomez-Ruiz et al. 2017). The direct oxidation of the anode or/and the indirect oxidation of active radicals are the mechanisms of electrochemical oxidation to PFASs removal (Niu et al. 2016). The removal efficiency is substantially determined by the anode material's electron transfer capacity, $^{\bullet}$OH-generating ability, and oxygen evolution potential (OEP) (Li et al. 2022). PFOA and PFOS may be successfully oxidized in an electrochemical manner by boron-doped diamond (BDD) anodes, with direct anodic oxidation being the predominant mechanism (Zhuo et al. 2020). However, these studies were carried out in synthetic supporting electrolyte solutions with high or low conductivity, but high initial PFASs concentrations. Nevertheless, concentrations of PFASs are relatively low and rarely exceed 1 μg/L (Table 3.1).

Obviously, the treatment of PFASs from water using a combination of electrochemical oxidation and advanced oxidation is more effective (Wang et al. 2020a; Zhou et al. 2021). The electrode materials, on the other hand, remain a source of worry due to their high cost, limited activity, and short service life. In addition, all of the investigations relied on a reasonably pure reaction system (carried out with deionized water spiked with chosen PFASs) and were still in the theoretical/lab experimental stage.

3.3.3.4 Biodegradation

The most reliable and cost-effectiveness approach for wastewater treatment is bioremediation process. However, WWTPs are an important point source of PFASs. The fluorine-saturated carbon chain element structure of PFASs impeded the oxidative degradation of microorganisms (Lenka et al. 2021). Therefore, it is difficult for microorganisms to use such substances as carbon sources and energy sources.

PFASs precursors have carbon–hydrogen (C–H) and carbon–oxygen (C–O) bonds, as well as carbon–nitrogen (C–N) bonds in their molecular structure, which may convert precursor organics to PFAAs via microbial reactions (Yin et al. 2019, 2018). However, according to several studies (Huang and Jaffé 2019; Yu et al. 2020, 2022), PFASs are difficult to entirely decompose by a single biodegradation pathway.

Although a few studies reported some special microbial degradation of PFOA/PFOS, these studies were almost all long-term microbial degradation under special pure bacterial culture and sensitive to environmental changes as well as no complete mineralization (Zhang et al. 2022; Huang and Jaffé 2019; Ruiz-Urigüen et al. 2022). For example, *Acidimicrobium* sp. strain A6 is selected and employed for PFASs biodegradation with the average 77% decrease in PFOA concentration under 18 days of operation (Ruiz-Urigüen et al. 2022). Obviously, more work is highly desirable with the aim to improve the microbial biodegradation ability of PFASs.

Overall, most degradation technologies' energy costs constrain their long-term sustainability and acceptability, while the formation of hazardous by-products (e.g., short-chain PFAAs, bromate, and perchlorate) remains a problem. Each single treatment technique has its advantage and disadvantage (Table 3.3), so combination of different treatment techniques is often the best solution for control PFASs from water.

3.4 Potential Approach of CW-MFC

Many POPs and CECs, such as antibiotics, pharmaceutical and personal care products (PPCP), as well as insecticides, could be effectively removed in CW systems (Vymazal and Březinová 2015; Brunhoferova et al. 2021; Liu et al. 2019). Substrate serves as an adsorbent, a media for wetland plant growth, and a carrier for biofilm formation, among other components to play a key role in CW system. Various wetland substrates (GAC, zeolite, and biochar) are also used for the adsorption removal of PFASs from water (Du et al. 2014). With enough adsorbent amount and adsorption capability in the wetland substrate, both conventional pollutants and trace PFASs should be removed concurrently. There is no doubt that the use of appropriate adsorbents in the construction of CW filler beds can provide long-term effective adsorption of long-chain and/or short-chain PFASs on the field scale.

Plants are another key component of wetlands. They can uptake and accumulate PFASs in a variety of environments and applications, including laboratory experiments (Knight et al. 2021; Krippner et al. 2015; Zhang and Liang 2020; Zhou et al. 2019) and field surveys (Yamazaki et al. 2019). Because of worries about PFASs traveling via animals or crops and into humans, most previous research focused on irrigated crops in PFASs-contaminated soil or water (Zhou et al. 2019; Brown et al. 2020; Miranda et al. 2021). Several studies have found that wetland plants have potential ability for accumulating PFASs, with significant levels of PFASs found in plant tissues such as root, straw, and grains (Wang et al. 2020b; Yin et al. 2017). Short-chain PFCAs have a higher bioaccumulation potential in plant leaves than long-chain PFCAs with a low octanol/water partition coefficient (K_{ow}). For long-chain PFCAs, however, root concentration factors (RCF) rose with chain length (Lesmeister et al. 2021; Mei et al. 2021). Because of their hydrophilicity and mobility, short-chain PFASs are more likely to be uptaken and bioaccumulated in plant above-ground components. More importantly, it may be anticipated that by rationally structuring wetland substrates and plants, various components of CW could work together to remove various kinds of PFASs. Wetland plants for PFASs removal must be carefully chosen since they are a significant aspect of the biological habitat. To avoid being eaten by other organisms (animals, insects), it is advised to choose fern plants. It should be highlighted that when PFASs have been removed, disposing and regenerating the plants and substrate used in CW remain a significant challenge. The use of destructive treatment technique to achieve mineralization of PFASs is a viable option.

On the other hand, although biological approaches to the treatment of PFASs are extremely limited and not currently considered feasible, CW-MFC system provides a potential bioremediation approach. Due to unique electroactive bacteria around

Table 3.3 Advantages and disadvantages of various existing technologies for remove PFASs from water (Ji et al. 2020)

Technology	Application media	Scale	Advantages	Disadvantages
Adsorption	Wastewater Surface water Drinking water	Full-scale	• Easy to operate • Tailor-made of adsorbents • Good removal of several long-chain PFASs	• Poor in clearing short-chain PFASs • Unable to remove trace level of PFASs • Difficulty regeneration • Impact with other pollutants
Membrane filtration	Wastewater Surface water Drinking water	Field pilot	• Good performance • Wide range of application scenarios	• High-operating costs • Based on the PFASs' molecular weight • High concentrations of residues
Advanced oxidation & reduction	Wastewater Surface water	Field pilot	• Able to mineralize PFASs • Quicker reaction capability	• Require extreme operating conditions, centralized equipment, and massive chemical • Poor in treating some PFASs • Forming intermediate product • Impact with other pollutants
Thermal treatment	Wastewater	Lab-scale	• Able to mineralize PFASs	• Required at high temperatures • May form a potential source of air pollution
Electrochemical	Wastewater Surface water Drinking water	Field pilot	• Able to mineralize PFASs • Could be used in combination with other treatment methods	• High-energy • High-operating costs • Poor in treating some PFASs • Forming intermediate product
Bioremediation	Surface water	Lab-scale	• Cost-efficiency • Green solution	• Few evidences could completely degrade PFASs • Requires specific environmental

anode chamber, CW-MFC has been investigated in recent years to remove a variety of biorefractory organic contaminants. CW-MFC could effectively treat wastewater with high antibiotic and PPCPs (Wang et al. 2020c; Zhang et al. 2017a, b). Biodegradation, substrate absorption, and plant uptake were found to have distinct roles in removing pollutants in these studies, notably biodegradation, and plant uptake. It has been demonstrated that a bioelectrochemical system not only creates a battery circuit that can promote microbial metabolism but also selectively enriches electrochemically active microbial communities for refractory organics (Li et al. 2019b; Wen et al. 2022; Xu et al. 2019).

The accumulation of PFASs in the substrate with long hydraulic retention time, and bioelectrochemical stimulation in CW-MFC offers a favored condition for incubation and/or domestication PFASs-degrading microorganisms. Moreover, there are few studies, showing that the special microbial can degrade of PFOA in lab experiment (Sect. 3.3.4). It seems that there is a condition and pathway for PFOA biodegradation or biotransformation due to the abundant microbial population and suitable microenvironment in CW-MFC system. However, further studies are highly desirable.

Based on the above clues, using CW-MFC to removal PFASs in water was proposed by Ji et al. (2020) (Fig. 3.2). Subsequently, related experiments were carried out, while the results showed that when the concentrations of PFOA and PFOS in the influent were 6.46 ± 0.52 μg/L and 9.34 ± 0.87 μg/L, respectively, both closed-circuit and open-circuit operations of the CW-MFC systems demonstrated over 96% removal performance of PFASs (Ji 2022). These results indicate that the CW-MFC system can effectively remove PFASs from wastewater.

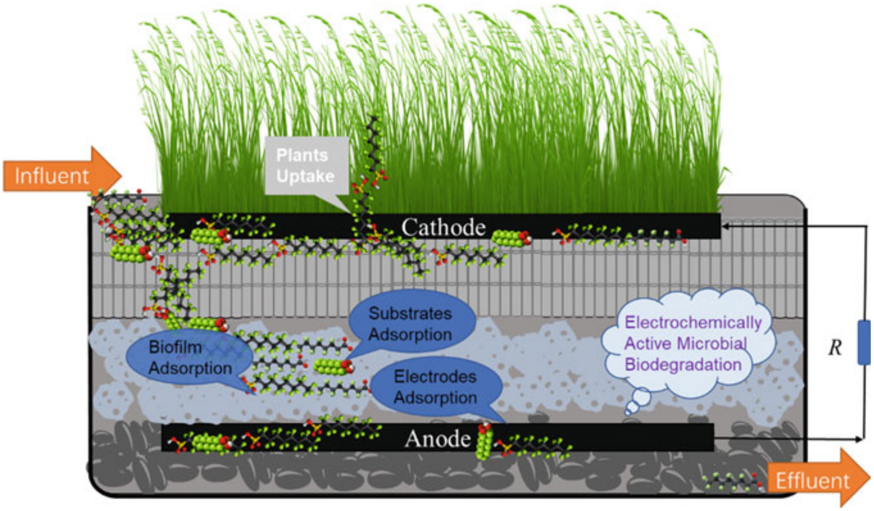

Fig. 3.2 Principle of PFASs removal in proposed CW-MFC system

3.5 Conclusion

The current review provides a brief overview of the occurrence and properties of PFASs in water environment, with an emphasis on problems and feasible removal solutions based on published literature. Some physical, chemical, and limited biodegradation methods have been documented to degrade or transfer PFASs to some extent. However, these methods are insufficiently thorough and not environmentally friendly. Given the fact that PFASs are very stable compounds with distinct physicochemical features, the integration approach or a combined system may be a viable option for PFASs control. CW-MFC system could provide an integrated and environmentally friendly while sustainable way to remove PFASs from water through substrate adsorption, plant uptake, and enhanced biodegradation.

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Chapter 4
Plastic Chemical Constituents in Wastewater, Surface Water, and Drinking Water

Rahul Kumar

Abstract Plasticizers constitute tens of thousands of synthetic chemical substances added to plastics to increase their elasticity and durability. Plasticizers are commonly found in polyvinyl chloride (PVC) materials, food packaging, medical devices, toys, automobiles, solvents, paints, and adhesives. Phthalates are the most used plasticizers and many have adverse impacts on human health. Plastic monomers include several chemical constituents that act as the building blocks in plastics manufacturing. For example, bisphenol A (BPA) and terephthalic acid (TPA) are monomers of polycarbonate and polyethylene terephthalate-based plastic products. Phthalates and BPA are regulated in consumer products in some countries due to their profound human health impact. Previous studies have reported endocrine-disrupting properties and carcinogenicity of phthalate plasticizers and BPA. Plasticizers and plastic monomers enter the environmental waters and wastewater, mainly through human exposure and leaching from the plastic materials. Plasticizers and plastic monomers are ubiquitously found in all environmental waters and wastewater ranging in concentration from ng/L to μg/L. Most plasticizers and monomers undergo biological or non-biological transformations, and these transformed products are frequently detected in wastewater. Although several analytical pipelines are employed to detect plastic chemical constituents in water, it is always recommended to ensure data quality due to the background interferences from laboratory settings. This chapter provides an overview of plasticizers and plastic monomers' occurrence, transformations, and fate in environmental waters and wastewater. This chapter also emphasizes the analytical challenges in detecting plastic constituents and provides recommendations to ensure reported data quality.

Keywords Phthalates · Bisphenols · Plasticizers · Fate · Occurrence · Analytical challenge

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4.1 Introduction

Plastic pollution is one of the significant environmental and public health concerns globally. Although plastics have several applications, they are unpleasant to the environment due to the leaching of their harmful constituents over a period of time (Erythropel et al. 2014). Plastics and their components, including additives and monomers, may also impose potential particle, microbial, and chemical hazards on humans exposed to them (Wright and Kelly 2017). Plasticizers are examples of additives that are incorporated to improve the flexibility and processibility of synthetic polymers to provide a wide range of applications for plastics (Rahman and Brazel 2004). Phthalates are a widely used plasticizer in food packaging, floorings, cosmetics, medical devices, and several other consumer items. Phthalates are detected in all environmental matrices, including air, water, soil, sediments, and living beings (Lee et al. 2019).

Phthalates, also called phthalate esters with the general chemical formula of $C_6H_4(CO_2R)_2$, are also used as additives in plastic bottle manufacturing. They can leach from drinking water bottles to bottled water under ambient conditions and may pose health risks to humans consuming bottled water (Luo et al. 2018). Most phthalates are potent endocrine disruptors that can interfere with developmental, metabolic, neurological, immune, and reproductive systems (Abtahi et al. 2019). The di-(2-Ethylhexyl) phthalate (DEHP), butyl benzyl phthalate (BBP), di-n-butyl phthalate (DBP), diisononyl phthalate (DINP), di-isodecyl phthalate (DIDP), and di-n-octyl phthalate (DNOP) are some of the examples of phthalate diesters found in consumer products. In one recent study, the detection frequency of dibutyl phthalate was the highest among more than 300 brands of bottled water brands collected from 21 countries, followed by di-2-(ethyl hexyl) phthalate (DEHP), diethyl phthalate (DEP), benzyl butyl phthalate (BBP), and dimethyl phthalate (DMP) (Luo et al. 2018). The leaching of phthalates from bottled water depends upon several factors, including storage time, temperature, pH of liquid inside the bottle, contact surface area of bottles, and type of polymer material (virgin or recycled plastic) (Keresztes et al. 2013).

Phthalates are classified into low molecular weight phthalates (LMW phthalates) and high molecular weight phthalates (HMW phthalates) based on their molecular weight. LMW phthalates are primarily used in personal care products and cosmetics. In contrast, HMW phthalates are used in polyvinyl chloride (PVC) plastics to increase the lifetime and flexibility of packaging materials, medical devices, and construction materials (Smith et al. 2022). DEHP belongs to the HMW phthalate category, whereas DMP, DEP, and DBP are examples of LMW phthalates (Tuan Tran et al. 2022). Humans are exposed to phthalates primarily via oral exposure. However, dermal contact and inhalation are also secondary sources of exposure (Smith et al. 2022; Giovanoulis et al. 2018).

Phthalate diesters are hydrolyzed to their respective monoesters and oxidized derivatives in the human body after exposure and excreted via urine. Human biomonitoring studies on exposure to phthalates focus on phthalate monoesters and oxidized derivatives in urine as they represent a unique biomarker of human exposure to phthalate. Recently, a few wastewater-based epidemiology (WBE) studies have also reported phthalate monoesters in community wastewater (González-Mariño et al. 2017, 2021; Tang et al. 2020; Kumar et al. 2022a).

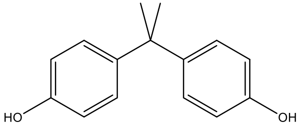
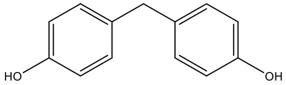
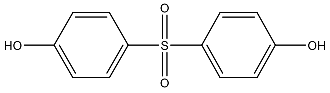
Polyethylene terephthalate (PET) and polycarbonate (PC) are two essential types of plastics produced in large quantities and are widely used globally (Zhang et al. 2019). The leaching of their monomers from consumer products is one reason for their occurrence in environmental compartments. Bisphenol A (BPA), the monomer used in the production of PC plastics, is ubiquitously present in the environment and the human body. However, industrial production and usage in consumer products have been regulated in the USA and Europe, keeping in mind its adverse impact on the human body (Chen et al. 2016). BPA is a potent endocrine disruptor that can damage the reproductive, immune, and neuroendocrine systems. Moreover, BPA has shown carcinogenicity in animal models (Ma et al. 2019). Other bisphenol analogues, including bisphenol S (BPS), bisphenol F (BPF), Bisphenol Z (BPZ), Bisphenol B (BPB), Bisphenol P (BPP), Bisphenol AP (BPAP), and bisphenol AF (BPAF), are increasingly replacing BPA in consumer products. However, many of these are not considered safe alternatives to BPA (Eladak et al. 2015). The world's average human daily intake of bisphenols and its analogous ranked in the order BPA > BPF > BPS > BPP > BPAP > BPB > BPZ > BPAF, ranging from 0.06 μg/d/person to 2.5 μg/d/person (Wang et al. 2020c). Community-wide exposure to BPA can be accurately accessed by analyzing the urinary biomarkers of BPA. Recently. BPA sulfate has been used to estimate population exposure to BPA as the metabolic biomarker (Kumar et al. 2022a; Lopardo et al. 2019).

Terephthalic acid (TPA) is one of the monomers used in manufacturing PET plastics in addition to dimethyl terephthalate (DMT) with ethylene glycol. There are no reported pieces of evidence of TPA toxicities in humans (Ball et al. 2012). However, TPA exposure to humans needs to be investigated further. There are limited studies on TPA occurrence in environmental matrices, with a few reports on detections in industrial wastewater manufacturing purified terephthalic acid (Zhang et al. 2010) and in sewage sludge (Zhang et al. 2019).

4.2 Occurrence of Phthalates, Bisphenols, Terephthalic Acids and Their Transformation Products in Wastewater, Surface Water, and Drinking Water

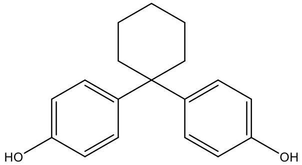
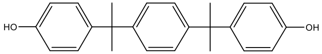
The dispersion of plasticizers in the aqueous environment is due to industrial and domestic wastewater, surface runoff, atmospheric dispersion, and leaching from microplastics (Chakraborty et al. 2021). The occurrence of plastic chemical constituents and their transformation products in wastewater, surface water, and drinking water is listed in Tables 4.1 and 4.2. Phthalates concentration in domestic wastewater ranges from 1 to 195,000 ng/L, with DBP and DEHP representing the

Table 4.1 Concentration of bisphenol A, bisphenol analogues, and phthalates in wastewater, surface water, and bottled drinking water

Compounds	Acronym	Structure	Concentration (ng/L)		
			Wastewater	Surface water	Bottled water/drinking water
Bisphenol A	BPA		4–60,000 (Hu et al. 2019)	0.71–29,920 (Catenza et al. 2021); 40–4460 (Chakraborty et al. 2021), N.D.–678 (Liu et al. 2021)	< LOD-8800 (Wang et al. 2020a; Akhbarizadeh et al. 2020)
Bisphenol F	BPF		2–384 (Hu et al. 2019)	N.D.–1740 (Liu et al. 2021)	N.D. (Wang et al. 2020b)
Bisphenol S	BPS		1–316 (Hu et al. 2019)	0.07–65,600 (Catenza et al. 2021), N.D.–3640 (Liu et al. 2021)	N.D.–10.6 (Wang et al. 2020b)

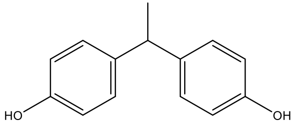
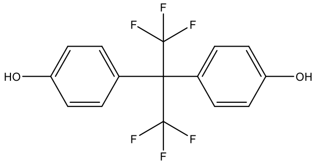
(continued)

Table 4.1 (continued)

Compounds	Acronym	Structure	Concentration (ng/L)		
			Wastewater	Surface water	Bottled water/drinking water
Bisphenol Z	BPZ		0.3–151 (Hu et al. 2019)	N.D.–9 (Catenza et al. 2021)	N.D. (Wang et al. 2020b)
Bisphenol P	BPP		1–8 (Hu et al. 2019)	N.D.–94 (Catenza et al. 2021)	N.D. (Wang et al. 2020b)

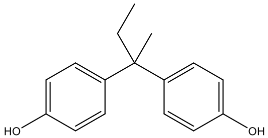
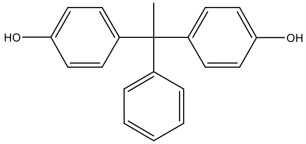
(continued)

Table 4.1 (continued)

Compounds	Acronym	Structure	Concentration (ng/L)		
			Wastewater	Surface water	Bottled water/drinking water
Bisphenol E	BPE		0.2–476 (Hu et al. 2019)	N.D.–2.69 (Catenza et al. 2021)	N.D.–7.8 (Wang et al. 2020b)
Bisphenol AF	BPAF		0.3–17 (Hu et al. 2019)	N.D.–205 (Catenza et al. 2021), N.D.–114 (Liu et al. 2021)	N.D.–4.9 (Wang et al. 2020b)

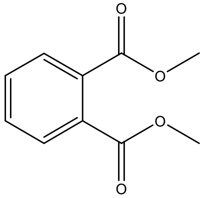
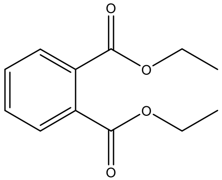
(continued)

Table 4.1 (continued)

Compounds	Acronym	Structure	Concentration (ng/L)		
			Wastewater	Surface water	Bottled water/drinking water
Bisphenol B	BPB		0.4–27 (Hu et al. 2019)	0.36–18.1 (Catenza et al. 2021)	N.D. (Wang et al. 2020b)
Bisphenol AP	BPAP		1–75 (Hu et al. 2019)	0.540–0.903 (Catenza et al. 2021)	N.D.–7.4 (Wang et al. 2020b)

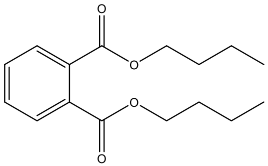
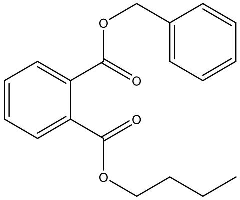
(continued)

Table 4.1 (continued)

Compounds	Acronym	Structure	Concentration (ng/L)		
			Wastewater	Surface water	Bottled water/drinking water
Dimethyl phthalate	DMP		228–5740 (Tuan Tran et al. 2022)	N.D.–224 (Tuan Tran et al. 2022; Le et al. 2021), 30–50 (Chakraborty et al. 2021)	< LOD–51,000 (Akhbarizadeh et al. 2020; Loraine and Pettigrove 2006)
Diethyl phthalate	DEP		182–12,820 (Tuan Tran et al. 2022)	29–241 (Tuan Tran et al. 2022). 40–2140 (Chakraborty et al. 2021)	< LOD–21,000 (Akhbarizadeh et al. 2020; Loraine and Pettigrove 2006)

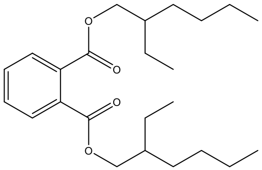
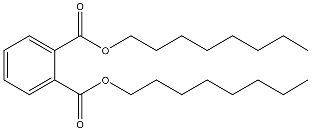
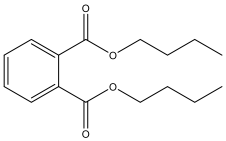
(continued)

Table 4.1 (continued)

Compounds	Acronym	Structure	Concentration (ng/L)		
			Wastewater	Surface water	Bottled water/drinking water
di-n-butyl phthalate	DnBP		1290 (Tuan Tran et al. 2022)	N.D.–2270 (Chakraborty et al. 2021)	20–5000 (Akhbarizadeh et al. 2020)
Benzyl butyl phthalate	BBP		388–37,870 (Tuan Tran et al. 2022)	22–39 (Tuan Tran et al. 2022), N.D.–130 (Chakraborty et al. 2021)	< LOD-52,000 (Akhbarizadeh et al. 2020; Loraine and Pettigrove 2006)

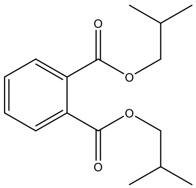
(continued)

Table 4.1 (continued)

Compounds	Acronym	Structure	Concentration (ng/L)		
			Wastewater	Surface water	Bottled water/drinking water
Di(2-ethylhexyl) phthalate	DEHP		28,000–72,000 (Tuan Tran et al. 2022)	134–22,700 (Tuan Tran et al. 2022), 110–6300 (Chakraborty et al. 2021)	< LOD-15,000 (Akhbarizadeh et al. 2020; Loraine and Pettigrove 2006)
Di-n-octyl phthalate	DnOP		12,710 (Tuan Tran et al. 2022)	2–119 (Tuan Tran et al. 2022), N.D.–98,000 ng/L	15–39 (Akhbarizadeh et al. 2020)
Dibutyl phthalate	DBP		748–195,000 (Tuan Tran et al. 2022)	109–500 (Tuan Tran et al. 2022)	< LOD–26,000 (Akhbarizadeh et al. 2020; Loraine and Pettigrove 2006)

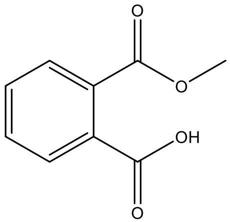
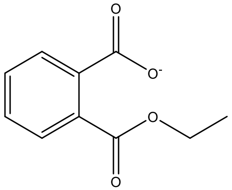
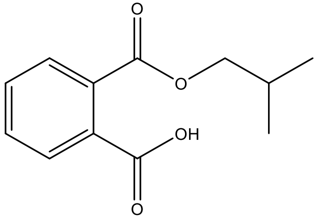
(continued)

Table 4.1 (continued)

Compounds	Acronym	Structure	Concentration (ng/L)		
			Wastewater	Surface water	Bottled water/drinking water
Diisobutyl phthalate	DiBP		1170–73,900 (Le et al. 2021)	77 (Tuan Tran et al. 2022)	< 3–900 (Akhbarizadeh et al. 2020)

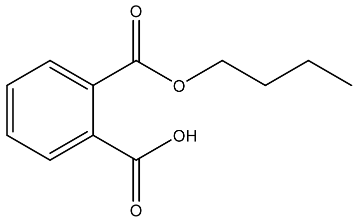
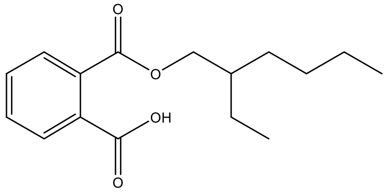
N.D. Non-detect; *LOD* Limit of Detection

Table 4.2 Concentration of phthalate urinary metabolite, BPA sulfate, and terephthalic acid in wastewater and drinking water

Compounds	Acronym	Parent compound	Structure	Concentration (ng/L)	
				Wastewater	Drinking water/bottled water
Monomethyl phthalate	MMP	DMP		48–11,000 (González-Mariño et al. 2017, 2021; Tang et al. 2020)	5.45 ± 3.54 (Ding et al. 2019)
Monoethyl phthalate	MEP	DEP		300–12,700, (González-Mariño et al. 2017, 2021; Tang et al. 2020)	0.550 ± 6.30 (Ding et al. 2019), 11,000 (Li et al. 2019)
Monoisobutyl phthalate	MiBP	DiBP		39–1974 (González-Mariño et al. 2017, 2021; Tang et al. 2020)	3.60 ± 4.28 (Ding et al. 2019), 14,000 (Li et al. 2019)

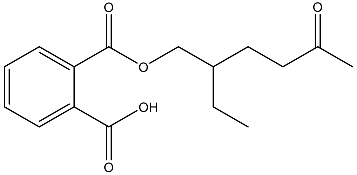
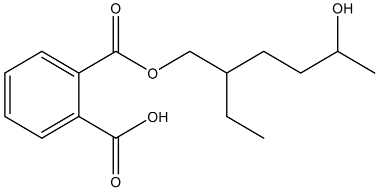
(continued)

Table 4.2 (continued)

Compounds	Acronym	Parent compound	Structure	Concentration (ng/L)	
				Wastewater	Drinking water/bottled water
Mono-n-butyl phthalate	MnBP	DBP		7–867 (González-Mariño et al. 2017, 2021)	9.49 ± 4.77 (Ding et al. 2019), 44,180 (Li et al. 2019)
Mono-2-ethylhexyl phthalate	MEHP	DEHP		5000 ± 8400 (Tang et al. 2020)	4.13 ± 3.63 (Ding et al. 2019), 2450 (Li et al. 2019)

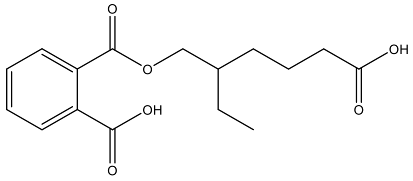
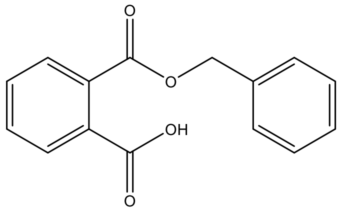
(continued)

Table 4.2 (continued)

Compounds	Acronym	Parent compound	Structure	Concentration (ng/L)	
				Wastewater	Drinking water/bottled water
Mono(2-ethyl-5-oxohexyl) phthalate	MEOHP	DEHP		6–128 (González-Mariño et al. 2017, 2021; Tang et al. 2020)	4700 (Li et al. 2019)
Mono(2-ethyl-5-hydroxyhexyl) phthalate	MEHHP	DEHP		11–170 (González-Mariño et al. 2017, 2021; Tang et al. 2020)	6150 (Li et al. 2019)

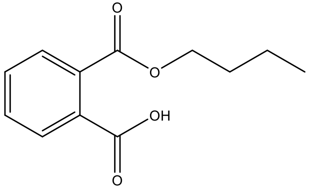
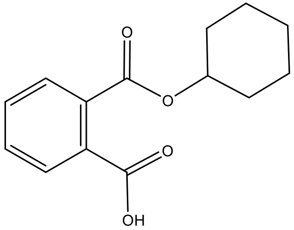
(continued)

Table 4.2 (continued)

Compounds	Acronym	Parent compound	Structure	Concentration (ng/L)	
				Wastewater	Drinking water/bottled water
Mono(2-ethyl-5-carboxypentyl) phthalate	MECPP	DEHP		8–43 (González-Mariño et al. 2017)	8660 (Li et al. 2019)
Monobenzyl phthalate	MBzP	BzBP		< MDL-69 (González-Mariño et al. 2017, 2021; Tang et al. 2020)	110 (Li et al. 2019)

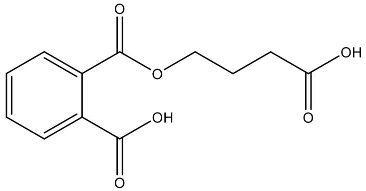
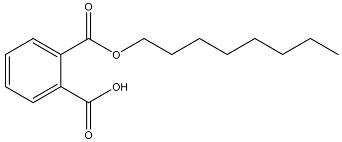
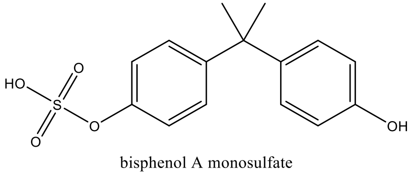
(continued)

Table 4.2 (continued)

Compounds	Acronym	Parent compound	Structure	Concentration (ng/L)	
				Wastewater	Drinking water/bottled water
Monobutyl phthalate	MBP	DBP		1500 ± 740 (Tang et al. 2020)	No data found
Monocyclohexyl phthalate	MCHP	DCHP		< LOQ (Tang et al. 2020)	No data found

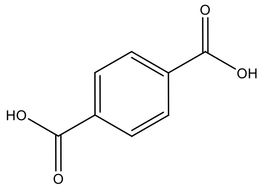
(continued)

Table 4.2 (continued)

Compounds	Acronym	Parent compound	Structure	Concentration (ng/L)	
				Wastewater	Drinking water/bottled water
Mono-3-carboxypropylphthalate	MCPP	DOP/DBP		< LOQ (Tang et al. 2020)	No data found
Monooctyl phthalate	MOP	DnOP		< LOQ (Tang et al. 2020)	No data found
Bisphenol A monosulfate	BPA monosulfate	BPA		700–121,000 (Lopardo et al. 2019)	No data found

(continued)

Table 4.2 (continued)

Compounds	Acronym	Parent compound	Structure	Concentration (ng/L)	
				Wastewater	Drinking water/bottled water
Terephthalic acid	TPA	TPA		444 ± 64 (mg/L) (Zhang et al. 2010)	No data found

LOQ Limit of Quantification; *MDL* Method Detection Limit highest concentration. Phthalate concentration in surface water ranges from 2 to 23,000 ng/L (Tuan Tran et al. 2022). Phthalate transformation products are also frequently detected in wastewater, with the average concentration ranging from < MDL (method detection limit) to 13,000 ng/L (González-Mariño et al. 2017, 2021; Tang et al. 2020). Globally, BPA concentrations range from < 10 to > 10,000 ng/L in wastewater influents, whereas the concentration of bisphenol analogs ranges from <1 to > 100 ng/L (Hu et al. 2019). The concentration of BPA sulfate, a urinary metabolite of BPA exposure to humans, in wastewater ranged from 1 to 121 μg/L in UK wastewater (Lopardo et al. 2019). The concentration of TPA, a monomer of PET plastic, in sludge has been reported in the range of < 0.085 to 75 μg/g, whereas the concentration of TPA in industrial wastewater has been reported as 440 ± 64 mg/L (Zhang et al. 2010, 2019).

4.3 Analytical Challenges in Detecting Plastic Chemical Constituents and Recommendations

The accurate and reliable reporting of levels of plasticizers in the environmental matrices is important to understand the degree of exposure of humans to plastics and the extent of plastic pollution. Phthalate diesters and phthalate monoesters are present in ng/L to μg/L concentration in environmental matrices. As a result, liquid chromatography–mass spectrometry (LC-MS) and gas chromatography–mass spectrometry (GC-MS) are often employed to determine trace concentrations of these compounds (Hidalgo-Serrano et al. 2022). Solid-phase extraction–liquid chromatography–tandem mass spectrometry (SPE-LC-MS/MS) has been primarily employed in the analytical pipeline for the analysis of endocrine disruptors in environmental media (Wee et al. 2022). The mobile phases usually used for the analysis of phthalates in wastewater on LC-MS/MS include water as the aqueous mobile phase and methanol as the organic mobile phase, with acetic acid as mobile phase additives in both the solvents (Kumar et al. 2022a). The analytical columns used to separate analytes in the previous studies include biphenyl columns, C18, phenyl-hexyl, and Kinetex F5 columns (González-Mariño et al. 2017, 2021; Tang et al. 2020; Kumar et al. 2022a). The chromatographic separation of the isomeric analytes (e.g., mono-n-butyl phthalate (MnBP) and monoisobutyl phthalate (MiBP)) on analytical columns is recommended. The LC-MS/MS analysis of bisphenols is usually carried out in negative electrospray ionization mode (ESI) mode using the water and methanol as mobile phase (Caballero-Casero et al. 2016). The addition of mobile phase additives (e.g., acetic acid, ammonium acetate) to the mobile phase has been reported to cause signal suppression. However, derivatization of bisphenols enhances the sensitivity of these compounds by ESI-MS/MS (Caballero-Casero et al. 2016; Owczarek et al. 2018).

There are several analytical challenges that need to be addressed to ensure data reliability. Several sources of phthalate and bisphenols in the laboratory setting may incorporate high background levels, and their accurate quantification may be challenging. Sample contamination with phthalates may occur at all stages of the analytical pipeline, including sample collection, storage, sample preparation, and analysis on the high-end analytical instrument (Net et al. 2015a). The ambient laboratory air carries significant levels of phthalates, including DEHP and DnBP that can contaminate glassware and solvents. All glassware should be rinsed with an appropriate organic solvent and baked at the temperature 450–550 °C overnight to remove adsorbed phthalates on their surface. The use of plastic materials in the phthalate and BPA analytical pipeline should be avoided as they may introduce the background concentrations in the samples. Frequently reported sources of contamination for bisphenols in the laboratory include gloves, plastic and microcentrifuge tubes, solid-phase extraction cartridges, syringe metal needles (due to adhesives in them), solvents, and connections in instruments (Caballero-Casero et al. 2016). The proper selection of gloves is also essential since they are also one of the prominent sources of phthalate contamination in the samples. A recent study has indicated significant phthalate levels (30–40% v/v) of DMP, DEP, DIBP, DBP, DEHP, DEHT, and DINP in vinyl gloves. However, nitrile, neoprene, and latex gloves had less than 0.2% (v/v) of total phthalate loading, indicating nitrile gloves are recommended for laboratory purposes (Poitou et al. 2021). The high-purity organic solvents used in the analysis of phthalates also contain a trace amount (ng/ml level) of phthalates. Organic solvents should be considered the important source of phthalate contamination in the analysis. The minimal use of solvents and further purification of solvents with sorbents may reduce phthalate contamination originating from solvents (Guo and Kannan 2012).

Interestingly, phthalate monoesters may also get introduced into the analytical channel in laboratory settings (Kumar et al. 2022a; Chen et al. 2012; Lien et al. 2018). For reliable quantification, the use of internal standards is highly recommended. The plastic sampling container should be avoided since phthalates may leach from the container during storage and may contribute to the actual phthalate level in the sample.

4.4 Fate of Plastic Chemical Constituents

Phthalates can be removed from environmental matrices by physicochemical processes, including biotransformation and biodegradation, volatilization, photolysis, and sorption (Net et al. 2015b). The fate of phthalates, bisphenols, and their urinary metabolites highly depends on their physicochemical properties under relevant environmental conditions. It has been reported that sorption of chemical compounds to suspended solids may be significant (> 20%) if organic compounds feature a pH-dependent logarithmically transformed organic carbon–water distribution coefficient (log D_{OC}) of ≥ 3.0 and > 5.0 in wastewater influent and effluent (Kumar et al. 2022b). Moreover, increased hydrophobicity of phthalates is expected with an increase in alkyl chain length (Prasad 2021). The aqueous hydrolysis of phthalate at environmental pH is negligible, with half-lives of several years. Although the photolysis of phthalates in surface water decreases the half-lives of phthalates, phthalate esters react with photogenerated hydroxyl radicals to form a potential toxic compound, 4-hydroxy phthalate esters. The biodegradation of phthalate esters varies from a day to several weeks, depending on the density and type of species (Net et al. 2015b).

Phthalates enter the marine ecosystem due to the discharge of plasticizer-laden water from rivers and streams. Marine water salinity is one factor affecting the fate of phthalates in the sea and ocean. The increase in salinity is linked to the high sorption of plasticizers to marine sediments (Prasad 2021). The HMW phthalates may tend to sorb to suspended solids and particulates in the sewer network and during transport in surface water. In the hydrological cycle, particularly, rainfall disperses atmospheric phthalates to surface water bodies, including rivers and lakes.

The combination of anaerobic biodegradation and membrane bioreactor in wastewater treatment plants has been reported to be more efficient in removing recalcitrant phthalate compounds from wastewater (Gao and Wen 2016). It has been reported that wastewater effluents are the major source of phthalates in receiving water bodies (Wang et al. 2020a). For DEHP, sorption to sludge solids is the major removal mechanism in the wastewater treatment system due to its high logarithmic octanol–water partitioning (log K_{ow}) (~7.0). LMW phthalates tend to get treated by bioremediation in the wastewater treatment plant facility, whereas HMW phthalates are more readily removed by sorption to sludge solids (Dargnat et al. 2009).

Membrane filtration techniques, including microfiltration, ultrafiltration, nanofiltration, and reverse osmosis, utilizing general principles of adsorption, size inclusion, and electrostatic interaction, generally show $> 95\%$ removal of phthalates from water (Zolfaghari et al. 2014).

The activated sludge process is highly effective in the almost complete removal of bisphenols. However, BPZ, BPAP, and BPAF are recalcitrant compounds due to the complexity of chemical structures (C–F bond in BPAF) (Qian et al. 2021). Two transformation products of BPA, bisphenol A monomethyl ether (BPA-MME) and bisphenol A dimethyl ether (BPA-DME), have been reported recently in wastewater treatment plants and surface water bodies. The methylation of BPA occurs in both wastewater and surface water bodies (Ashfaq et al. 2018).

A recent study investigated the stability of phthalates and phthalate metabolites in laboratory sewer reactors. The study found that phthalates are transformed in the sewer reactors into their respective monoesters, and phthalate monoesters are prone to get converted to other compounds (He et al. 2021). This study further indicated that phthalate monoesters might not be considered the unique biomarker for phthalate exposure in WBE studies.

4.5 Conclusions and Recommendations

Plastics and their chemical constituents may impose a significant health impact when humans are exposed to them. Plastics and their chemical ingredients are ubiquitously detected in wastewater, surface water, and drinking water in concentrations ranging from ng/L to µg/L. The occurrence, fate, and mobility of plastic chemical constituents in aqueous media depend on compounds' physiochemical properties and relevant environmental conditions. The precise laboratory analysis of plasticizers is a challenging task and requires profound analytical skills to perform the analysis and report the data. Accurate measurement of plasticizers and related chemicals is the foremost concern in environmental and human health biomonitoring since reported data may be used for framing risk assessment decisions. Precautionary steps should be taken to avoid sample contamination with phthalates and bisphenols in laboratory settings. It is recommended to explore more into the fate and toxicity of transformation products of phthalates and bisphenol analogs in environmental waters. Future studies should also focus on the environmental fate of emerging non-phthalate plasticizers since they may potentially impose ecological risks.

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Chapter 5
Occurrence of Phthalates in the Environment, Their Toxicity, and Treatment Technologies

Ravindra Singh, Alok Sinha, and Dharmendra Singh Ken

Abstract In recent years, phthalates have attracted attention as an emerging contaminant that adversely affects the environment and human life. Phthalates are found in various kinds of day-to-day products, like personal care products (soaps, shampoos, detergents, etc.), cosmetics, lubricants, medical tubing adhesives, vinyl flooring, etc. Different kinds of phthalate compounds that have been detected in the environment like diethyl phthalate (DEP), dimethyl phthalate (DMP), di(2-ethylhexyl) phthalate (DEHP), dibutyl phthalate (DBP), di-isobutyl phthalate (DIBP), butyl benzyl phthalate (BBP), di-isononyl phthalate (DINP), and dinoctyl phthalate (DNOP). Because of their extensive usage in day-to-day life and their property to leach, phthalates have been detected in groundwater, surface water, wastewater, and even in drinking waters. The primary source of their occurrence in water is the discharge from industries and domestic wastewater. It has become important to treat water contaminated with phthalates before it is discharged into an aqueous environment. Various advanced wastewater treatment methods like adsorption, membrane processes, advanced oxidation processes (e.g. photocatalysis, photo-Fenton, ozonation), and biological treatment processes have been successful to address this problem with wastewater sufficient removal efficiencies ranging from 70 to 90%. This chapter highlights the occurrence of phthalates in the different matrices of the environment and their harmful effects on human life. It also discusses the different treatment methods being used for the removal of phthalate esters. Being a top-priority pollutant, and with its serious harmful impact on human life, there is an urgent requirement to develop proper remediation strategies for phthalate treatment.

Keywords Phthalates · Photocatalysts · Diethyl phthalate · Dimethyl phthalate · Di(2-ethylhexyl) phthalate · Dibutyl phthalate · Di-isobutyl phthalate · Butyl benzyl phthalate · Di-isononyl phthalate · Dinoctyl phthalate · Advanced treatment methods · Emerging contaminants

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5.1 Introduction

There has been rapid development in recent decades in the field of industrialization, which has led to an increase in the problems associated with the environment. The proliferation of toxic compounds released from the industries into the environment is one of the serious problems that has attracted attention over the years. Phthalates esters (PAEs) are one of the major pollutants being released from the industrial sector and have been observed to impact the natural environment on a large scale. The term "phthalates" refers to the di-ester derivatives of phthalic acid representing a group of structurally related compounds. They are odourless, colourless, tasteless, and generally exist in liquid form at a large temperature range (Tran et al. 2021). Figure 5.1 shows the chemical structure of different phthalate compounds. The chemical structure of a phthalate compound can differ in physical and chemical properties according to the different alkyl groups attached.

Phthalates have got immense use in different household products like cosmetics, clothing, toys, food packaging, etc. These are also used in the industrial sector (paints, lubricants, adhesives, electronics, etc.) and the agricultural sector (fertilizers, insecticides, pesticides, etc.). Because of its vast application in every field, phthalate can be found in every matrix of the environment. According to the report by the Organization for Economic Cooperation and Development, worldwide use of phthalates reaches about 5.5 million metric tonnes in a year (OECD 2018).

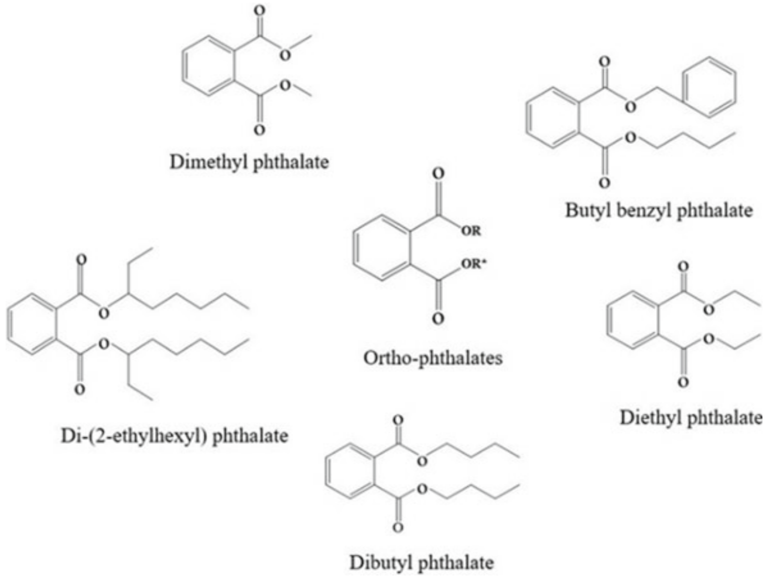

Fig. 5.1 Chemical structures of different PAE compounds (Modified and reproduced with authorization from Pang et al. (2021), Copyright 2022, Elsevier)

Phthalates can be grouped into different categories according to their weights. Low molecular weight phthalates are that having 3–6 carbon chains like dimethyl phthalate (DMP), diethyl phthalate (DEP), and dibutyl phthalate (DBP) and high molecular weight phthalates with 7–13 carbon chains like di(2-ethylhexyl) phthalate (DEHP), dioctyl phthalate (DOP), and dinoctyl phthalate (DNOP) (Schettler 2006). Phthalate esters or phthalates are not easily degradable because of the long chain structures and high molecular weight, which makes them recalcitrant and hard to degrade naturally. Also, these compounds are not bound to the host products with the covalent bond, hence leach out easily as vapours or in the particulate form based on whether they are volatile or semi-volatile and contaminate the air, water, and soil and find a path to affect human life.

5.2 Occurrence of Phthalates in the Environment

Phthalates can leach out or evaporate easily and, thus, are detected in water, soil, and air all over the world. It has become important to study the fate and movement of these compounds in the environment for proper evaluation and analysis of the exposure risks associated. Recently, different research works have been performed for the detection of phthalates in different mediums of environments (Tables 5.1, 5.2, and 5.3). Fromme et al. (2002) reported the presence of phthalates in surface water (22.7 mg/l) and wastewater (288 mg/l). A study from Serbia reported six types of phthalates with concentrations varying from 0.0002 mg/kg to 4.82 mg/kg in the soils of Novi Sad with DEHP being the highest in concentration. The highest concentration of total phthalate concentration was detected in City park (2.12 mg kg^{-1} in soil and 5.45 mg kg^{-1} in street dust) (Škrbić et al. 2016). In a similar study, DEHP and DPB were detected in the soil in China (Lü et al. 2018) and Denmark (Laturnus and Grøn 2007).

Daily exposure is not only limited to mediums like water and soil, but phthalates have also been detected in air. Zhang et al. (2014) investigated the presence of phthalates in the indoor environment. He examined ten families from Tianjin, China, and concluded that six kinds of phthalates were present in the indoor environment (concentration ranging from 13.878 to 1591.277 ng/m^3 in PM_{10} and 7.266–1244.178 ng/m^3 in $PM_{2.5}$). DPB was found to be dominant followed by DEHP (the median values were 573.467 and 368.364 ng m^{-3}, respectively, for DPB and DEHP). Wang et al. (2008) detected six kinds of phthalates in the gaseous phase in the urban part of Nanjing, China (DMP (10.1 ng m^{-3}, average), DEP (3.4 ng m^{-3}), DBP (58.8 ng m^{-3}), BBP (3.2 ng m^{-3}), DEHP (20.3 ng m^{-3}), and DOP (1.2 ng m^{-3})), which was found to be approx. 3.5 times more than concentration of phthalates in suburban areas. Similarly, Fromme et al. (2013) confirmed the occurrence of phthalates like DIBP, DBP, and DEHP (median values of 468, 227, and 194 ng/m^3, respectively) in the indoor air in German day-care centres. High DBP was detected in deep waters offshore of France with total concentrations being 75.3 ng/l offshore in surface water to 1207.1 ng/l a few metres above the bottom of Marseilles Bay

Table 5.1 Occurrence of different phthalate compounds in water across the world (ng/l)

Country	DEP		DBP		BBP		DEHP		References
	Min	Max	Min	Max	Min	Max	Min	Max	
Surface water									
India	36	520	0	372	5.4	145	0	822	Selvaraj et al. (2015)
Netherlands	70	2300	7	310	10	1800	900	5000	Vethaak et al. (2005)
Netherlands	0	0	23	450	0	0	280	650	Peijnenburg and Struijs (2006)
France	71	181	67	319	0	0	160	314	Dargnat et al. (2009)
China	14	123	235	4430	0	12	237	1600	Zeng et al. (2009)
Austria	0.02	0.27	0	0.27	0	0.33	0.45	24	Clara et al. (2010)
China	10	211	105	286	10	21	10	836	He et al. (2011)
Malaysia	10	49	47	213	4	13	66	389	Santhi and Mustafa (2013)
Spain	0	0	0	554	0	0	0	0	Domínguez-Morueco et al. (2014)
China	1	7	2	12	0	4	2	12	Gao et al. (2014)
Drinking water									
India (Okhla)	0	198	0	317	0	633	0	257	Das et al. (2014)
India (JNU)	0	7	0	0	0	0	0	146	Das et al. (2014)
Germany	0	200	0	380	0	20	0	50	Luks-Betlej et al. (2001)
Poland	0	160	0	64	0	50	0	60	Luks-Betlej et al. (2001)
Japan	0	5	6	93	0	0	0	5220	Hashizume et al. (2002)
Greece	0	0	0	0	0	0	0	0.64	Psillakis and Kalogerakis (2003)
China	0	3	0.11	93	0	7	7	280	Shi et al. (2012)
China	0	55	5	450	0	0	129	6570	Liu et al. (2013)
Spain	0	381	0	633	0	0	0	0	Domínguez-Morueco et al. (2014)
Taiwan	0	2	0	35	0	1	0	172 k	Liou et al. (2014)

(Paluselli et al. 2018a). In a study in China, 8 different phthalates were detected in the urban lakes in Guanzhou with mean concentrations of 2.91 μg l^{-1} and 20.85 μg g^{-1} dry weight, in water and sediments, respectively (Zeng et al. 2008). DBP and DEHP have been reported to be found in fishes in a study by Peijnenburg and Struijs (2006). Mean values around 1.8 μg kg^{-1} for wet fish were found for both DEHP and DBP (Peijnenburg and Struijs 2006).

The movement of phthalates from one phase to another has given a new challenge in the detection quantification, monitoring, and removal process of phthalates

Table 5.2 Phthalate concentration in indoor atmosphere

Country	Concentration ng/l				References
	DMP	DEP	DEHP	DBP	
Germany	436.0	643.0	156.0	–	Fromme et al. (2004)
USA	–	330.0	110.0	–	Rudel et al. (2010)
France	8.2	157.0	–	–	Blanchard et al. (2014)
Norway	69.0	496.0	–	–	Sakhi et al. (2019)
China	2560.3	321.3	9028.8	–	Huang et al. (2020)
Japan	42.0	74.0	323.0	–	Yoshida et al. (2020)
Saudi Arabia	–	17.0	520.0	320.0	Ali et al. (2021)
Vietnam	26.5	66.5	14.2	–	Anh et al. (2021)

Table 5.3 Phthalates concentration found in soils and sediments

Country	Location	Soil and sediments (concentrations in µg/kg dry weight)				References
		DMP	DEP	BBP	DEHP	
India	Kaveri River	1.60	16.50	2.60	278	Selvaraj et al. (2015)
South Africa	Jukskei River	0.22–12.80	2.48–44.80	–	6.54–3660	Sibali et al. (2013)
India	Gomti River	316	137	–	947	Srivastava et al. (2010)
Taiwan	Rivers	–	100–1100	1800	500–23,900	Yuan et al. (2002)
China	Aquaculture fish ponds sediment	1–14	50–160	20–150	1310–26,600	Cheng et al. (2019)
Taiwan	Kaohsiung Harbour	–	–	–	400–34,800	Chen et al. (2013)
China	Guanting Reservoir	94.50	0.20–89.5	380	278	Zheng et al. (2014)

(Gao and Wen 2016). Researchers have also investigated the presence of phthalates in wastewater treatment plants (WWTPs). Salaudeen et al. (2018) detected six phthalate compounds majorly DBP in influents (2.7 and 2488 $\mu g\ l^{-1}$) and effluents (4.90–8.88 $\mu g\ l^{-1}$) of wastewater treatment plants in South Africa. Çifci et al. (2013) analysed the presence of phthalates in Istanbul and Turkey and detected the occurrence of five phthalate compounds (1.4–2.7 mg/kg dry weight) with DEHP being the highest in concentration. DEHP was also detected in high concentration in all the WWTP samples (3.4–34 $\mu g\ l^{-1}$ in influent 0.083–6.6 $\mu g\ l^{-1}$ in effluent) in Austria in a study by Clara et al. (2010).

5.3 Exposure of Phthalates to Humans

Recently, the use of phthalate compounds has increased at an alarming rate as these are used in day-to-day used products. So human life is easily exposed to these compounds via many routes like inhalation from ambient air, ingestion of food, skin adsorption from personal care products, and many more. Figure 5.2 shows the different routes of exposure of human to phthalates. Many studies have detected the presence of phthalates in food items and personal care products (Pereira et al. 2019). Food is reported to be a major contributor (about 67%) to human exposure (Das et al. 2014). Similar studies were done to analyse the role of food and clothing in the exposure of humans to phthalates (Wormuth et al. 2006; Gong et al. 2011). Tran and Kannan (2015) showed that food packaging materials also contribute to DEHP exposure in humans. Because of the large exposure of humans to various sources, daily intake of phthalates into humans has reached a value of 70 μg/kg/d (Net et al. 2015). In a study, Ji et al. (2014) reported that diet has been an important source of DBP, DEP, DOP, and DEHP exposures. Likewise, water ingestion was the main source of DBP, DOP, and DEHP exposures. Contaminated air is also one of the main sources of DMP, DEP, and DBP exposures.

Koniecki et al. (2011) detected the presence of 18 different phthalates in 252 daily-use items with DEP, DBP, and DEHP being the highest in use. Xu et al. (2020) investigated the packaging bags from different delivery companies in China. The

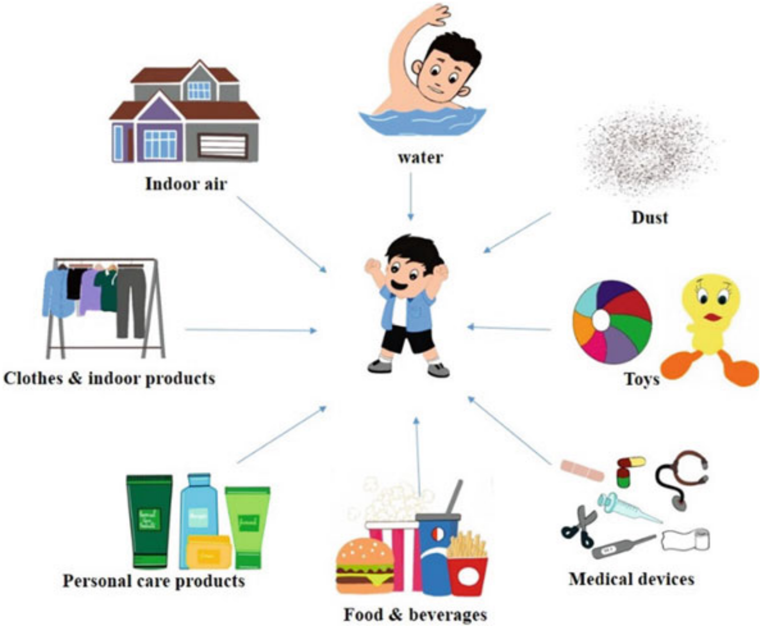

Fig. 5.2 Different routes for phthalate exposure

concentration of phthalates leaching out from these bags ranged from 181.44 to 5320.64 ng/g which can be a potent source of phthalates exposure to human health. Paluselli et al. (2018b) analysed that DBP and DiBP were the main compounds leached out from polyethylene bags and DMP and DEP were the main compounds being leached out from PVC cables.

Further, there can be an indirect exposure of humans to phthalate compounds as these can leach out and mix with other products like drinking water and food. Li et al. (2019a) reported the presence of 21 phthalate compounds in water samples packed in PET bottles with DMP, DiBP, and DBP as the main compounds. The study concluded that PET bottles can be the reason for the presence of these compounds in the water. Indoor dust can also be considered a potential source of phthalates exposure. Li et al. (2019b) detected the presence of DEHP in the indoor dust sample in the bedroom as a major component. Wormuth et al. (2006) investigated the daily exposure to phthalate compounds in various age groups and found that children and infants were more prone to the phthalates exposure as compared to adults. One of the reasons for this could be the cotton garments generally worn by kids and infants that adsorb phthalates easily when compared to other fabrics.

5.4 Toxicity of Phthalates and Their Effect on Human Life

Phthalate-containing items are produced on a large scale worldwide and possess toxic characteristics. The exposure to these compounds is also very wide. Several studies have been carried out to check the harmful effects on human health and the environment. Table 5.4 gives a small overview of the effects of phthalates on human life. Phthalates have an endocrine-disrupting effect and thus disturb the hormone synthesis process causing various problems. Exposure to phthalate in pregnant women causes problems for both the woman and the child like the risk of delivery preterm can increase on exposure to phthalate compounds. A study by Wang et al. (2018a) showed that phthalate toxicity can even lead to reproductive failure. Toxicology studies also showed the increased risk of asthma and respiratory tract infection on exposure to high molecular weight phthalates (Gascon et al. 2015). Further, phthalate exposure was investigated to cause developmental problems in children. Olesen et al. (2018) reported that there can be a negative effect on the language development of children on phthalate exposure. Similarly, inverse relation was found between the phthalate metabolites and IQ scores in a study done in South Korea by Cho et al. (2010). Other research also led to the conclusion that phthalates can cause other health issues like hypertension, thyroid concentration, and many more (Zhou et al. 2019; Zhang et al. 2021).

Other than human life, phthalates can also have an adverse impact on flora and fauna. They can bio-accumulate in the long term and can cause negative impacts on the environment. As per the literature survey, EPA has provided a guideline for the concentration of phthalates in the water (Table 5.5) (https://www.epa.gov/sites/default/files/2019-03/documents/ambient-wqc-phthalateesters-1980.pdf).

Table 5.4 Toxic effects of phthalates

Toxic effects of phthalates	
Autoimmune diseases	Thyroid hormone production and secretion, allergy, asthma
Cancer	Skin, liver, prostate, ovarian, cervical
Metabolic disorders	Type 2 diabetes, atherosclerosis
Gynecological issues	Premature birth, PCOD, infertility
Andrological issues	Gynecomastia, disrupted spermatogenesis, infertility
Others	Non-alcoholic fatty liver disease

Table 5.5 Guidelines for the concentration of phthalates in water

Phthalate	Through water and contaminated aquatic organisms alone	Through aquatic organisms alone
Dimethyl phthalate	313 mg/l	2.9 g/l
Diethyl phtha1ate	350 mg/l	1.8 g/l
Dibutyl phtha1ate	34 mg/l	154 mg/l
Di(2-ethylhexyl) phthalate	15 mg/l	50 mg/l

Looking at the increasing use of phthalates and their exposure and effect on human health, there has been an increase in the technologies for the efficient removal and degradation of these compounds. This chapter further explores the different methods that are being used for phthalate removal.

5.5 Movement of Phthalates in the Environment

Because of the worldwide use of phthalates in different sectors, phthalates are found to be present in every matrix of the environment. This makes the analysis of the fate and transportation of the phthalates important for the research. Phthalates leach out from different products and then travel to different mediums via different routes as shown in Fig. 5.3 and contaminate the environment. The main source of phthalate entry into the environment matrix includes manufacturing, distribution, consumption, and discharge of phthalate-containing compounds into the environment. The transportation of these compounds depends on various physical, chemical, and environmental conditions.

Anthropogenic activities like industrial activities, transportation, etc. affect the distribution of phthalates in the environment resulting in a higher concentration of these compounds in urban areas. DnBP and DEHP are the common phthalates predominantly found in the urban atmosphere. Generally, long-chain phthalates are found to be adsorbed on particles, while short-chain phthalates are found in the gaseous phase. Phthalate concentration in the indoor environment depends on the

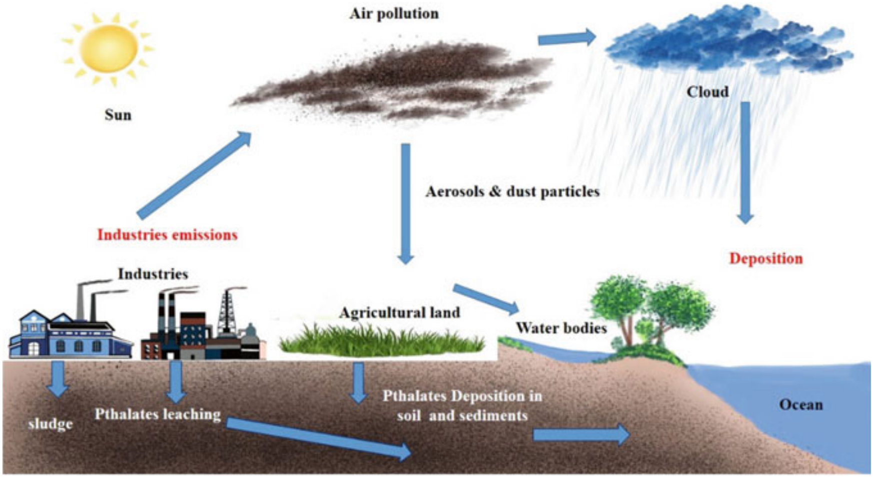

Fig. 5.3 Movement of phthalates in different matrices of the environment

sources present and the activities of the household. Materials used, lifestyle, working conditions, etc. are some factors that contribute to the phthalate concentration in the indoor air. According to Bi et al. (2015), BBP and DEHP constituted approximately 46% of indoor phthalate concentration. Over time, phthalate compounds get adsorbed on the surface of particles, and household products, and affect the fate and movement of phthalate in the indoor environment.

The outdoor environment is open, and thus, the movement of phthalates gets affected by many factors. Photodegradation, photolysis, and gas–solid partitioning are some of the phenomena that lead to phthalate degradation in the outdoor environment. Further, phthalate in the atmosphere enters other media like soil and water through atmospheric precipitation.

Phthalates further move to the water environment via the discharge of domestic or industrial wastewaters. Phthalates that enter the surface sources like rivers, streams, etc. further move to the marine environment. The distribution of phthalates in the aquatic environment is affected by different processes like photolysis, hydrolysis, sediment–water adsorption/desorption, and microbial metabolism.

The presence of phthalates in wastewater has been studied in a broader aspect. Gani et al. (2017) detected phthalates in domestic water with average concentration varying from 1 to 100 μg/l with DEHP in the highest amount. In a similar report by Salaudeen et al. (2018), concentration of phthalates was higher in wastewater reaching a value of 288.95 μg/l. Wastewater treatment plants are said to be a major source of phthalate discharge into the environment. A high concentration of phthalates can be found in the sewage sludge coming from various domestic and industrial sources. Staples et al. (1997) reported the concentration to be varying from 12 to 1250 mg/kg in a sewage sludge sample. Various conditions for the treatment like oxygen concentration, temperature, etc. affected the biodegradation of these compounds.

Phthalate pollution is not only limited to the surface and marine waters, but it can leach and enter the groundwater sources. The high amount of phthalate compounds found in the landfill leachate further seeps into the groundwater causing groundwater contamination. Wowkonowicz and Kijeńska (2017) showed high concentrations of DMP (0.6–4.72 μg/l) and DEHP (1.3–73.9 μg/l) from old landfills. Landfill of household waste can lead to the accumulation of phthalates and that can further seep into the different environments causing a potential risk to the environment.

Phthalates pollution has also affected the soil medium. Activities like mulching and the addition of chemical products like fertilizers contribute to phthalate discharge in the soil. In a report by Ferreira and Morita (2012), phthalate concentration was found up to 3349 mg/kg in the soil in a contaminated soil sample. Distribution of phthalates varies according to the soil type, weather conditions, physical–chemical properties, and microbiological conditions. DEHP, DMP, and DEP are major phthalates found in contaminated soil. The presence of these toxic compounds not only affects the soil but also impacts the organisms and humans by entering the food chain.

5.6 Method of Analysis of Different Types of Phthalates

Looking at the recent growth of the use of phthalate compounds and their harmful effects, there is a need to develop methods for the proper treatment. And the effective treatment and disposal of these toxic compounds require proper analysis and quantification. The identification and quantification of phthalate esters in different mediums consist of two steps: the first is the sample preparation, and the second is the determination and quantification. The selection of the appropriate method for the analysis largely depends on the physical and chemical properties of the pollutant. A few methods for the direct analysis of phthalates include gas chromatography, liquid chromatography, micellar electrokinetic capillary chromatography, Fourier transform infrared spectroscopy, UV spectrophotometry, nuclear magnetic resonance methods, etc.

Gas chromatography and liquid chromatography are generally coupled with other methods for specific identification of the target pollutant. Generally, GL and LC are combined with a mass spectrometer (MS) for identifying phthalate compounds in foods and drinks. A mass spectrometer is an analytical tool that measures the mass-to-charge ratio of the sample for identifying and quantifying the unknown compound from the sample. Gas chromatography (GC) analysis is a frequently used method for the analysis of phthalates (Sanchis et al. 2017). Phthalate esters like DBP, BBP, DEHP, etc. in non-carbonated water were identified in a work by GCMS technology (Farajzadeh and Mogaddam 2012). MS is generally combined with GS because of the high sensitivity and specificity of MS, which adds the advantage of detecting several phthalates present in lower concentrations in foods and beverages using electron impact ionization (Sanchis et al. 2017). GS-MS has many advantages like high resolution and sensitivity and reduced time of analysis, but has the limitation that it is a destructive technique and has a high cost of analysis. Liquid chromatography (LC) analysis provides greater selectivity for phthalates. Just like GCMS, it is also combined with MS. In comparison with GC, LC gives ease in sample preparation, but provides lower sensitivity. The limitation of LC is that it shows a lower efficiency when compared to GC (Jia et al. 2014).

Micellar electrokinetic capillary chromatography (MEKC) is another method of analysis of phthalates that can be used in the place of HPLC or GC because of its higher efficacy, less use of the reagents, and rapid analysing capacity. MEKC has been used for PAE determination from landfill leachate and water samples (Sun et al. 2014), soil (Guo et al. 2005; Lin et al. 2010). Another method of phthalate detection is Fourier transform infrared spectroscopy (FTIR). It is a simple method of infrared spectroscopy. In this, IR radiations are passed through the sample, where some rays are absorbed and some are transmitted. The spectrum obtained gives the absorbance transmission pattern, giving the unique fingerprint of the sample which is used for the analysis. This method provides high speed, and sensitivity is less time-consuming and has mechanical simplicity. The leaching of PAEs from plasticized polymers is often examined by FTIR (Zhang and Chen 2014). FTIR can be also used to obtain a prescreening to determine gross PAE contamination with accurate measurements as low as 0.1% (Higgins 2013; Rijavec et al. 2022). To date, applications are limited, but the couplings are possible with separation techniques (e.g. GC) or a second detection for considering new applications.

The calorimetric analysis is also one of the techniques being used for the analysis of phthalates, with the help of a colour reagent (Zhang et al. 2011; Guo et al. 2021). This method is widely used in medical laboratories and industries for the analysis of industrial water treatment. It is cost-effective, highly sensitive, and less time-taking method of analysis. Nuclear magnetic resonance (NMR) analysis uses magnetic fields for the detection of compounds (Monakhova et al. 2011). This method can be used to analyse the physical, chemical, and biological properties of any compound and also its molecular structure. This method is widely used for the detection of phthalates. Direct methods like GC and LC have been widely used for the determination of phthalates but have too high instrumentation cost. So some simple methods have been developed for the detection of phthalates. This includes molecular imprinting technology (MIP) and immunoassay-based techniques.

5.7 Treatment Technologies for Phthalate Removal

People are exposed to phthalates through different variety of products that are part of their everyday routine. Hence, there has arisen an urgent need to develop new technologies for the effective removal and degradation of these compounds from the environment. Traditional methods that are used for water treatment are not very efficient for the removal of phthalates because of recalcitrant and stable nature of these compounds. Table 5.6 summarizes the advantages and disadvantages associated

Table 5.6 Advantages and disadvantages associated with each method of phthalate removal

Method	Advantage	Disadvantage
Adsorption	• Sludge-free process • Clean removal of pollutants • Large-scale plant is not required • Adsorbents can be regenerated and reused	• Problem in the disposal of adsorbed pollutants
Coagulation/flocculation	• Simple and cost-effective	• Generates high amount of sludge • Requires high amount of chemicals • Presence of heavy metals in the sludge can be hazardous
AOP	• Zero discharge of waste • Complete destruction of pollutants into simpler substance	• Costly • Production of harmful reaction intermediates
Biological treatment	• Cost-effective • Easy to operate • Low maintenance	• Requires larger area • Time-consuming • Little efficiency
MBR	• High efficiency	• Costly • Problem in disposal of filtrate

with different methods for the treatment of phthalate esters. Liu et al. (2013) analysed the efficiency of the conventional methods for the treatment of phthalates from two water systems in Harbin, China. The efficiency was observed to be 25.8–76.5% for DMP and DOP which is very low.

Several studies are being carried out for developing new methods for the removal of phthalate compounds. Many methods have been analysed for the purpose like membrane processes (Bodzek et al. 2004), biological processes (Jianlong et al. 2004), etc., but advanced oxidation processes like photolysis (Lau et al. 2005), Fenton process (He et al. 2009), ozonation (Li et al. 2009), and photocatalysis (Sin et al. 2012) seem to be promising for the removal of these recalcitrant products.

5.7.1 Conventional Physical and Chemical Methods

Physical and chemical methods include the conventional techniques that are used for water treatments like adsorption, coagulation, and flocculation. Each process has its own advantage and disadvantage. These processes are basically common traditional methods and has not been very effective for lower concentration of pollutants. Also, these methods do not completely mineralize the phthalate compounds.

5.7.1.1 Adsorption

Adsorption is one of the most common physico-chemical processes for the treatment of wastewater. It is a process in which the pollutant is accumulated on the surface of the adsorbing material. The advantage associated with this process is the sludge-free and clean removal of the pollutant. Also, large-scale plants are also not required for this system. Adding to it, the adsorbents can be regenerated and reused, and phthalates are recovered. The important parameter that influences the whole adsorption system is the surface area of the adsorbent. Adsorbents like biochar and activated carbon are generally used because of their large surface areas. The process is further affected by the temperature and pH of the system. Temperature controls the thermodynamics of the system, and pH influences the surface charge of the adsorbents. Efficient adsorption depends on the type of functional group attached. Phthalates are basically structures with ester groups having benzene rings and alkyl chains of different lengths. Depending on the kind of group attached, different mechanisms of adsorption can take place. The main interactions involved for the phthalate adsorption on the adsorbents are as follows:

(a) Hydrophobic interaction: Phthalates are generally hydrophobic in nature. Longer alkyl chain phthalates have more hydrophobicity (having high K_{ow} value) and hence are said to be easily adsorbed.
(b) Ester group interaction: Ester group attached with the phthalate also affects the adsorption. The kind of ester group attached acts as an electron acceptor coming from the adsorbent and generates a л–л electron donor–acceptor bond from the adsorbent. DMP and DEP are said to be more efficient in forming the л–л interaction (Wang et al. 2010). Other than this, hydrogen bonding with specific groups also facilitates adsorption.
(c) Benzene ring interaction: л electrons from the adsorbent can be for л–л stacking with the л electrons present in the benzene ring of the esters, though this may be significantly weaker than the above-mentioned techniques.
(d) Electrostatic interaction: Phthalates can have attraction or repulsion interaction with the charged adsorbent according to their pKa value.

These different interactions generally coexist in the adsorption system and rarely occur independently. Also, there may be different types of phthalates in the water that increases the challenge for the selection of proper adsorbent for the treatment process. Table 5.7 shows different works done using different adsorbents for the removal of phthalates. The first research for the adsorption of phthalate was done by Sullivan et al. (1982). He studied the adsorption of DBP and DEHP on some clay minerals. Now many more adsorbents have come into use like activated carbon, biochar, carbon nanotubes, chitosan, etc. Activated carbon has been analysed by researchers for the adsorption of phthalates in China. One of the research by Tang et al. (2017) used AC derived from the coconut shells for DBP removal and obtained sufficient efficiency for the DBP removal but resulted in the change of flavour. Also, the phthalate esters and acids adsorbed caused corrosion of the tanks. Graphene is also a good option in the field of adsorption for phthalates removal (Yang and Tang 2016). More than 80% efficiency was obtained for DBP and DEHP removal on 0.1 g/l graphene.

Modifications are employed to these adsorbents for enhancing phthalate removal efficiency. For example, Shaida et al. (2018) used low-grade coal modified by chitosan as an adsorbent for the removal of DEP. Qmax observed in the process was 42.67 mg/g, showing a significant improvement in DEP adsorption (Shaida et al. 2018). Similarly, in a work by Chen and Chung (2006), adsorption by chitosan was carried for DHP giving a capacity of 1.52 mg/g, and 75% chitosan was recovered with the mixture of ethanol and water in the further process. The point to be noted in the process of adsorption is the regeneration of adsorbents which becomes difficult to separate in case of nanoscale adsorbents. Wang et al. (2018b), Yin et al. (2014) performed a modification of the graphene oxide with a hydrophilic and hydrophobic group which enhanced the recycling of the adsorbents. Modifications in adsorbents can lead to the efficient removal of phthalates. For example, Cu-impregnated carbon gave 2.1 times high adsorption when compared to plane carbon (Adhoum and Monser

Table 5.7 Overview of different adsorbents for the removal of phthalates

Phthalate	Adsorbent	Experimental conditions	Efficiency	References
DEP	9:1 coal chitosan composite	Adsorbent dose 4 mg/l, pH 5.8, contact time 4 h	91.1%	Shaida et al. (2018)
DEP	Zeolite/Fe_3O_4 magnetic nanocomposite (MZNC)	Adsorbent dose 50 mg/l	99.7%	Mesdaghinia et al. (2017)
DEP and phthalic acid	ZIF-8 (zinc-methylimidazolate framework-8)	Adsorbent dose 5 mg/50 ml	654 mg/g much higher than commercial activated carbon or other metal organic framework	Khan et al. (2015)
DMP	Magnetic strong base anion-exchange resin named MAER-OH	0.1–0.9 g adsorbent DMP concentration 0, 20, 40, and 50 mg/l	134.9 mg/g	Li et al. (2018)
DBP	Fe_3O_4@powdered activated carbon (PAC)	Adsorbent dose of 0.2 g/l, pH = 5, DBP concentration of 8 mg/l, contact time of 90 min	87.55% in synthetic wastewater	Nozari et al. (2022)
DEHP	Fe_3O_4@MIPs	Initial concentration 100 mg/l	17.21 mg/g	Zulfikar et al. (2022)

2004). Similarly, the efficiency of activated carbon for adsorption increased 1.7 times when combined with TBA. Adsorption of phthalates is not only limited to carbonaceous adsorbents, but different mineral and polymer adsorbents have also been used for phthalate removal.

Phthalates have hydrophobic nature; hence, it becomes difficult to mineralize them in wastewater treatment plant units because of their insoluble nature. Thus, there is a requirement to work on the phthalate adsorption on suspended organic matters and their degradation. Also, there is a need to work on the improvement of adsorption efficiency and the regeneration of the adsorbent. The problem also comes in disposing of the adsorbed pollutant. Hence, the focus shifts to other methods for phthalate removal.

5.7.1.2 Coagulation/Flocculation

Coagulation/flocculation method is generally adopted when the particles are suspended in the water in the colloidal form. This method is used to agglomerate fine suspended particles and colloidal-sized particles that are present in the wastewater into larger-sized particles in order to reduce the turbidity or the organic and inorganic content present in the water. This process mainly consists of two stages: first is the mixing of the coagulating agent into the solution via agitation, and the second is the flocculation or agglomeration of the small particles into bigger-sized particles. Later, these flocs are allowed to settle down and removed, and the supernatant is sent for further processes or for discharge as per requirement. This process is relatively simpler in design and has lower energy consumption and thus is used in many industries.

The general method involves the addition of a coagulant into the wastewater that changes the physical behaviour of the suspended impurity. Colloidal-sized particles generally remain suspended in water because of their surface charge. Similar nature of the suspended charged particles makes them repel each other and prohibit their settlement. In this method, different kinds of coagulating and floc forming agents are added to the wastewater which facilitate the destabilization of colloidal particles by charge neutralization allowing them to agglomerate and settle down. Coagulation allows the charge neutralization of the suspended colloidal particle, and flocculation allows them to bind together and settle down. Four mechanisms are involved for the agglomeration of the particles and its settlement depending upon the nature of the pollutant and the coagulant dose, namely double-layer compression, charge neutralization, colloid entrapment, and intraparticle bridging. The flocs formed not only settle down the colloidal impurity but inter-particle bridging of flocs can also take away other impurities as well. This method is generally effective for the removal of heavy metals, but it is not generally used for the treatment of organic pollutants. Zheng et al. (2009) used aluminium chloride as coagulating reagent for phthalate removal from a landfill leachate and reported 30% removal efficiency from fresh leachate and 50% from stabilized leachate. Zhang and Wang (2009) worked on phthalate removal using the complexation—flocculation process using three different coagulants—ferric chlorides, aluminium sulphate, and polyaluminium chloride (PAC). PAC was found to give better results for phthalate removal. Though being a very common method for water treatment, this method is not very cost-effective as it requires a large amount of chemicals. One more drawback that follows is the generation of high amount of sludge which can be hazardous because of the presence of other heavy metals if present and would require more cost for handling. Hence, a little work has been done using this method for phthalate removal.

5.7.2 Advanced Oxidation Methods

Advanced oxidation processes (AOPs) have attracted the attention of scientists for the oxidation of a wide range of products. It employs hydroxyl radicals for the oxidation of recalcitrant compounds. Being a zero-discharge technology, these methods are getting huge amounts of research in the world of science. Theoretically, advanced oxidation processes can fully oxidize the organic compounds and mineralize them to carbon dioxide and water.

Advanced oxidation processes use different reagents like hydrogen peroxide, ozone, and Fenton reagent and produce hydroxyl radical which is highly oxidizing in nature and oxidizes the targeted pollutant and converts it into simpler substances. This process can be performed in the presence of UV light, ultrasounds, and catalysts, which enhances the speed of the oxidation process.

5.7.2.1 Photocatalysis

Photocatalysis has been a promising technology for phthalate degradation according to some recent research. The term photocatalyst is a combination of two words: photo relating to a photon and catalyst relating to a substance that alters the reaction rate in its presence. Hence, we can say photocatalyst is a material that changes the rate of a chemical reaction on exposure to light. In simple words, we can say that this process harvests the sunlight as an energy source for the degradation of pollutants. All photocatalyst materials are basically semiconductors.

The mechanism of photocatalysis has been illustrated in (Figs. 5.4 and 5.5) (Pang et al. 2021). Energy state in any catalyst material is characterized by two bands: the valence band and the conduction band. These two bands are separated by an energy gap. Electrons occupy valence band in the natural state, and when it receives energy from any external source, it jumps from the valence band to the conduction band and generates a pair of electrons and holes. Electrons move to the conduction band leaving a hole behind in the valence band. Holes react with the H_2O to generate OH° radical which is highly oxidizing in nature. Similarly, electron can react with the O_2 to generate superoxide anion radical $^{\circ}O_2^{-}$. These generated pairs of electrons and holes react with the adsorbed molecule and prompt a redox reaction. The formation of H_2O_2 further leads to formation of more OH radicals.

$$\text{Photocatalyst} + h\nu \rightarrow h^+ + e^- \tag{5.1}$$

$$\mathrm{h}^+ + \mathrm{e}^- \rightarrow \text{heat} \tag{5.2}$$

$$\mathrm{O_2\ (free)} \rightarrow \mathrm{O_2\ (ads)} \tag{5.3}$$

$$e^- + \mathrm{O_2\ (ads)} \rightarrow \mathrm{O}_2^{\bullet} \tag{5.4}$$

$$\mathrm{O}_2^{\bullet} + \mathrm{H}^+ \rightarrow \mathrm{HO_2}^{\bullet} \tag{5.5}$$

$$\mathrm{HO_2}^{\bullet} + \mathrm{HO_2}^{\bullet} \rightarrow \mathrm{H_2O_2} + \mathrm{O_2} \tag{5.6}$$

$$\mathrm{H_2O_2} + e^{\bullet} \rightarrow \mathrm{OH}^{\bullet} + \mathrm{OH}^{\bullet} \tag{5.7}$$

$$\mathrm{O_2}^{\bullet} + \text{pollutant} \rightarrow \text{products} \tag{5.9}$$

$$\mathrm{OH}^{\bullet} + \text{pollutant} \rightarrow \text{product} \tag{5.10}$$

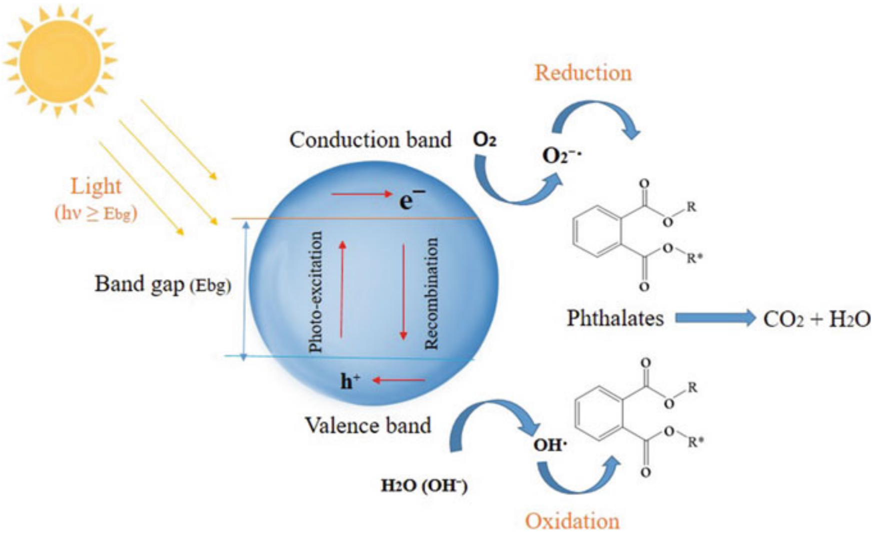

Fig. 5.4 Mechanism of photocatalytic oxidation of a phthalate compound (Modified and reproduced with authorization from Pang et al. (2021) (Copyright 2022, Elsevier)

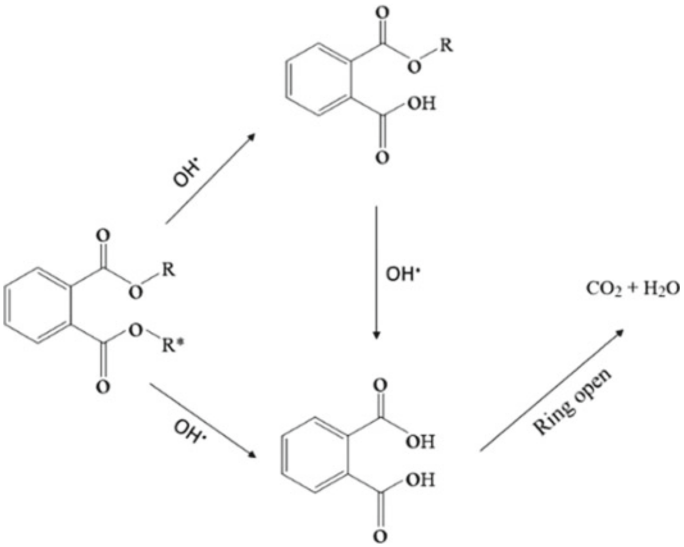

Fig. 5.5 Photocatalytic degradation pathway of a phthalate compound (Modified and reproduced with authorization from Pang et al. (2021) (Copyright 2022, Elsevier)

TiO_2 is a popular photocatalyst material. About 95.5% efficiency for DEP removal by photocatalytic degradation was achieved in a work by Huang and Chen (2010) using TiO_2. Other metal oxides like Fe_2O_3, ZnO, CuO, etc. are also used as photocatalyst material. Sarmin et al. (2021) subjected the effluent from an MFC to photocatalytic degradation and reported that degradation is affected by irradiation time and dose. In a work by Wang et al. (2019), 87.9% DBP removal was attained by a graphene-loaded tube subjected to photocatalysis. Works by Halmann (1992), Muneer et al. (2001), and Kaneco et al. (2006) have given more idea about the photocatalytic degradation of phthalates and different parameters affecting the process. Table 5.8 describes the removal of different phthalates using different photocatalysts in different irradiation conditions. The main limitation of these photocatalytic processes is the recombination of electrons and the holes that are generated during the process which reduces the efficiency of the catalyst material. Another disadvantage is that some popular photocatalysts like TiO_2 can harvest only UV light which increases the cost of the process. To overcome this, different metals are doped with the catalyst which not only reduces the recombination of electrons and holes but also increases the visible light harvesting efficiency of the materials. Other than metal doping, the formation of composite is also another technique for improving the light harvesting.

Table 5.8 Overview of the photocatalytic degradation of different phthalate compounds

Pollutants	Photocatalysts	Light sources	Initial load of pollutant	Catalyst load	Observation	References
Diethyl phthalate (DEP)	TiO_2 (anatase)	Xenon lamp: 254 nm	20 mg/l	0.2 g/l	Removal of DEP was observed after 50 min of photocatalytic activity	Huang and Chen (2010)
	ZnO	Hg lamp: 254 nm	50 mg/l	1 g/l	50% removal of DEP observed after 18.1 min	Liao et al. (2010a)
	WO_3/TiO_2	UV LED and blue LED	10 mg/l	5 g/l	Enhanced photodegradation of DEP was observed under visible light by loading small amount of WO_3 on surface of TiO_2	Ki et al. (2019)
	Ni/TiO_2	Mercury lamp: 365 nm	30 mg/l	1 g/l	Improved degradation of the pollutant because of Ni doping as compared to undoped TiO_2. Doping improved the degradation efficiency	Singla et al. (2016)
	Mn/TiO_2 Ni/TiO_2 Co/TiO_2 composite	Hg lamp: 365 nm	1 g/l	1 g/l	Doping with the metal resulted in decrease of the band gap of TiO_2 (2.49 eV with Mn doping) Doping improved the degradation efficiency in all the cases, Highest rate of DEP degradation was observed with Ni doping	Kaur et al. (2018)
	Nanorod ZnO/SiC nanocomposite	Eight UV lamps: 254 nm visible light	5, 10, 15, 25 mg/l		More than 90% DEP degradation observed with the given conditions	Meenakshi and Sivasamy (2018)

(continued)

Table 5.8 (continued)

Pollutants	Photocatalysts	Light sources	Initial load of pollutant	Catalyst load	Observation	References
	Pt/In_2O_3–TiO_2 nanotubes	Xenon lamp: 320 – 680 nm	10 mg/l	1 g/l	99.8% DEP degradation when using Pt/In_2O_3-TiO_2-nanotubess after 45 min of irradiation	Ma et al. (2012)
Dimethyl phthalate (DMP)	TiO_2	UV lamp: 365 nm	10 mg/l	1 g/l	62.1% DMP removal by hydrothermal-synthesized TiO_2 that was 2.5 times more than that of sol–gel-synthesized TiO_2 giving 33.6% DMP removal	Jing et al. (2011)
	Sonically fabricated N-doped TiO_2 and non-sonically fabricated N-doped TiO_2	Visible light	15 mg/l	0.5 g/l	41 and 58% removal of DMP with non-sonically fabricated N-doped TiO_2 and sonically fabricated N-doped TiO_2, respectively, after 5 h irradiation	Wanqin et al. (2013)
	LDHs/TiO_2 (layered double hydroxides carbon nanotubes)	UV lamp (8 W): 365 nm	10 mg/l	2 g/l	80% of DMP removal was achieved after 4 h illumination	Huang et al. (2013)
	HGM-TiO_2 (hollow glass microspheres)	Low-pressure mercury lamp: 350 nm	10 mg/l		DMP was eliminated after 20 min illumination using HGM-TiO_2. ($\geq$ 8.0 g/l)	Jiang et al. (2013)
	TiO_2/carbon aerogel	Xe lamp (300 W): filter used to remove infrared light	2 mg/l	0.1 g/l	83% DMP removal observed after 3 h irradiation with the composite	Liang et al. (2016)

(continued)

Table 5.8 (continued)

Pollutants	Photocatalysts	Light sources	Initial load of pollutant	Catalyst load	Observation	References
	MWCNTs/TiO_2 (multiwalled carbon nanotubes composite)	UV lamp (96 W)	1 mg/l	0.5 g/l	97% DMP removal was observed with MWCNTs/TiO_2 nanocomposites	Tan et al. (2018)
	ZrOx/ZnO	Hg lamp (15 W): 254 nm	50 mg/l	1 g/l	88% total organic carbon removal efficiency was observed with 30 min of illumination	Liao et al. (2010a)
Dibutyl phthalate (DBP)	TiO_2 (P25)	Xe lamp: 320–410 nm	5 mg/l	0–30 mg/100 ml	Complete removal of DBP within 3 h	Nozari et al. (2022)
	(Fe, Ag) co-doped ZnO	Visible LED lamp (7 W): 450–500 nm	15 mg/l	0.15 g/l	95% removal of DBP was observed	Akbari-Adergani et al. (2018)
	α-Fe_2O_3 nanoparticles	High-pressure mercury lamp (250 W)	13 mg/l		94% degradation achieved with complete mineralization	Liu et al. (2018)
	g-C_3N_4/$Bi_2O_2CO_3$; g-C_3N_4/BiOCl	Halogen tungsten lamp (500 W): 420 nm	5 mg/l	1 g/l	60% removal of DBP within 300 min of irradiation	Shan et al. (2016)
Butyl benzyl phthalate (BBP)	P25 TiO_2	UV lamp (8 W): 350 nm	1 mg/l	2 g/l	80% removal of BBP was observed after 2 h irradiation	Xu et al. (2009)
	Cl-doped TiO_2	Xe lamp: 400 nm	10 mg/l	1 g/l	Approx. 92% BBP removal was observed by Cl-TiO_2	Wang et al. (2012)

(continued)

Table 5.8 (continued)

Pollutants	Photocatalysts	Light sources	Initial load of pollutant	Catalyst load	Observation	References
	P-doped TiO_2 thin-films	Xe lamp: 400 nm	20 mg/l	0.1 g/l	17 and 98% removal of BBP using TiO_2 and PTIO-0.03 catalyst, respectively	Mohamed and Aazam (2013)
Di(2-ethylhexyl) phthalate (DEHP)	Nx-TiO_2–x	Xenon lamp (55 W): $\lambda \geq 440$ nm	5.0×10^{-4} M		High DEHP degradation obtained using N-doped TiO_2 when compared to pure TiO_2	Anandan et al. (2013)
	Fe-Ag@ZnO	Visible LED lamp: 430–500 nm	20 mg/l		90% DEHP removal within 120 min of visible illumination	Eslami et al. (2017)

5.7.2.2 Fenton Process

Recently, the Fenton process has come to attention for the degradation of organic pollutants. In this method of oxidation, hydroxyl radical ($^{\bullet}OH$) is generated from the reaction between aqueous ferrous ions and hydrogen peroxide which is used further to oxidize different pollutants in the wastewater. Fenton method of oxidation improves the degradation rate of the targeted pollutant using UV-Vis part of the electromagnetic spectrum. In a study by Zhao et al. (2004), 80% removal of DMP was achieved by the photochemical degradation using the Fenton reagent (hydrogen peroxide and Fe^{2+}). In another work by Zhao et al. (2017), 98% efficiency in removing DMP was achieved by the use of iron-doped activated carbon aerogel. Chen et al. (2009) reduced the toxicity of DEHP and then subjected it to biodegradation leading to a faster removal rate.

5.7.2.3 Ozonation

Ozonation is another technique being used worldwide for the treatment of water. It is an advanced oxidation process (AOP) which uses ozone gas for the oxidation of pollutants. Ozone is a reactive gas and has low solubility. It is generated in situ for the oxidation process through dry air or pure oxygen via high-voltage corona discharge. This generated gas is passed through the solution where it undergoes decomposition and oxidizes the pollutant. Mansouri et al. (2019) studied the degradation kinetics of four phthalate compounds. O_3/Al_2O_3 was suggested to be an efficient method for DEP removal. Although other processes like adsorption have shown sufficient efficiency for phthalate removal but takes a long time for the removal process. Advanced oxidation processes overcome this limitation and have shown high removal of DEP when compared to conventional methods (Medellin-Castillo et al. 2013).

The point to be taken care of in these processes is the production of reaction intermediates. For example, two intermediate products namely phthalic acid and 4-hydroxy phthalic acid were determined during the degradation of DEP by O_3 (Mohan et al. 2019). Similarly, in other work, other intermediates include 4-hydroxy phthalate, phthalic anhydride, and phthalic acid (Jung et al. 2010).

Advanced oxidation processes though give high efficiency for phthalate removal, but require a large amount of chemicals increasing the cost of the system. Another challenge that accompanies is the generation of reaction intermediates that sometimes can be more harmful than the phthalates themselves. Hence, work is required in analysing the treatment of these intermediates also.

5.7.3 Biological Treatment for Phthalate Removal

Biological treatment is the process of conversion of organic pollutants into simpler materials using different aerobic and anaerobic processes. Use of microorganisms has proven to be successful for the degradation of organic pollutants. Biodegradation is an effective method for phthalate removal, but has a little less efficiency when performed in the field. Major pathways for phthalate decomposition include a breakdown of the phthalate compounds by microorganisms under various environmental conditions. Different redox conditions provide different kinds of metabolic pathways for the degradation of phthalates. Wang et al. (1996) reported 90% efficiency for DMP and DBP removal under aerobic conditions with activated sludge. Marttinen et al. (2003) analysed the decomposition of DEHP emitted from a treatment plant and reported the removal rate to be around 90% of which 20% was done by biological degradation.

According to a work by Gani and Kazmi (2016), biotransformation led to 37%, 65%, and 74% removal of phthalates in UASB, ASP, and SBR. Different systems were combined to enhance the removal of phthalate compounds. For example, UASB when combined with pond enhanced the efficiency by up to 83%. In a similar work by Yousefzadeh et al. (2017), performance of up-flow anaerobic fixed-film fixed bed reactor (UAnFFFBR) and anaerobic fixed-film baffled reactor (AnFFBR) was analysed for the removal of DEP, and 90.31 and 86.91% of COD removal and 91.11% and 88.72% of DEP removal were achieved in the both systems, respectively. But the degradation process under anaerobic conditions has proven to be 4–5 times slow as compared to aerobic degradation (Madsen et al. 1999). Other approaches include use of aquatic plants like *Phragmites australis*-based, *mesocosm* scale, and *Wolfa arrizha* for the removal of phthalates that have given efficiency up to 97% for the removal of DEP and 99% for the removal of phthalates, respectively (Li et al. 2020).

Li et al. (2007) combined the UV/O_3 and biological activated carbon for phthalate removal and achieved up to 79–100% phthalate removal, but the cost associated was a big disadvantage limiting its practical use. Fang and Zheng (2004) suggested that short-chain phthalates are easier to degrade when compared to long-chain esters. Anaerobic reactors have been more successful in degrading phthalates. Liang et al. (2007) successfully degraded DMP in a UASB reactor. At first, DMP was de-esterified to MMP (monomethyl phthalate). Further, it was de-aromatized and converted to CH_4 and CO_2. Gao and Wen (2016) analysed the degradation of phthalates in anoxic conditions, and limited degradation was observed. According to Liang et al. (2008), microbial degradation is suggested to be a better option for phthalate degradation as compared to abiotic degradation.

Biodegradation can be a time-taking process. High OLR and HRT enhanced the phthalate removal process because of the longer contact time with the substrate. Higher aeration time also affects the performance. Aeration can increase the catabolic activity of the microorganisms leading to efficient degradation of the pollutant, but a very high aeration rate can wash out the biofilm, reducing the removal rate. Other microbes have given complete degradation of PAE. Some microorganism species used in the treatment have been tabulated (Table 5.9). Factors like temperature and seasonal variation can affect the removal rate of phthalates. Work is needed to be done to improve the working conditions for the practical application. The development of effective microbes is needed for the efficient removal of phthalates.

Table 5.9 Overview of different species used for phthalate removal

Compounds	Genus/species	Operating conditions	Initial conc. (mg/l)	Results	References
DEP, DBP, BBP, and DEHP	*Corynebacterium* sp.	pH 7.0 Temp 30 °C	5	100% DEP, DBP, BBP; 89.2% DEHP	Chang et al. (2004)
DEP, DBP, BBP, and DEHP	*Sphingomonas* sp.	pH 7.0 Temp 30 °C	5	100% DEP, DBP, BBP; 56.9% DEHP	Chang et al. (2004)
DBP and DEHP	*Enterococcus* sp.	pH 6–8 Temp 30 °C	–	100% DBP and 93.8% DEHP	Chang et al. (2005)
DEP	*Sphingomonas* sp.	pH 7.0 Temp 25–30 °C	450	14 mg DEP l^{-1} h^{-1}	Fang et al. (2007)
DEHP	*Microbacterium* sp.	pH 6.5–7.5 Temp 25–35 °C	1350	$t_{1/2}$ = 1.59 days	Chen et al. (2007)
DEP and DBP	*Rhodococcus ruber* sp.	pH 7.0 Temp 37 °C	300	Degradation half-life ($t_{1/2}$) = 1.28 days	Lu et al. (2009)
DBP	*Deinococcus radiodurans* sp.	pH 6.5–8.0 Temp 30 °C	5	0.77 day^{-1} and $t_{1/2}$ = 0.89 days	Liao et al. (2010b)
DBP	*Pseudomonas stutzeri* sp.	pH 6.5–8.0 Temp 30 °C	5	0.58 day^{-1} and $t_{1/2}$ = 1.18 days	Liao et al. (2010b)
DBP	*Gordonia* sp.	pH 7.0 Temp 30 °C	100–750	8.93–35.87 m g^{-1} h^{-1}	Jin et al. (2012)
DBP	*Gordonia* sp., *Burkholderia* sp., *Achromobacter* sp., *Burkholderia* sp.	pH 8 and 9 Temp 25–35 °C	1000	95%	He et al. (2013)

5.7.4 Membrane Processes

Membrane bioreactors are also an effective approach for the removal of toxic compounds. Membrane bioreactors involve the combination of two processes biological and membrane separation thus giving a better efficiency. A membrane is a material that allows the selective flow of certain substances.

In water treatment processes, water flows through the membranes leaving behind impurities on one side. The filtration efficiency depends on the type of membrane used. The membrane used should be durable, resistant to acidic and basic conditions, and could withstand different pH range. Polymeric membranes are generally used in water treatment processes. Water treated with membrane filters can provide high-quality effluent that can be directly discharged into the water. In MBR, it has become easy to operate water with high MLSS concentration thus reducing the volume requirement for same loading rate. The combination of membrane and biological processes has improved the removal rates for organic compounds, but some phthalates are not fully removed by MBR and hence need further treatment processes. Ultrafiltration, nanofiltration, and reverse osmosis have been applied for phthalate removal and have given efficiency up to 97–99%. Overview of different works using biological methods has been tabulated (Table 5.10).

Table 5.10 Overview of different biological systems for the removal of phthalates

Phthalates	Treatment technology	Substrate	COD	HRT	Removal (%)	References
PAEs	AnMBR	Landfill leachate	3.3 g/l	7 days	PAEs increased inside the reactor	Zayen et al. (2015)
DEP, DAP	MBBR	Synthetic wastewater	200 mg/l	< 7 h	94.96, 93.85	Ahmadi et al. (2015)
DEHP	IFAS-MBR	Municipal wastewater		10–20 days	10–30	Torre et al. (2015)
DEHP	MBR integrated with electrooxidation	Landfill leachate	1550 ml/l	48 h	59 ± 24.3 (in summer) 66.4 ± 28.8 (in winter)	Zolfaghari et al. (2016)
DEHP	MBR	Landfill leachate	6740 mg/l	24 h	> 90	Boonnorat et al. (2016a)
DBP	MBR, DEHP	Landfill leachate	14200 mg/l	12 h	98.3, 96.5	Boonnorat et al. (2016b)
DEP, DBP, DEHP	Anoxic-aerobic two-stage MBR	Landfill leachate	2400 mg/l	24 h	100, 94, 93	Kanyatrakul et al. (2020)
DEHP, DINP	AnMBR	Middle/old landfill leachate	7041 mg/l	48 h	100	Cirik and Gocer (2020)

5.8 Conclusion and Future Recommendations

Phthalates have been classified as a top-priority pollutant by researchers. These compounds are not chemically bound to the host materials and, thus, are easily released into the environment from different products. Consequently, they are present in high concentrations in occupational and residential environments. Phthalates are odourless and tasteless and are used in many day-to-day consumable products and are even detected in foods. Phthalates have observed to be very toxic and harmful for human health and aquatic species. Looking at the toxic effects, they have been classified as top-priority pollutants. More research is needed to analyse the after-effects and treatment processes, including how exactly these compounds affect the humans. Advanced treatment technologies have been successful in phthalate degradation giving 75–95% efficiencies. But there is still a need to draw attention to the limitations related to each process to get an optimal condition for the practical application of these systems. Further, it becomes necessary to analyse whether the results obtained in laboratory study are fit for the practical application of these processes or if there is any need to couple the systems with other treatment technologies.

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Part III

Advanced Oxidation Processes for Removal of Persistent Pollutants

Chapter 6
Application of Electrochemical Technologies for the Efficacious Removal of Persistent Organic Pollutants from Wastewater

Makarand M. Ghangrekar, Monali Priyadarshini, Azhan Ahmad, and Shraddha Yadav

Abstract The intensification of industrial activities and urbanization have significantly increased the discharge of huge amount of toxic and recalcitrant pollutants into the water bodies. Among these, persistent organic pollutants (POPs) are considered highly toxic to aquatic ecosystem as well as human and animals due to their pervasive and bio-accumulative in behaviour. Moreover, these pollutants are not effectively eliminated by conventional wastewater treatment systems due to their recalcitrant nature; thus, trace concentrations of these persistent pollutants are detected in the effluent of wastewater treatment plants (WWTPs). In this regard, to achieve the safe discharge of POPs laden wastewater into the receiving water bodies, electrochemical technologies, such as electrocoagulation (EC), anodic electrochemical oxidation (AO) and electro-Fenton (EF), have demonstrated the potential to effectively eliminate the POPs from contaminated water. Thus, this chapter aims to annotate the basic principles, advantages, disadvantages, application status of electrode materials, electrocatalysts and latest advancement in the field of electrochemical technologies. Moreover, the factors affecting the performance, bottlenecks, future research directions and status of commercialization of electrochemical technologies also have been articulated in the present chapter for the benefit of the researchers for commercial utilization of these technologies in near future.

Keywords Electrocatalysts · Electrocoagulation · Electro-Fenton · Electrochemical oxidation · Persistent organic pollutants · Wastewater treatment plants

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6.1 Introduction

Persistent organic pollutants (POPs) are the noxious chemicals that remain in the environment for longer period of time, which can adversely affect the human health, wildlife species and aquatic ecosystem. The bioaccumulation and transportation of POPs via food chain is a global concern due to its recalcitrant nature (Sun et al. 2020). To address this issue, the USA along with 90 other countries signed an agreement in Stockholm, Sweden, in 2001 (Stockholm convention) aiming to scale down or eradicate the production, use and release of twelve key POPs, which is also termed as "the dirty dozen" (UNEP USEPA 2012). The major sources of POPs include industries, agricultural practices and unscientific management of medical and municipal solid waste. The POPs include wide range of substances, such as dyes, pharmaceuticals, personal care products, endocrine disrupting chemicals (EDC), polychlorinated biphenyls, perfluoroalkyl acids, and organochlorine pesticides (Covaci et al. 2005; Buck et al. 2011; Zaynab et al. 2021). Thus, elimination of these pollutants is the current need of the hour to restrict their release into the receiving water bodies.

The conventional treatment technologies, such as coagulation, ultrafiltration, adsorption, and solvent extraction, have inevitable shortcomings as these only separate the pollutant from the water phase or gas phase, however, does not degrade the pollutant; thereby, it can increase the chances of secondary pollution. Also, the biological treatment technologies are inefficient in degrading the POPs due to their toxic and recalcitrant nature (Priyadarshini et al. 2021). The rectification of these shortcomings has been observed by adopting the electrochemical oxidation technologies, which completely mineralize the recalcitrant pollutants without generation of secondary waste (Moreira et al. 2017; Kharel et al. 2021). Basically, oxidation refers to the movement of electrons from an electron donating species to electron acceptor, whereas in some cases the species with an odd number of electrons are produced known as radicals. These highly potent radicals (e.g. hydroxyl radical ($^{\bullet}OH$)) degrade the POPs into stable end products (Rajendran et al. 2022). Other radicals, such as hydroperoxyl ($HO_2^{\bullet}$), sulphate anions ($SO_4^{\bullet-}$) and superoxide ($O_2^{\bullet-}$), are also formed in different electrochemical processes, and the generation can be photo-assisted, irradiation assisted or non-photochemical (Vidales et al. 2015). On the other hand, in situ metal hydroxides are also formed in the electrochemical process, which adsorbed the POPs on to its surface and settle down, thereby rendering its removal through precipitation.

In this regard, the researchers have utilized electrochemical technologies, such as anodic electrochemical oxidation (AO), electro-Fenton (EF) and electrocoagulation (EC) to remediate POPs from wastewater (Zhang et al. 2021). These electrochemical processes serve dual purpose of contamination removal and disinfection of the wastewater and can be controlled at ambient temperature (Qiao and Xiong 2021). The current chapter deals with the most prominent electrochemical processes for the remediation of POPs from the wastewater. Also, the basic mechanism, factors affecting the performance efficiency, implementation challenges, and the future perspective have been articulated. Thus, the basic objective of this chapter is to help the researchers to attain knowledge in the field of electrochemical technologies to treat wastewater in the most efficient and economical way.

6.2 Classification and Occurrence of Persistent Organic Pollutants (POPs)

6.2.1 Classification

Based on the chemical composition, the POPs can be classified into pharmaceuticals, biocides, PCPs, EDCs, food additives, dyes, surfactants and phenols. Beside this, a variety of compounds, such as sucralose, artificial sweeteners, flame retardants, nano materials, perfluorinated compounds, sunscreens and UV filter and drinking water and swimming pool disinfection by-products, can also be categorized as POPs (Priyadarshini et al. 2020). However, most of these compounds are not regulated appropriately due to the lack of regulatory standards. As a result, these compounds find their way into water bodies, which could adversely affect the aquatic organisms due to their potential toxicity. The general classification, uses and major sources of generation of POPs are summarized in Table 6.1.

6.2.2 Occurrence

The occurrence and transportation of POPs into the aquatic and subsurface environment depend on different factors, such as characteristics of wastewater, the source of generation, employed treatment method and climatic conditions (Salimi et al. 2017). Among these factors, the source of generation is one of the major factors responsible for the occurrence of POPs in the environment. The sources of generation of POPs are classified into five categories, such as industries, hospital effluent, domestic discharge, livestock farming, and agricultural run-off. For example, in case of domestic discharge, the medicine consumed by humans is excreted via urine and faeces due to metabolization (Ahmad et al. 2021). From there, these POPs subsequently enter the wastewater treatment plants (WWTPs) and then are introduced into the environment through the effluent of WWTPs after incomplete degradation (Fig. 6.1).

Likewise, PCPs such as sunscreen lotions, toothpaste, fragrances and shampoos also enter in to the environment via washing activities of human beings (Krithiga et al. 2022). Furthermore, the steroid supplements used for improving in the productivity of livestock and pesticides used in agricultural activities are the other major contributors of POPs. Apart from these, improper management of waste from pharma industries and medical facilities, leakage from sewage treatment facilities, landfill leaching, and aquaculture discharges are also the dominant contributors of POPs (Bolong et al.

Table 6.1 General classification, uses and their major sources of generation of persistent organic pollutants

POPs category	Application	Sub-category	Compounds	Major sources
Pharmaceuticals	Substance used in the diagnosis, treatment or prevention of disease	Antibiotics, antidiabetic, antidepressant, anticonvulsant, beta-blockers	Clarithromycin, metformin, diazepam, carbamazepine, metoprolol	Domestic wastewater, pharmaceutical industry effluent, hospital effluent, effluent from livestock farms and aquaculture
Biocides	Group of chemicals used to kill germs, microorganisms and algae	Pesticides, fungicides, molluscicide	Epoxiconazole, butachlor, metaldehyde	Agricultural run-off, aquaculture effluent and surface water
PCPs	Substances used by individuals for personal health or cosmetic reasons	Sunscreens and UV filters, insect repellents, fragrances	4-benzophenone, N, N′ diethyltoluamide, Galaxolide	Surface water, WTP effluent and landfill leachate
EDCs	Chemicals that interfere with the way the body’s hormones work	Xenohormone, bisphenol and phthalates	Xenoestrogen, bisphenol A, dioctyl phthalate	Domestic wastewater, surface water, secondary sludge, soil and sediments
Surfactants	Compounds used in an array of cleaning products	Ionic surfactants and non-ionic surfactants	Sodium lauryl sulphate, tweens or polysorbates	Domestic wastewater and industrial effluents
Dyes	substance used to impart colour to textiles, paper, leather, foods, drug and cosmetics	Anionic and cationic	Methyl orange, crystal violet	Textile, printing and paper industries effluent
Industrial chemicals	Chemicals used for manufacturing of products	Fire retardants and plasticizers	Tris (1-chloro-2-propyl) phosphate and dimethyl adipate	Industrial effluent and domestic wastewater
Artificial sweeteners	Chemical substances used instead of sugar to sweeten foods and drinks	Aspartame, saccharin, sucralose	–	Sewage treatment plant effluent, wastewater and landfill leachate

(continued)

Table 6.1 (continued)

POPs category	Application	Sub-category	Compounds	Major sources
Perfluorinated compounds	Chemicals used in non-stick cooking utensils, food packaging, carpets, fabrics, PCPs, paints, firefighting foams and adhesives	Perfluorosulphonic acids, perfluorocarboxylic acids	Perfluorooctanesulphonate, perfluorooctanoic acid	Surface water, ground water, wastewater and sediments

WWTP Wastewater treatment plant, *WTP* Water treatment plant, *PCPs* Personal care products, *EDCs* Endocrine-disrupting chemicals, *UV* Ultraviolet

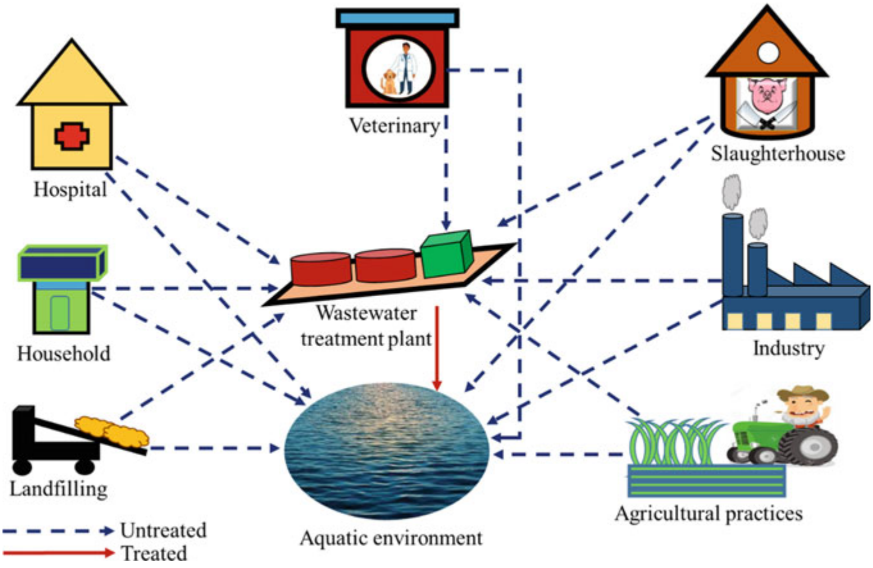

Fig. 6.1 Pathways by which persistent organic pollutants end up in aquatic environment

2009). Moreover, due to low-biodegradability and recalcitrant nature of POPs, the conventional WWTPs are not efficient in removal of these pollutants, as a result trace level of POPs is detected in the effluent of WWTPs, which finally reflect in groundwater, surface water, drinking water, and soil with concentration in the range of few ng/L to μg/L (Priyadarshini et al. 2022a).

The countries India, the USA, China, UK, Germany, Canada, etc., have reported the frequent detection of POPs with higher concentrations in WWTPs. Among the different types of POPs, pharmaceuticals are predominantly detected due to their higher consumption by the consumers. For example, an analgesics named ibuprofen was detected with the concentration of 75.8 μg/L in the influent of WWTPs in North America, which was relatively higher than that of Asia (26.45 μg/L), Australia (10.3 μg/L) and Europe (33.76 μg/L) WWTPs influents (Saidulu et al. 2021). Similarly, the antibiotics drug, ciprofloxacin, was found with the highest concentration of 31,000 μg/L in the influent of water treatment plant (WTP) in Hyderabad, India (Mutiyar and Mittal 2014); whereas, about 0.028–0.175 μg/L and 0.160–13.6 μg/L concentration of ciprofloxacin was found in the WTP influent of China and Spain, respectively. Moreover, about 0.323 μg/L of ciprofloxacin was also identified in the groundwater of Castellon province, Spain (Gracia-Lor et al. 2012).

Similarly, other prominent research articles also reported the occurrence of other POPs like pesticides and EDCs in wastewater. For example, 43–45 ng/L of atrazine metabolite was detected in the Yangtze River of China and atrazine with concentration of 1.65 μg/L was found in Australian surface water (Qi et al. 2014; Allinson et al. 2015). On the other hand, EDCs like nonylphenol with the concentration between 32 and 63 μg/L were found in the influent of domestic wastewater or sewage treatment plant (STP) in the UK, which was found to be higher than that observed in the STP influent in China (1.5 μg/L) and Spain (5.5–6.6 μg/L) (Saidulu et al. 2021). Another class of emerging contaminant is surfactant, which is most widely detected in the concentration range of 20–300 mg/L in municipal wastewater because of their application in domestic as well as commercial sectors (Dereszewska et al. 2015). Similarly, other researchers have also reported the existence of different POPs in other water matrices, which are summarized in Table 6.2.

6.3 Electrochemical Treatment Technologies

Over the past few decades, electrochemical-based technologies, such as AO, EF and EC, have received considerable attention from the researchers owing to their requirement of relatively short time duration for mineralization POPs, consume less land area and produce negligible sludge compared to conventional chemical and biological wastewater treatment processes. Additionally, it can be suitable for treatment of wastewaters in wide pH range and also requires few chemical reagents for the degradation of POPs. Therefore, all these major benefits of electrochemical technologies make them more suitable and eco-friendlier for the degradation of complex organic pollutants present in the wastewaters. In this regard, the detail mechanism, merits, demerits, application and factor affecting the process efficacy during the remediation of POPs are discussed in the subsequent sections.

6.3.1 Anodic Electrochemical Oxidation (AO)

6.3.1.1 Mechanism

The process of AO occurs via direct transfer of charge of the target pollutant from the anode or by the oxidation of water (H_2O) at anode surface produced metal absorbed reactive oxygenate species (ROS), which further helps in the mineralization of POPs into simpler products like CO_2 and H_2O (Eqs. 6.1 and 6.2) (Panizza and Cerisola 2009) (Fig. 6.2). Moreover, the ROS, $^{\bullet}OH$, $HO_2^{\bullet}$, $SO_4^{\bullet-}$ and $O_2^{\bullet-}$ produced in the solution during the oxidation process are involved in the degradation of POPs owing to their high oxidizing potential.

$$M + H_2O \rightarrow M(^{\bullet}OH) + H^+ + e^- \tag{6.1}$$

$$M(^{\bullet}OH) + P \rightarrow M + mCO_2 + nH_2O + H^+ + e^- \tag{6.2}$$

where M and P represent the metal used as anode and organic pollutant, respectively.

Table 6.2 Occurrence of emerging contaminants in different water matrices over the world

Category	Contaminant	Country	Occurrence	Maximum Concentration (ng/L)	References
Pharmaceuticals	Carbamazepine	USA	Treated drinking water	26.5	Benson et al. (2017)
		Kenya	Surface water	600	K'oreje et al. (2016)
		Italy	Sea water	0.0071	Brumovský et al. (2017)
	Ibuprofen	USA	Urban wastewater	14,330	Mohapatra et al. (2016)
		India	Surface water and groundwater	49.4	Sharma et al. (2019)
		China	Surface water	–	Sun et al. (2015)
	Paracetamol	Kenya	Surface water and groundwater	106,970	K'oreje et al. 2016)
		Italy	Sea water	0.111	Brumovský et al. (2017)
	Caffeine	USAs	Urban wastewater	19,580	Mohapatra et al. (2016)
		Brazil	Surface water	1040	Sposito et al. (2018)
	Ofloxacin	India	Hospital wastewater	73,200	Mutiyar and Mittal (2014)
	Norfloxacin	India	Lake water	520,000	Mutiyar and Mittal (2014)
Pesticides	Simazine	Australia	Surface water	$\geq$ 100	Sardiña et al. (2019)
	N,N-Diethyl-m-toluamide	USA	WWTP effluent	675	Sutton et al. (2019)
	Atrazine	Brazil	Surface water	171.3	Sposito et al. (2018)
		USA	Source water and treated drinking water	323	Glassmeyer et al. (2017)
	Metolachlor	USA	Wetland water	10,500	Glinski et al. (2018)
		USA	Source water and treated drinking water	130	Glassmeyer et al. (2017)

(continued)

Table 6.2 (continued)

Category	Contaminant	Country	Occurrence	Maximum Concentration (ng/L)	References
Artificial sweeteners	Acesulfame K	India	Surface water and groundwater	2.92	Sharma et al. (2019)
		Italy	Sea water	–	Brumovský et al. (2017)
	Cyclamate	India	Surface water and groundwater	1.216	Sharma et al. (2019)
	Saccharine	India	Surface water and groundwater	85.43	Sharma et al. (2019)
		Italy	Sea water	5.23	Brumovský et al. (2017)
Fluorinated compounds	Perfluorobutaic acid	USA	Source water and treated drinking water	104	Glassmeyer et al. (2017)
		Spain	Surface water	742.904	Pico et al. (2019)
		India	Surface water and groundwater	1.18	Sharma et al. (2016)
	Perfluorooctane sulphonate	USA	Source water and treated drinking water	48.3	Glassmeyer et al. (2017)
		Australia	Surface water	≥ 2	Sardiña et al. (2019)
Dyes	Malachite green	Saudi Arabia	Textile effluent	1,680,000	Khan et al. (2019)
	Disperse brown 1	China	Textile effluent	109,000	Lou et al. (2018)
	Disperse blue 291	Brazil	STP effluent	50	Vacchi et al. (2017)
EDCs	Bisphenol-A	USA	Urban wastewater	1290	Mohapatra et al. (2016)
		Spain	Surface water	4800	Salgueiro-González et al. (2015)

(continued)

Table 6.2 (continued)

Category	Contaminant	Country	Occurrence	Maximum Concentration (ng/L)	References
	Dibutyl phthalate	Taiwan	Surface water and drinking water	163	Gou et al. (2016)
	2,4-Di-tert-butylphenol	Canada	WWTP effluent	270	Lu et al. (2019)
	4-tert-octylphenol	Spain	Surface water	88	Salgueiro-González et al. (2015)
	Butylated hydroxytoluene	Canada	WWTP effluent	520	Lu et al. (2019)
Surfactants	Linear alkylbenzene sulphonates	China	WWTP influent	527,000	Zhu et al. (2018)
	Benzalkonium chlorides	China	WWTP influent	692	Zhu et al. (2018)

EDCs Endocrine-disrupting chemicals, *STP* Sewage treatment plant, *WWTP* Wastewater treatment plants

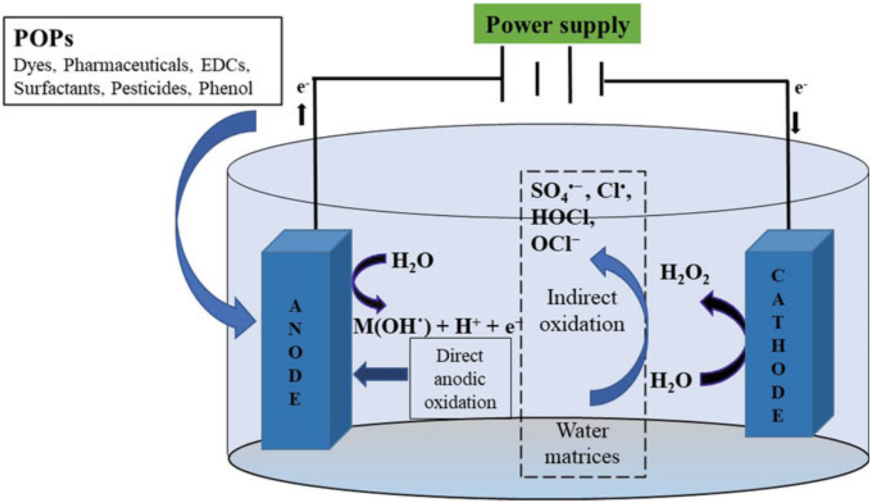

Fig. 6.2 Typical schematic of anodic oxidation and mechanism involved therein

The performance and selectivity of the AO are greatly dependent upon the nature of the anode materials (Jiang et al. 2021). Some active anode materials, such as graphite, platinum, RuO_2 and IrO_2, possess better chemical stability and electrocatalytic activity. However, these materials still have bottlenecks of low oxygen evolution potential (LOEP) (about 1.8 V vs. standard hydrogen electrode (SHE)), which leads to partial oxidation of POPs. The LOEP is a crucial element in the determination of current efficiency for the degradation of pollutants. However, anodic materials, such as SnO_2, PbO_2 and boron-doped diamond (BDD), have emerged as the ideal materials for the complete degradation of pollutants in wastewater.

The efficiency of AO also depends upon the factors like concentration and nature of the supporting electrolyte, current density, temperature, pH, metallic cations and initial concentration of POPs. For instance, increasing the initial concentration of the pollutants would inhibit the degradation efficiency of the pollutant owing to the limited availability of $^{\bullet}OH$ radical in the solution at constant applied current density. This can be attributed to the lower $^{\bullet}OH$ to pollutant ratio as well as simultaneous formation of intermediate, which inhibit the direct attack of $^{\bullet}OH$ on the pollutant. However, temperature variation has negligible effect on the degradation capability of the AO process; though, at certain extent the temperature hike is favourable for the process, as reaction kinetics of some oxidants (e.g. peroxodisulphuric ions) depends on the temperature (Serrano et al. 2002).

In an exploration by Ansari and Nematollahi (2020), the effect of acidic, basic and neutral pH of the solution on the AO of para-dinitrobenzene at 4 mA/cm^2 was explored. The result obtained revealed the decrease in efficiency in basic solution due to the reaction of hydroxide ions with para-dinitrobenzene, which hinders the degradation of polymeric intermediates. Consequently, acidic pH is beneficial for the degradation of organic pollutant, which might be due to enhanced production rate of oxygen at the anode surface that attracts the pollutants towards anode and further degrades pollutant (Jiang et al. 2021).

6.3.1.2 Application

Recently, the AO has been extended towards the remediation of various types of POPs, such as pharmaceuticals, PCPs, EDCs, disinfection by-products, dyes, pesticides and phenols from domestic and industrial wastewater (McBeath et al. 2021). Additionally, AO is also applied for the pollutant remediation from soil and gaseous streams (Karim et al. 2021). In this regard, the BDD anodes proved to be a successful electrode material for AO owing to its higher oxygen evolution potential, chemical stability and long life compared to other electrode alternatives. For example, Zhou and co-workers investigated the degradation of methyl orange using BDD electrode, which resulted in 90% of chemical oxygen demand (COD) removal and 50% of total organic carbon (TOC) reduction (Zhoua et al. 2011).

Advancement in BDD material has been made by co-doping with other compounds (such as boron and nitrogen) to enhance the synergetic electrocatalytic activities. In an investigation, AO process was adopted for the removal of highly toxic and carcinogenic perfluoroalkyl and polyfluoroalkyl substances from the wastewater with modified boron and nitrogen co-doped diamond (BND) anode (Liu et al. 2019). Results revealed the improved efficiency of BND anode compared to the BDD and nitrogen-doped diamond (ND) anode, and about 99% reduction of perfluorooctanoic acid was observed with current density of 4 mA/cm^2, 0.05 M Na_2SO_4 and pH of 4.8 using BND. Similarly, Yang et al. investigated the efficiency of AO for degradation of 20 mg/L of methylene blue using a novel sulphur-doped Ti-based PbO_2 (S–TiO_2–PbO_2) anode. Nearly, 99% removal was observed in 90 min, wherein 50% degradation was through direct oxidation at the anodic surface and the remaining through indirect oxidation. Moreover, other pollutants, such as 4-chlorophenol, p-nitrophenol and bisphenol A, were also remediated using S–TiO_2–PbO_2 anode in AO (Yang et al. 2021). Similarly, other investigations also reported excellent performance of AO for the removal of POPs, which are summarized in Table 6.3.

6.3.2 Electro-Fenton Oxidation (EF)

6.3.2.1 Mechanism

In 1894, the concept of Fenton was discovered by H. J. H Fenton, where the degradation of tartaric acid was observed in the presence of Fe^{2+} salt (Eq. 6.3) (Fenton 1894). The concept was further investigated by Haber and Weiss in 1934, wherein they suggested that activation of H_2O_2 by Fe^{2+} resulted in the generation of $^{\bullet}OH$ radicals. The produced radicals enhanced the degradation efficacy of the pollutant owing to their high oxidation potential of 1.8–2.7 V/SHE (Eqs. 6.4 and 6.5 (Uri

Table 6.3 Removal of emerging contaminants through electrochemical technologies

Pollutant	Electrochemical process	Process Parameters	Electrode material	Removal efficiency	References
Pesticides					
Malathion	Electrocoagulation	Initial concentration = 40 ppm Current density = 10 mA/cm^2 Electrolysis time = 10 min	Aluminium electrode	90%	Behloul et al. (2013)
Tricyclazole	Electro-Fenton	Initial concentration = 0.2 mM Current density = 2.2 mA/cm^2 Operating time = 188 min	Iron anode Carbon plated iron cathode	99.6% operating cost of 121.392 $/kg TC	Bui and Huynh (2022)
Nitenpyram	Electrochemical oxidation	Initial concentration = 75 ppm Current density = 70 mA/cm^2 Operating time = 120 min	Gd-PbO_2	95%	Yang et al. (2020)
Cypermethrin	Electrochemical oxidation	Initial concentration = 50 ppm Current density = 80 mA/cm^2 Operating time = 180 min	SnO_2	75%	Bouya et al. (2012)

(continued)

Table 6.3 (continued)

Pollutant	Electrochemical process	Process Parameters	Electrode material	Removal efficiency	References
Pharmaceutical					
Metformin	Electro-Fenton	Initial concentration = 10 ppm Current density = 6 mA/cm^2 Operating time = 10 min H_2O_2 dosage = 250 µL/L	Iron electrodes	98.57%	Dolatabadi and Ahmadzadeh (2019)
Ciprofloxacin	Electrocoagulation	Initial concentration = 5 ppm Operating time = 10 min Current density = 4.3 mA/cm^2	Iron electrodes	86.6%	Barışçı and Turkay (2016)
Metronidazole	Electrocoagulation	Initial concentration = 21.6 ppm Current density = 6 mA/cm^2 Operating time = 14.6 min	Iron electrodes	More than 90%	Ahmadzadeh and Dolatabadi (2018)
Folic acid	Electro-Fenton	Initial concentration = 1041.15 ppm Current density = 10.26 mA/ cm^2 Operating time = 90 min	3-D electrode	94.87%	Xiaochao et al. (2018)

(continued)

Table 6.3 (continued)

Pollutant	Electrochemical process	Process Parameters	Electrode material	Removal efficiency	References
Dyes					
Brilliant green dye	Electrocoagulation	Initial concentration = 100 ppm Current density = 41.7 mA/cm^2 Operating time = 30 min	Mild steel electrode	99.59%	Nandi and Patel (2017)
Acid blue dye 25	Electrocoagulation	Initial concentration = 25 ppm Voltage = 60 V Electrolysis time = 90 min	Aluminium electrode	90%	Balarak et al. (2019)
Acridine orange	Electrochemical oxidation	Initial concentration = 30 ppm Current density = 50 mA/cm^2 Operating time = 90 min	Ce-PbO_2/ZrO_2 anode	Approx. 100%	Yao et al. (2019)
Reactive Red 120	Electrocoagulation	Initial concentration = 1299.8 ppm Current density = 13.45 mA/cm^2 electrolysis time = 69.62 min	Aluminium electrode	Colour removal = 93.47% COD removal = 81.31%	Gautam et al. (2020)

(continued)

Table 6.3 (continued)

Pollutant	Electrochemical process	Process Parameters	Electrode material	Removal efficiency	References
Perfluoroalkyl acids					
Perfluorobutanoic acid	Electrochemical oxidation	Initial concentration = 0.000496 ppm	BDD electrode	–	Veciana et al. (2022)
Perfluorooctanoic acid	Electrochemical oxidation	Initial concentration = 100 ppm Current density = 7.9 mA/cm^2 Operating time = 360 min	BDD electrode	97.6%	Garcia-Costa et al. (2020)

1949). However, this process needs high amount of Fe^{2+} salt to produce enough $^{\bullet}OH$, which could increase the operating cost as well as generate iron-laden sludge as secondary waste that further require supplementary treatment.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^{-} \quad (6.3)$$

$$^{\bullet}OH + H_2O_2 \rightarrow H_2O + HO_2{}^{\bullet} \quad (6.4)$$

$$^{\bullet}OH + Fe^{2+} \rightarrow Fe^{3+} + OH^{-} \quad (6.5)$$

Moreover, use of high concentration of reagent also favours liberation of less reactive species, like $HO_2{}^{\bullet}$, which drops the efficiency of mineralization due to the formation of persistent toxic intermediates. Therefore, to overcome these shortcomings of Fenton process, researchers have paid attention on the Fenton-like processes. One of such Fenton-like process is electro-Fenton (EF) process, where two-electron reduction pathway of O_2 at cathode surface produced continuous H_2O_2 in the aqueous solution to be treated, that further decomposed by Fe^{2+} to generate $^{\bullet}OH$ in the electrochemical cell (Eq. 6.6) (Fig. 6.3).

$$O_2 + 2H^{+} + 2e^{-} \rightarrow H_2O_2 \quad (6.6)$$

The electrochemically generated H_2O_2 in the system is an added advantage, which could reduce the cost along with the risks associated with its handling, storage and transportation (Priyadarshini et al. 2022b). Moreover, for proceeding the Fenton reaction, about 10^{-4} M of Fe^{2+} salt is externally added in to the solution, that converted to Fe^{3+}, which again undergoes cathodic reduction, and regenerated to

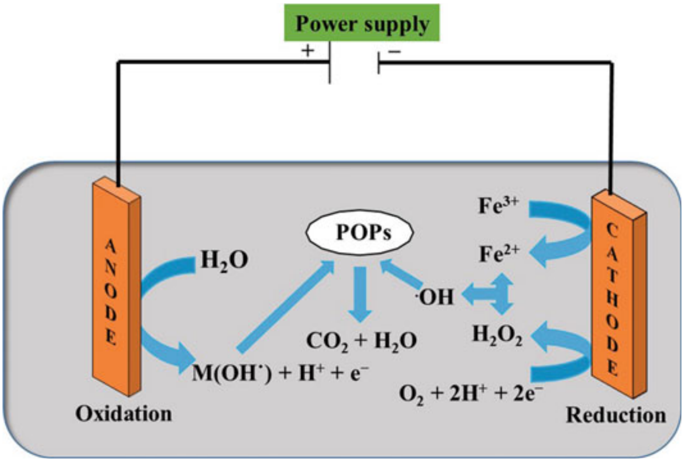

Fig. 6.3 Typical electro-Fenton (EF) and mechanism involved therein

Fe^{2+} ions (Eq. 6.7). At the same time, the generated Fe^{2+} ions produce $^{\bullet}OH$ by decomposing electrochemically generated H_2O_2 in the system. During EF process, the water molecules get oxidized at the anode surface and produce metal absorbed $^{\bullet}OH$ species, which also participate in the degradation of POPs (Eq. 6.1).

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \tag{6.7}$$

6.3.2.2 Application

The EF technology has been successfully adopted for the removal of POPs from contaminated water. For instance, a low-cost graphite bar cathode was used to degrade 230 mg/L of 2,4-di-chlorophenoxyacetic acid (2,4-D) from wastewater and almost more than 95% mineralization was observed after 4 h of electrolysis time at 1 mM of Fe^{2+}, 0.05 M of Na_2SO_4 and 450 mA of current (Brillas et al. 2000). Further, the pathway of mineralization has been identified using gas-chromatography mass spectroscopy (GC–MS), and the result showed the formation of hydroxylated derivatives as a primary intermediate, which further oxidized in to polyhydroxylated, followed by quinones and short-chain carboxylic acid due to attack of $^{\bullet}OH$ on 2,4-D (Brillas et al. 2000). However, these intermediates, particularly quinones, are very toxic in nature; therefore, complete degradation of such derivatives is highly necessary for environmental protection point of view.

Similarly, the degradation of 100 mg/L of amoxicillin was observed using cathode manufactured from multi-walled carbon nanotubes and co-modified carbon black-graphite felt cathode, and about 98.7% degradation of amoxicillin and 309 mg/L production of H_2O_2 was reported at optimal operating condition of 30 min of reaction time, 0.5 mM of Fe^{2+} and 15 mA/cm^2 of current density (Pan et al. 2020). About 66.1% of TOC removal and 566 mg/L of H_2O_2 production were achieved by adopting a dual gas diffusion cathode for the degradation of 1000 mg/L of tartrazine at optimum operating conditions (time = 120 min, Fe^{2+} = 22 mg/L, CD = 7.1 mA/cm^2) (Yu et al. 2015).

6.3.3 Electrocoagulation (EC)

6.3.3.1 Mechanism

The process of electrocoagulation (EC) can be utilized for the remediation of contaminated water by the production of in situ coagulants, which acts as a destabilizing agent to neutralize the surface electric charge of the colloidal pollutants. Thus, agglomeration of pollutants can take place for their removal through sedimentation (Kobya et al. 2008). In context, for the first time in 1889, the sewage treatment was carried out in London by mixing wastewater with seawater for electrolysis (Ingelsson et al.

2020). However, during the nineteenth century, A.E. Dietrich treated the contaminated water released from ships and patented the innovative concept of EC. Moreover, in 1909, J. T. Harries patented the application of sacrificial aluminium and iron electrode in EC for wastewater treatment. Further, in 1940s, dissolution of aluminium as the sacrificial anode into the solution was carried out in a cell known as electrochemical coagulator (Ahmad et al. 2022). Since then, the researchers have employed the technology for the remediation of different pollutants, like heavy metals, dyes, pharmaceuticals, pesticides, bacteria and other pollutants from wastewaters.

The fundamental principle of the EC technology relies on the Faraday's law of electrolysis, wherein breakage of molecules can take place by applying external electricity. In a basic EC set-up, multiple or single sacrificial electrode pairs are arranged vertically in a cell, which are also attached to an external energy source for the electro-generation of metal coagulants to facilitate charge neutralization and floc formation (Sankar and Sivasubramanian 2021), thus rendering the pollutant removal through sedimentation at the bottom of the set-up (Fig. 6.4). In detail, on the application of current, electrochemical oxidation as well as metal dissolution of the anode into the solution occurs, the generated metal ions can destabilize the stable pollutants (Eqs. 6.8 and 6.9). Simultaneously, hydroxyl ions (OH^-) and hydrogen (H_2) gas were also produced at the cathode electrode through electrolysis of H_2O, the OH^- and metals ions from the anode react to generate metal hydroxide complexes ($M(OH)_n$) with significant surface area to assist agglomeration of the dissolved contaminants (Eqs. 6.10 to 6.12) (Aoudj et al. 2010). In addition, the H_2 gas (bubble) floats the suspended particles through buoyancy onto the surface of the contaminated water; thus, pollutants removal through floatation can also take place within an EC set-up, which is an added advantage of this technology.

$$\text{At anode: } M\ (\text{s}) \rightarrow M^{n+}\ (\text{aq}) + ne^- \tag{6.8}$$

$$2\text{H}_2\text{O (I)} \rightarrow 4\text{H}^+\ (\text{aq}) + \text{O}_2\ (\text{g}) + 4e^- \tag{6.9}$$

$$\text{At cathode: } M^{n+}\ (\text{aq}) + ne^- \rightarrow M\ (\text{s}) \tag{6.10}$$

$$2\text{H}_2\text{O (l)} + 2e^- \rightarrow \text{H}_2\ (\text{g}) + 2\text{OH}^- \tag{6.11}$$

$$\text{In solution: } M^{n+} + n\text{OH}^- \rightarrow M(\text{OH})_n \tag{6.12}$$

Moreover, theoretical mass of the coagulants produced from the leaching of anode is estimated using Faraday's law of electrolysis (Eq. 6.13) (Ghernaout et al. 2019).

$$\Delta M_{\text{th}} = \frac{ItM}{nF} \tag{6.13}$$

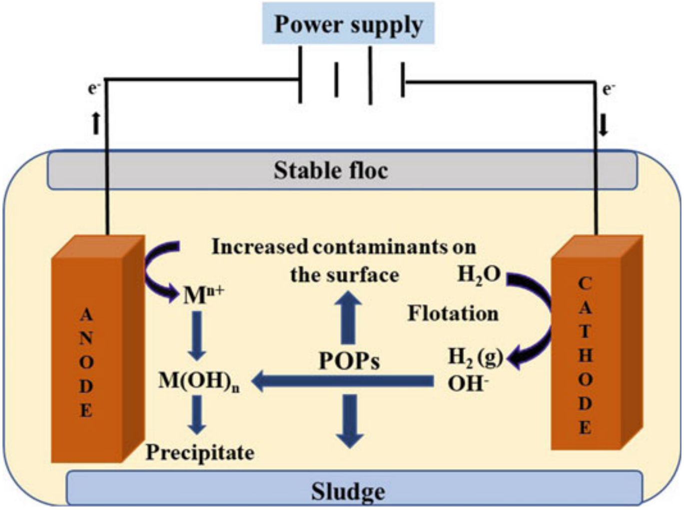

Fig. 6.4 Elimination of persistent organic pollutants (POPs) by an electrocoagulation system

where, ΔM_{th} is the produced coagulant mass (g), I is the external supplied current (A), t is the time of electrolysis (s), M_w is the molecular weight of the metal (g/mol), Z is the number of electrons involved in the reaction, and F is Faraday's constant (96,485 C/mol). The theoretical mass of metal coagulants generated can be deviated from the experimental mass of coagulants produced in the EC set-up owing to the occurrence of other side reactions on the anode. For instance, at alkaline pH, evolution of oxygen at anode occurs, which might be the reason for the deviation in the actual mass to the theoretical value for the metal ions (Eq. 6.9) (Ahmad et al. 2020).

6.3.3.2 Application

The extensive utilization of EC as a sustainable electrochemical technology for the treatment of POPs laden wastewater attributes to its easy mode of operation, lower installation cost, minimal sludge production, and no chemical addition is required during the treatment compared to conventional coagulation process. The EC is implemented for the treatment of wastewater arising from industries, such as tannery, oil and grease, textiles, pharmaceuticals, restaurant, and laundry. Moreover, recovery of nutrients in the form of struvite (phosphate derivative) is also possible through EC (Ahmad and Gupta 2019). In addition, EC is also effective for the remediation of POPs laden wastewater, which is discussed elaborately in the subsequent section.

Recently, EC was adopted for the elimination of ciprofloxacin from wastewater employing iron electrodes. At optimum current density of 4.3 mA/cm^2, electrolysis time of 10 min and pH of 4.0, nearly about 86.6% of 5 mg/L of ciprofloxacin removal was obtained (Yoosefian et al. 2017). Similarly, when aluminium electrodes are utilized for the remediation of ciprofloxacin, about 88.57% of 32.5 mg/L of ciprofloxacin was achieved at optimum current density of 12.5 mA/cm^2 and reaction time of 20 min (Ahmadzadeh et al. 2017). The high removal of ciprofloxacin in case of aluminium compared to iron electrodes can be attributed to the high current density and electrolysis time, which can generate more aluminium flocs for the adsorption of pollutants on to its surface (Ahmad et al. 2020), thus rendering the removal of ciprofloxacin through precipitation. On the other hand, EC was also deployed for the degradation of pesticides from polluted water. In an investigation, dicofol pesticide removal from synthetic wastewater through aluminium electrodes was explored, and with 2 h of electrolysis time, voltage of 15 V and electrode gap of 8 cm, about 95.52% dicofol removal was obtained (Rao et al. 2017). Similarly, about 90% of 40 mg/L of malathion was removed with aluminium electrodes at optimum operating condition of current density 10 mA/cm^2 and 10 min of electrolysis time following pseudo-second-order kinetics (Behloul et al. 2013).

Additionally, other POPs like phenolic compounds, which are widely used in different household applications, such as detergents, emulsifiers, wetting agents and dispersants, are also effectively removed through the EC process. For instance, phenol removal from paper mill wastewater was explored with aluminium and iron anodes. The effect of operating parameters was also investigated, and at optimum applied voltage of 12 V, current density of 10 mA/cm^2 and initial concentration of 2.5 mg/L, about 98% and 92% of phenol was removed with aluminium and iron electrodes, respectively (Ahmad et al. 2020; Uğurlu et al. 2008; Vasudevan 2014). Hence, it can be concluded that both aluminium and iron electrodes have shown efficient removal of phenol from wastewater. Similar other observations pertaining to the POPs laden wastewater are summarized in Table 6.3.

6.4 Factors Affecting the Performances

There are several parameters that affect the performance and functioning of electrochemical technologies in terms of treatment of pollutants from wastewater. The factors, such as current density, type and concentration of electrolyte, initial pollutant concentration and electrode gap, are important for achieving effective removal efficiency at minimum operating cost. In this section, a discussion on different factors affecting the performance of electrochemical technologies for pollutant removal from wastewater has been articulated.

6.4.1 Current Density

The current density (mostly measured in mA/cm^2) stipulates the ratio of applied current to the projected surface area of the electrodes. The current density is a vital parameter in electrochemical technologies as it determines the amount of metal species, ROS, hydroxyl ions and bubble generation in the set-up. Also, it can be controlled directly by an external power supply, which might help in minimizing the operational cost. The current density can be evaluated by the ratio of applied current to the projected surface area of the electrodes (Ahmad et al. 2022). Generally, current density is expressed in mA/cm^2. The increase in current density can improve the pollutant removal efficiency up to optimum, which can be ascribed to the production of sufficient metal coagulants and ROS in the system to facilitate the removal of pollutants, either by adsorption on to the coagulants surface in EC, or via oxidation in the electrochemical oxidation process (Kalivel et al. 2020). However, the rise in current density above the optimum value might decrease the removal efficiency owing to the occurrence of other side reactions in the system, which would inhibit the mass transfer rate of pollutants to the coagulants or to the ROS. Thus, a lower number of pollutants are adsorbed or oxidized in the set-up, and a decrease removal is obtained at current density above optimum.

6.4.2 Electrolysis Time

The rate of reaction between the pollutants and the coagulants or ROS also depends on the electrolysis time. Generally, the prolonged electrolysis time will amplify the remediation efficiency due to higher production of flocs or ROS up to an optimum electrolysis time (Bener et al. 2019). However, beyond the optimum time, the efficiency of the set-up remains constant and does not improve efficiently with time, which can be attributed to the generation of other side reactions in the system. Additionally, prolonged time will result in a higher energy consumption; thus, it is crucial to optimize the electrolysis time required for electrochemical process.

6.4.3 Electrolyte Concentration

The dose of electrolyte also plays a crucial role in the electrochemical technologies, as electricity consumption is highly influenced by the solution conductivity, which depends on the concentration of electrolyte. Generally, sodium chloride (NaCl) and sodium sulphate (Na_2SO_4) have been utilized as an electrolyte to increase the conductivity of the solution owing to their low cost and easy availability in the market (Sandoval et al. 2021). The increase of electrolyte dose can enhance the conductivity of the solution, which can also help in improving the rate of electron transfer even at a low potential. Thereby, desired current can be provided to the electrodes at smaller applied potentials that might amplify the efficiency of the set-up in terms of pollutant removal, as well as low energy can be consumed during the treatment.

6.4.4 Initial Concentration of Pollutant

The efficacy of the electrochemical technologies is also affected by the initial concentration of pollutants. For a constant current density, the removal efficiency decreases with an increase in initial concentration of pollutant (Ahmad et al. 2020). This can be ascribed to the insufficient availability of ROS and metal complexes for the oxidation and absorption of pollutants on to its surface compared to higher number of pollutants, thus decreasing the efficiency of the process.

6.4.5 Inter-electrode Distance

The distance between the two electrodes, i.e. anode and cathode, limits the internal resistance and energy requirement of the electrochemical technologies. The maximum efficiency can be achieved by maintaining the optimum gap between the electrodes. When the electrode gap is smaller than the optimum value, the electric field produced on the application of current between the electrodes might shatter the metal complexes owing to inter collision; as a result, less flocs or ROS is available for the removal of contaminants (Ahmadzadeh et al. 2017). Consequently, extended inter-electrode distance more than optimum might not be viable for the potential flocs or ROS formation; thereby, decrement in removal capability can be observed with large electrode gap. Hence, it is important to optimize the inter-electrode gap prior to real-scale applications of the electrochemical technologies for wastewater treatment.

6.5 Conclusion and Future Perspective

The frequent occurrence of POPs in aquatic environment over the past two decades has arisen serious environmental concern. The POPs are being highly toxic and persistent in nature; thus, it is very difficult to eliminate by conventional WWTPs. Therefore, WWTPs is one of the major sources for releasing POPs into the receiving water bodies. In this regard, electrochemical technologies are coming up as the most efficient technologies for the removal of POPs from wastewater, as these processes offer numerous advantages, like shorter treatment time, require fewer chemical reagents and generate minimal amount of sludge compared to conventional chemical and biological technologies. Apart from these advantages, till date very few large-scale applications of electrochemical technologies currently exist because of many limitations, such as high operating cost owe to the electricity consumption and frequent replacement of electrode materials due to electrode fouling. Thus, development of low-cost, stable and durable electrodes, such as waste-derived and reusable catalytic materials, is necessary, which can minimize the operating cost as well as improve the electrocatalytic activity.

Moreover, the renewable energy sources, such as solar and wind turbines energy, can also be utilized as a power source for operation that could also minimize the treatment cost. Real-time analysis of the anodic surface interaction with pollutants is necessary to know possible pathway of radicals generation during degradation of pollutants, which could help in the selection and fabrication of better electrodes. Additionally, prior to large-scale implementation, different operating parameters, such as electrode materials, inter-electrode distance, reactor design, concentration of electrolytes and pollutants, are required to optimize, thus to obtain desirable results at minimal operating cost. The intermediates generated during the degradation process are not generally identified due to difficulty in detection; therefore, future efforts should be given for the identification and quantification of these toxic intermediates.

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Chapter 7

Recent Progress in Electrochemical Oxidation Technology: Its Applicability in Highly Efficient Treatment of Persistent Organic Pollutants from Industrial Wastewater

Dharmendra Singh Ken, Alok Sinha, Bhupendra Singh Ken, and Ravindra Singh

Abstract Over recent years, industry, agriculture, and other human activities have released a large number of organic or inorganic pollutants into natural water resources. Out of them, water pollution through industrial origin is a great matter of concern since it contributes largely to pollution than other activities. Wastewaters generated from different types of industries like coal processing, pharmaceutical, textile, fertilizers, petrochemical industries, etc., release several types of persistent organic pollutants (POPs) due to their different water handling practices like coke making, dye making, drug and fertilizer manufacturing, etc. Till now there are several treatment technologies that have been applied for the effective elimination of these POPs from water. But most of these technologies have some limitations. Out of them, electrochemical oxidation (ECO) technologies have recognized as highly efficient. This chapter has discussed about the recent progress made in the field of electrochemical oxidation techniques, their modified versions, and future possibilities to get easy and cost-effective wastewater treatment techniques. Authors mainly focused on the working mechanism of the ECO process, different types of electrode materials and their preparation, electrocatalysts, catalytic particle electrodes (CPEs), electrolytes, and their involvement in the reaction. Moreover, authors have also revealed the investment of different operating conditions for the optimization of any electrochemical oxidation technology. Additionally, the preparation of electrodes, their connections (anodes and cathodes) as well as the reactor designs have also been summarized in order to improve the performance of the electrochemical system. Finally, the participation of electrochemical technology specially for the treatment of several persistent organic pollutants generated from different type of wastewaters has been discussed.

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Lastly, the existing challenges and the limitations in the field of electrochemical oxidation (ECO) technology are also summarized.

Keywords Electrochemical oxidation (ECO) technology · Electrode materials · Electrocatalysts · Catalytic particle electrodes (CPEs) · Coke-oven wastewater · Dimensionally stable anode (DSA) · Direct oxidation · Indirect oxidation · etc.

7.1 Introduction

Nowadays, pollution of water bodies via natural or anthropogenic sources is very common which causes low availability of freshwater for human use which ultimately accountable for global water scarcity issues. The uncontrolled release of various carcinogenic and persistent pollutants (organic or inorganic) into natural water bodies makes them unusual for drinking and other human activities which ultimately destroys the aquatic life as well as dangerous to human and other living beings. Persistent or refractory organic substance basically represents the organic matter which comprises very less biodegradability. It was already established that if any wastewater contain BOD_5/COD ratio less than three ($BOD_5/COD < 3$), it can be considered as refractory or persistent organic matter (Li et al. 2021). Persistent pollutants in water mainly include polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides (including DDT, aldrin, chlordane), polychlorinated biphenyls (PCB), polybrominated diphenyl ethers (PBDEs), dioxins, and perfluoroalkyl acids (PFAS), phenols, cyanide, ammonia, anilines and dyes, etc. These compounds have lot of resistance toward conventional treatment methods. Once if they are released into the water bodies, they can remain unchanged for a long period of time. They can easily migrate through different media in the environment. Also, they can accumulate and possess toxicity at cellular level in the living organisms even at very low concentration due to their carcinogenic, teratogenic, and mutagenic effects. Hence, treatment of these pollutants from water is a great matter of concern worldwide for which number of treatment technologies have been developed and many of them are in their developmental phase. In past few decades, adsorption, ion exchange, coagulation, photocatalysis, nanotechnology and electrochemical oxidation techniques, etc., have gained much attention among scientific communities. Most of these techniques have some limitations or difficulties for the treatment of persistent pollutants or persistent organic pollutants available (POPs) from different types of wastewater. Out of them, electrochemical techniques such as electrochemical oxidation (ECO), electrocoagulation (EC) and electro-flotation (EF), electro-fenton (EF), photoelectro-fenton and solar photoelectro-fenton, etc., have gained so much popularities due to their extensive and powerful contaminants (organic and inorganic) treatment nature from wastewater. Moreover, these treatment technologies are most efficient as compared to other techniques due of their easy operation, less time and space consumption, automation, less chemical requirement, cost-effective, and eco-friendly nature. The electrochemical oxidation techniques basically work on the generation of strong oxidizing species such as active oxygen (*OH radical), active chlorine, active sulfate-related species (OH*, $Cl_{2(aq)}$, HOCl, ClO^-, H_2O_2, $S_2O_8{}^-$, and O_3) via exchange of electrons through the medium. According to the nature of electrolytic medium, the generation rate and characteristics of free radicals may change which influence the degradation/removal of pollutants (Eqani et al. 2013; Alardhi et al. 2020; Zaynab et al. 2021; Moreira et al. 2015; Stergiopoulos and Giannakoudakis 2014; Wang et al. 2019; Wang and Xu 2012; Qiao and Xiong 2021). In electrochemical oxidation process, pollutant abolition is mainly carried out at the interface of working electrode and water medium under the effect of an external electric field. Various previous literatures observed that electrocatalytic/electrochemical oxidation has beautifully treated printing and dyeing wastewater (Hamza et al. 2009; Moreira et al. 2013), pharmaceutical wastewater (Zhan et al. 2019; Murugananthan et al. 2011), pulp or paper wastewater (Wang et al. 2007), landfill leachate (Zhang et al. 2010), chlorinated-phenol wastewater (Ajeel et al. 2015), nitrobenzene wastewater (Quiroz et al. 2014), phenolic wastewater (Berenguer et al. 2016), aniline wastewater (Brillas et al. 1998), coking wastewater (Zhang et al. 2020), and secondary industrial wastewater (Li et al. 2021; Can et al. 2014).

The removal efficiency of electrochemical oxidation process can also be improved by making the modification in the electrode materials and reactors design. In the initial phase of this technology, several easily available metal and carbon-based electrodes (such as iron, aluminum, copper, stainless steel, carbon clothe, and glassy carbon) were utilized. Now, these electrode materials are outdated due to their huge corrosive and sludge generation nature during electrochemical oxidation. In last two/three decades metal oxides and mixed metal oxides (MMO) coated electrodes such as boron-doped diamond (BDD) electrode, metal oxides coated on titanium sheet (like Ti/PbO_2, Ti/TiO_2, and Ti/SnO_2) were vastly applied for wastewater treatment through electrochemical oxidation. Since these electrodes are highly stable against corrosion, hence, these electrodes are also acknowledged as dimensionally stable anodes (DSAs) (Jarrah and Mu'Azu 2016). Because of their outstanding catalytic performance, non-corrosive nature, high stability, and noteworthy removal efficiency pollutants from wastewater, the popularity of these DSAs or MMO coated electrodes have been increased (Ken and Sinha 2021).

In Fig. 7.1, a typical electrochemical reactor has shown containing anode, cathode, and other supportive devices in a typical undivided plexi-glass chamber in galvanostatic mode. This is also known as two-dimensional electrochemical reactor (2D-EC reactor), which can be easily converted in 3D-EC reactor by filling the pre-synthesized catalytic particles (also known as catalytic particle electrodes (CPEs)) between the available space of anode and cathode to increase the process performance through catalysis.

In this chapter, authors have discussed about the recent progress in the field of electrochemical oxidation techniques, their modified versions, and the future possibilities for the easy and cost-effective ECO-based wastewater treatment. The working mechanism of the electrochemical process, varieties of electrode materials, and their preparations have also elaborated here. Moreover, a brief report on electrocatalysts,

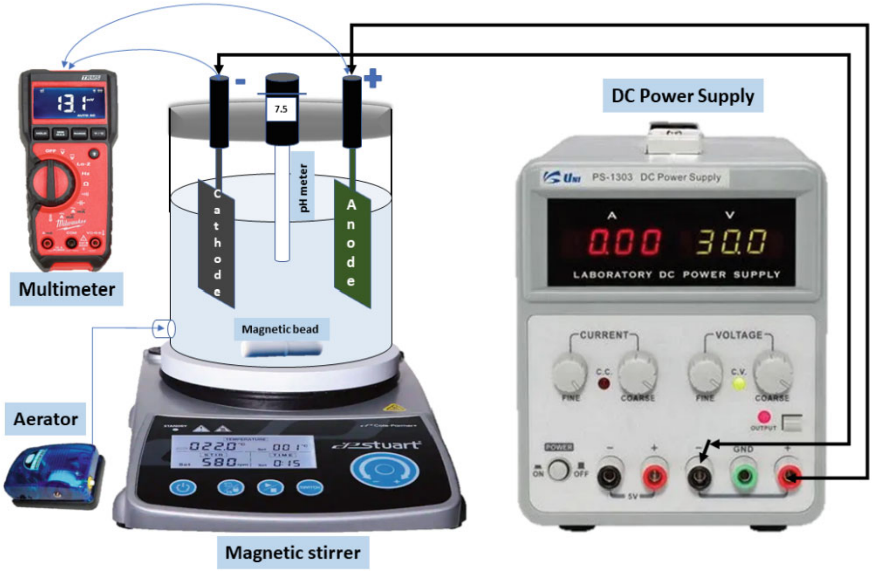

Fig. 7.1 Typical 2D-electrochemical reactor

catalytic particle electrodes (CPEs), electrolytes, and their utilities in the electrochemical technology have been discussed. In order to improve the performance of the electrochemical system, the applied operating conditions during electrochemical oxidation process, reactor designs as well as the selection and connections of electrodes (anodes and cathodes) inside the cell have also summarized. At the end the involvement of electrochemical technology specially for the treatment of coking and other types of wastewaters have been discussed as well as the existing challenges and the limitations in this context of electrochemical/electrochemical oxidation (ECO) technology have also been described.

7.2 Mechanism Behind the Treatment

The mechanism behind the degradation of persistent organic pollutants through electrochemical method can be reparented in two ways: (1) direct oxidation and (2) indirect oxidation (Qiao and Xiong 2021; Brillas and Martínez-Huitle 2015; Garcia-Segura and Brillas 2011). It is noteworthy that the degradation of persistent pollutants is basically based on the anodic oxidation. Except dechlorination, scientific community did not find any scientific evidence which can prove the cathodic degradation of POPs through electrochemical method. Dechlorination minimizes the toxicity of wastewater but increases the biodegradability (Qiao and Xiong 2021).

7.2.1 Direct Oxidation

In direct electrochemical oxidation first of all the persistent organic matter is directly adsorbed at the surface of anode then involve in the direct charge transfer mechanism at the surface of anode and finally get oxidized as shown in Fig. 7.2a. The carbon chain is fragmented and the molecular weight get reduced.

The simple representation of this is given here:

$$R \rightarrow R_{oxd} + e^- \tag{7.1}$$

where R = persistent organic compound; R_{oxd} = oxidized content.

Direct electrochemical oxidation basically contains two important features: (1) The diffusion of organic content from electrolytic medium or solution to the surface of anode. This step limited the oxidation rate of organics (Panizza and Cerisola 2009). (ii) The rate of oxidation/mineralization in direct oxidation is primarily associated to the electrocatalytic nature of working electrode (anode) as well as the applied current intensity/density. Also, it doesn't influence by other oxidized constituents. However, the interaction of organics and electrons is mainly occurred at the electrode (anode) potential which is substantially lower than the oxygen evolution reaction (OER) potential (Qiao and Xiong 2021; Garcia-Segura et al. 2018b).

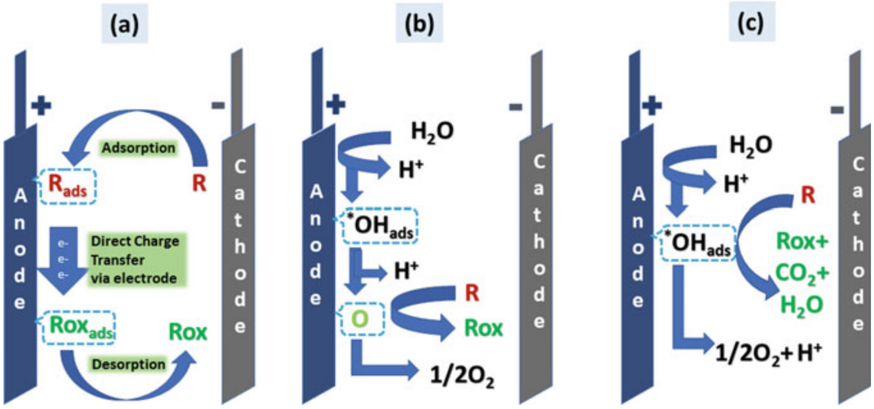

Fig. 7.2 Direct electrooxidation and **a** the working mechanism of reactive O_2 species on the surface of working electrode (anode) and **b** non-active anode and **c** in the ECO system (bulk medium). Adapted and modified from Qiao and Xiong (2021)

7.2.2 Indirect Oxidation

Under the influence of strong external current, the intermediate active oxidants of oxygen or other species such as *OH, O_3, H_2O_2, $S_2O_8^{2-}$, Cl_2, HClO-, ClO^-, and $P_2O_8^{4-}$ are generated at the surface of anode/working electrode or at the interface of the electrode and aqueous electrolytic solution (Sirés et al. 2014; Matzek and Carter 2016; Barreto et al. 2015; Nidheesh et al. 2018). The production of these active oxidizing species basically depends upon the availability of parental salt/compounds in the wastewater. The consecutive set of oxidation mechanisms such as electron transfer, double or triple bond formation, breakdown of cyclic ring and the functional group replacement and removal, etc., are mainly responsible for the complete degradation and mineralization of organic impurities in the medium. As discussed above, in case of indirect oxidation, the preliminary phase of oxidation mechanism occurs at the surface of anode, whereas the subsequent phase of oxidation takes place in the bulk of the medium (Qiao and Xiong 2021). Based on this, indirect oxidation can be again divided in two parts.

7.2.2.1 Indirect Oxidation at the Electrode Surface

During indirect oxidation several oxidants are generated, out of them *OH species which contains high redox potential (i.e., 2.8 V) after fluorine is generated in the high amount at electrode surface through water splitting. Due to its shorter life span (i.e., 10^{-9} s), its diffusion through electrolytic medium is very difficult. Hence, all its oxidation-related activities toward organic matter are mostly occurs at the electrode surface (Panizza and Cerisola 2009). The production and surface adsorption of *OH radical at anode can be explained by below equation:

$$M + H_2O \rightarrow M\left(HO^*\right) + H^+ + e^- \quad (7.2)$$

where M = electrode, M(*OH) = *OH at electrode surface.

This adsorption of *OH radicals on the surface of electrode may be physisorption or chemisorption. Based on the nature of the electrode (either active or non-active anode), it gets decided (Cavalcanti et al. 2013; Fóti et al. 1999). On the basis of previous literatures, it is observed that in case of active anodes (i.e., graphite, Pt, IrO_2, and RuO_2), the chemical adsorption or chemisorption takes place, whereas in case of non-active anodes (such as BDD and PbO_2), physical adsorption of *OH or physisorption occurs. This double nature of *OH adsorption on the electrode surface mainly linked with two different types of oxidation pathway (Comninellis 1994; Marselli et al. 2003), as described in Fig. 7.2b, c. The most studied active and non-active electrodes and their basic electrochemical oxidation characteristics are also enlisted in Table 7.1. In case of chemisorption (in active anodes), after the adsorption of *OH radicals on the electrode surface, a chemical bond is formed between the electrode and the oxygen atom of the chemisorbed *OH species, and

Table 7.1 Anode materials classification on the basis of their oxidation potential and O_2 evolution potential under acidic medium (Martínez-Huitle et al. 2015). Adapted from Qiao and Xiong (2021) and reproduced with Elsevier permission

Type of anode	Composition	Electrocatalytic ability of OER	Oxidation potential(V)	Overpotential for OER (V)	Adsorption enthalpy for M-*OH	Oxidation power of anode
Active anode	Ru-TiO_2 (DSA®-Cl_2)	Good	1.4-1.7	0.18	Chemisorption of *OH ↓	Lower ↕
	Ir-Ta_2O_5 (DSA®-O_2)	Good	1.5-1.8	0.25		
	Ti/Pt	Good	1.7-1.9	0.30		
	Carbon and Graphene	Good	1.7	-		
Non-active anode	Ti/PbO_2	Poor	1.8-2.0	0.50		
	Ti/SnO_2-Sb_2O_5	Poor	1.9-2.2	0.70	Physisorption of *OH	Higher
	P-Si/BDD	Poor	2.2-2.6	1.3		

lastly, the oxidation takes place after their interaction with the available organic matter. Whereas in case of physisorption (in non-active anodes), these *OH radicals do not form any chemical bond with the electrode (Malpass and Motheo 2021); this can be understood by below equation:

$$M(HO^*) \rightarrow MO + H^+ + e^- \tag{7.3}$$

where M = electrode, MO = chemisorbed *OH at electrode surface.

In case of active anodes due to the formation of MO (chemisorption), the oxidation power of *OH radical is comparatively get reduced than its original form or physiosorbed *OH as in case of non-active anodes (Qiao and Xiong 2021; Cavalcanti et al. 2013).

7.2.2.2 Indirect Oxidation in the Bulk of the Electrolytic Medium

The electrolytes generally utilized to increase the conductivity of the medium at the same time they also play catalytic role due to the presence of valuable ionic species (like Cl^-, SO_4^-, etc.) in aqueous medium. In the bulk of the medium due to their hydrolysis, they may produce active oxidant species such as $S_2O_8^{2-}$, $Cl_2(aq)$, $HClO^-$, and ClO^-, based on the available electrolyte. Although these oxidizing species has low oxidation potential than *OH radical but their life span and diffusion

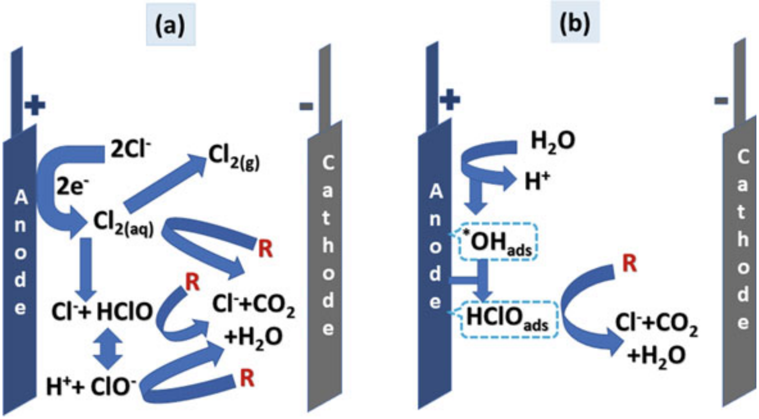

Fig. 7.3 **a** Pathway of generation of active chlorine oxidants via direct Cl^- oxidation and **b** generation of active chlorine oxidants through reactive oxygen species. Adapted and modified from Qiao and Xiong (2021)

characteristics in the aqueous medium is very high. Hence, they diffuse through medium and oxidize the organic matter at the electrode surface as well as in the bulk of the medium. The major part of this oxidation usually occurs in the bulk of the medium; thus, it is also known as bulk oxidation (Chanikya et al. 2021; Neodo et al. 2012). For better understanding, please see Fig. 7.3a, b and the equation no. (4–8). It was seen that a certain amount of these species is beneficial for better performance which can be control through the optimization of electrolyte (Qiao and Xiong 2021; Radjenovic and Sedlak 2015).

$$M\left(HO^*\right) + Cl^- \rightarrow M\left(HClO^-\right) \tag{7.4}$$

$$M(HClO) \rightarrow \frac{1}{2}Cl_2 + OH^- \tag{7.5}$$

$$2Cl^- \rightarrow Cl_{2(aq)} + 2e^- \tag{7.6}$$

$$Cl_{2(aq)} + H_2O \rightarrow HClO + Cl^- + H^+ \tag{7.7}$$

$$HClO \rightarrow H^+ + ClO^- \tag{7.8}$$

7.3 Influence of Key Operating Parameters

The monitoring and control of operating parameters in any electrochemical system are essential because they may tune the performance of the system. Their influence can affect any electrochemical system either positively or negatively. It necessarily depends upon the contribution of any factor or parameter to complete the electrolysis reaction. In electrochemistry, there are so many key factors exist that may affect the system performance broadly or shortly, such as initial pH, electrolyte, current density, catalyst dose, aeration rate, interelectrode distance, electrolysis time, temperature, mixing speed, pollutants concentration, etc., as shown in Fig. 7.4.

7.3.1 Influence of Initial pH

Since the pH controls the generation of active oxidants (*OH radical) and other species in the system which are mainly responsible for electrooxidation; hence, the initial pH of the system is need to be adjusted. People have adjusted the initial pH from acidic to alkaline range based on the chemical nature of the generated oxidants and their interactions with the available organic or inorganic matter of

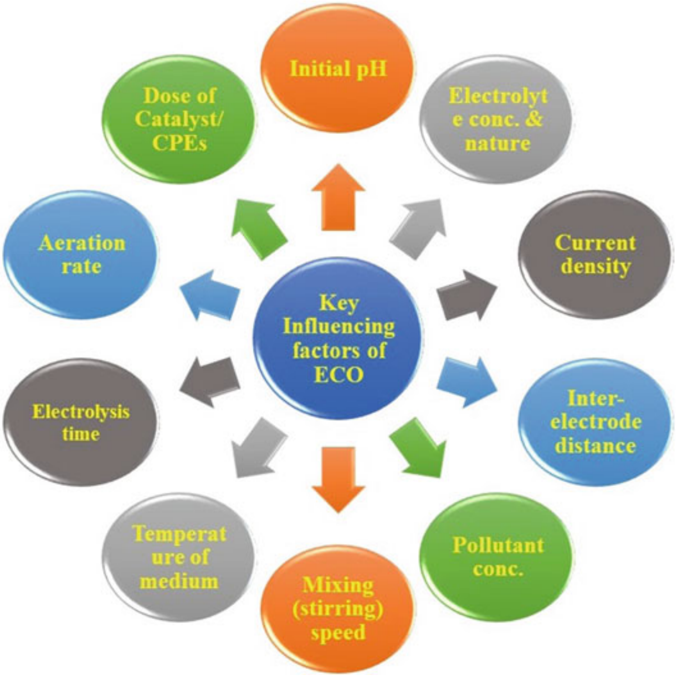

Fig. 7.4 Flowchart of key parameters which influence the electrochemical oxidation process

the medium. Some literatures have suggested that acidic while others suggested alkaline conditions are better for the generation of high amount of reactive oxygen species which ultimately linked to the better removal efficiency of the system. It is noticed that in acidic conditions, oxygen evolution is high which proves the direct oxidation as dominating mechanism. Meanwhile, it has been also reported that under extreme acidic conditions, the working electrode corrodes, resulting in a reduction in removal efficiency and an increase in the cost of the system due to the need for replacement of the working electrodes. On the other hand, in alkaline conditions, the direct oxygen evolution potential is low as compared to acidic pH, but the side reactions are very prevailing and responsible for indirect oxygen evolution which displays here indirect oxidation as dominating mechanism (Li et al. 2021). In case of electro-fenton, most of the published data is at the pH = 3, because at this pH the $^{*}OH$ generation rate is very high, whereas at alkaline pH, the precipitation of iron (Fe^{2+}) into iron hydroxide was also noticed which leads to the decline in removal efficiency at alkaline pH (Antonin et al. 2015; Garcia-Segura et al. 2015; David et al. 2015; Ghime and Ghosh 2019). Moreover, in many cases of phenolic, landfill leachate and coking wastewater through ECO the pH were set as alkaline for best removal. Hence, the initial pH of the system can be acidic/alkaline mainly depends upon the nature of wastewater, electrolyte and generated oxidants, etc. (Li et al. 2021).

7.3.2 Influence of Electrolyte Nature and Concentration

In order to increase, the process performance conductivity of the medium is important, which can only be possible through addition of adequate amount of supporting electrolyte. Several types of salts such as NaCl, Na_2SO_4, NaOCl, KH_2PO_4, K_2HPO_4, KCl, and $NaClO_4$, have already been utilized by different investigators. Out of them, NaCl and Na_2SO_4 are very common and easily available salts. In our earlier work, it was observed that NaCl is highly efficient than Na_2SO_4 for the abolition of coke-oven of wastewater because the active chlorine species ($Cl_{2(aq)}$, HOCl, ClO^-) generated through NaCl comprises the greater redox potential than active sulfate species ($S_2O_8{}^{2-}$) generated through Na_2SO_4 in the medium (Ken and Sinha 2021). Also, non-active anodes (such as BDD, PbO_2) are very efficient to generate high amount of $S_2O_8{}^{2-}$ species as compared to active anodes. Giraldo et al. (2015) estimated the influence of different supporting electrolytes on antibiotic oxacillin degradation through electrochemical method using Ti/IrO_2 as anode (Ghime and Ghosh 2019; Giraldo et al. 2015). The increased amount of electrolyte increases the current flow which leads to the increment in the mass transfer rate and then improves the removal efficiency of the system. The improvement of the working current tends to be at a stable state with the increment in electrolyte concentration. The optimization of electrolyte conc. is must because if the electrolyte amount continues to rise, it leads to waste of electrolyte and creates the trouble of subsequent wastewater treatment (Li et al. 2021).

7.3.3 Influence of Current Density (CD) of the System

Usually, ECO reactors are operated in the galvanostatic mode. Current density (CD or j) can be defined as the current (electron) flow per unit correctional area of working electrode which basically depends upon the strength of the electrons inside the system. The movement of electrons from anode to cathode inside the cell is mainly responsible for redox reactions and degradation of pollutants inside the cell. If we increase the current density, the mineralization of organic contents increases. The main reason behind this is the increased production of active oxidants due to high electron transfer inside the medium. But after a certain value, further increment in the current is not significant due to the formation of parasitic reactions in the medium or the development of electrode saturation condition. This certain value of CD is also known as optimum current density which is also influenced by other operating parameters like pH, flow rate and temperature of cell, etc. Many studies have been done which are investigated CD effect on treatment efficiency of different pollutants in different types of wastewater (Khaled et al. 2019; Kobya et al. 2016; Moussa et al. 2017).

7.3.4 Influence of Initial Concentration of Pollutants

Many investigations suggested that the removal efficiency decreases with increase in concentration of pollutant. This results the longer treatment time for ECO at higher concentration. Since the surface area of the electrode and rest of the parameters are constant throughout the process, hence the generation and availability of active oxidants are constant, whereas in case of a high concentration of pollutant, the population of organic molecules is very high due to which the interaction of organics and oxidants does not occur properly. That's why the reaction time increases with increased pollutant concentration which is reported by many authors worldwide (Labiadh et al. 2015; El-Ghenymy et al. 2013; Moreira et al. 2017). Moreover, if the redox potential and the amount of generated active oxidants (*OH) are very high, then the rate of reaction per unit time increases, which finally leads to the higher removal efficiency.

7.3.5 Influence of Interelectrode Distance (IED)

The interelectrode distance obviously affects the removal efficiency of the system, which is directly correlated to the electrolysis effect, electrode potential, and the mass transfer phenomenon of the medium (Li et al. 2021). The larger the interelectrode gap, the weaker the intensity of the electric field and the poor the electrolytic effect inside the 2D or 3D electrochemical system. Also, the resistance in the mass transfer inside the cell is decreased when the interelectrode gap is small. Thus, the rate of electrochemical oxidation reaction and treatment efficiency of the system could be enhanced. However, much small interelectrode distance has also influenced the stability of treatment. In case of 3D-reactor system, this interelectrode distance is highly correlated to the filling amount of 3D particle electrodes between the anode and cathode. If the distance is too small, the cell short-circuit problem is generated, and the short-circuit current increases than the effective current. The higher current density could be achieved at a shorter electrode gap, but at the same time, the filling amount of 3D particle electrodes between the electrode gap is also decreased. Therefore, the optimal interelectrode gap could be decided by checking these two factors essentially via repeated trails (Li et al. 2021).

7.3.6 Influence of Cell Temperature

It is observed that temperature may also influence the treatment efficiency either positively or negatively. At a higher temperature, the mass transfer rate of reactants increases toward the electrodes which result in better pollution removal efficiency. However, the higher temperature is problematic for the dissolved oxygen level of the system. As the temperature increases the DO concentration of the medium decreases, hence the formation of reactive oxygen and H_2O_2 type species is also reduced. So, there is a need for optimization of temperature to get a suitable value. Many researchers established that usually ambient temperature or mild conditions (20–30 °C) are perfect for significant electrochemical oxidation (Moreira et al. 2017; Malato et al. 2009; Boye et al. 2002).

7.3.7 Influence of Stirring Speed

The adjustment of stirring speed is essential to maintain a better mass transfer rate of reactants or pollutants as well as to maintain the uniformity of the solution. A higher mass transfer and mixing rate usually give a better system performance for pollutants degradation. If the mixing will be proper, the interaction of organic matter and oxidants will be better which ultimately increases the system performance and also avoid the sedimentation of reactor stuff. In electrocoagulation studies, the mixing speed is highly correlated to the formation and breaking of flocks during the reaction (Khaled et al. 2019).

7.3.8 Influence of Aeration/Oxygen Flow Rate

The bubbles formed through aeration continuously scrub the surface of working as well as particle electrodes in 3D or 2D electrochemical oxidation. Therefore, to avoid the deposition of suspended solids, reactants, pollutants, and intermediates on the electrode surface and for the betterment and longtime run of the process, aeration rate is necessary. Moreover, it also increases the mass transfer rate and supplies the required amount of oxygen to generate adequate reactive oxygen species inside the system. Additionally, microbubbles also exhibit excellent underwater fracture characteristics which are helpful in hydroxyl radical generation when they rupture inside the aqueous medium (Li et al. 2021).

7.3.9 Influence of Electrolysis Time

In the early stage of the electrolysis, the diffusion rate and the concentration of organics in the wastewater are very high. Meanwhile, as the reaction proceeds the accumulation of intermediates occurs which ultimately slows down the rate of diffusion and mineralization of organics. Hence, the concentration of organic content is reduced. Due to low concertation and slow diffusion in the later stage of the electrolysis, the degradation efficiency is decreased which finally increases the electrolysis time. In this manner, it can be inferred that the electrolysis time is directly related to the concentration of pollutants/organic matter inside the cell. A previous study was carried out with a focus on a single factor to uncover the relationship between the concentration of chloroaniline and the duration of electrolysis during the treatment of wastewater (Li et al. 2021).

7.3.10 Influence of Catalyst Dose

A catalyst basically accelerates the rate of electrolysis in 2D system, it can also be recovered completely at the end of the reaction. Some electrochemical systems like electro-fenton or photoelectro-fenton, etc., usually utilize iron or metal catalyst as an accelerator to produce additional reactive oxygen species or other types of oxidants to increase the removal efficiency. A high amount of catalyst dose may be unusual for the cell performance because it unreasonably increases the cost and power consumption load of the system. Therefore, an optimum dose of catalyst is always required for significant results (Dhaouadi and Adhoum 2009).

7.3.11 Influence of Filling Amount of 3D Particles Electrodes in 3D System

3D particle electrodes usually fill inside the electrode gap of the electrolysis chamber. It is noticed that these CPEs significantly minimized the electrode gap. Also, they reduced the transport distance of reactants and accelerate the mass transfer rate and finally promoted the performance of the electrochemical oxidation system. Their filling amount critically influences the electrolysis effect. The increase in the filling amount affects the diffusion of the pollutants on the surface of the 3D particles and the mass transfer rate inside the system. If the filling amount is too high, then it reduces the diffusion and mass transfer rate of pollutants, thus decreasing the system performance. On the contrary, if the filling amount is too low, it provides a poor electrolytic effect. Hence, an optimum amount is needed to be determined for the best performance of the system (Li et al. 2021).

7.4 Modifications in the Design of Electrochemical Oxidation Reactor

The modifications in the design of the electrochemical reactor are very crucial because the slight changes in the design of the EC reactor may increase or decrease the process performance of the reactor which indirectly affects the cost of the system. In recent years, some noteworthy modifications have been done in the design of EC reactor such as nature, the composition of coatings and size of electrodes, size and shape of the reaction chamber, arrangements of electrodes, amount and proper placement of catalytic particle electrodes between the anode and cathode, power supply modes, and reactor operation modes. Among them, a few most essential modifications are discussed below.

7.4.1 Selection and Synthesis of Working Electrodes

Selection and synthesis of electrodes are highly important. During the synthesis of any electrode, the base material, composition or ratios of coating materials, binders, the electrode dimensions or size are highly essential because they directly influence the electrolytic nature of the system. If the fabrication or coating is not done reasonably, the sufficient generation of active oxidants will be interrupted which reduced the system performance.

7.4.2 Involvement of Catalytic Particle Electrodes (CPEs) (Conversion of 2D-EC System to 3D-EC System)

The participation of catalytic particle electrodes has completely updated the 2D system of electrochemical technology. 3D particles are mainly improved the catalytic reactions inside the medium by increasing surface area and mass transfer rate for electrochemical oxidation. In the effect of strong electrochemical field, they get polarized and several micro-electrolytic cells are formed between working anode and cathode where the additional electrocatalytic reactions occur. There are many types of frequently used CPEs available such as metal ions, metal oxides, mixed metal oxides, ferrite, metal coated glass or plastic balls, granular graphite and activated carbon, γ-Al_2O_3 particles, granular coke powder, and steel slag (Li et al. 2021). On the basis of their electrochemical nature, these CPEs can be distributed in two categories: (1) low impedance CPEs and (2) high impedance CPEs. Low impedance conductive particles are generally employed in unipolar 3D electrochemical systems. The main problem with these CPEs is the short-circuit which may be resolved by placing a separator between the anode, CPEs, and cathode. These are mainly two types: (1) carbon-based CPEs (such as activated carbon, biochar, graphite, and carbon composites) and (2) metal conductors CPEs (such as metal, mixed metals, or alloys and coated metals), and composite particle electrodes (Li et al. 2021). Whereas in case of high impedance particle electrodes, short-circuit problem was resolved. The development of bipolarity at both ends of the CPE along with electrochemical fields is the main reason behind this. Ceramic particles, bentonite, perlite, PbO_2, kaolin, and molecular sieve are the examples of most employed high impedance CPEs.

An undivided electrochemical reactor (2D-EC system) can be easily converted into a 3D-EC system based on the filling method of the CPEs, as shown in Fig. 7.5. This 3D-EC system can be further divided into fixed bed or fluidized bed systems, as described in Fig. 7.5.

7.4.2.1 Fixed Bed 3D-EC Reactor

The CPEs are fixed in between anode and cathode as shown in Fig. 7.5a. In a typical fixed bed 3D-EC reactor, the space–time yield, volume-area ratio, and current efficiency are very high as compared to 2D-EC system. In order to increase the mass transfer aeration and stirring are also incorporated. During electrolysis, pollutants get adsorbed and desorbed on the CPEs which affects their stability. Therefore, regeneration is also required in order to maintain the stability of CPEs (Xu et al. 2008; Chu et al. 1974). Figure 7.5b exhibits a simple design of another type of 3D bioelectrochemical reactor where the anode is placed at the top, whereas the cathode is placed at the bottom, and GAC particles are filled in the cathode chamber which is separated from the anode through a permeable membrane as shown in Fig. 7.5b. The filled GACs act here like a biofilm carrier. In these reactors, the cathodic hydrogen is usually utilized by denitrifying microbes for the conversion of ammonia, nitrite, and

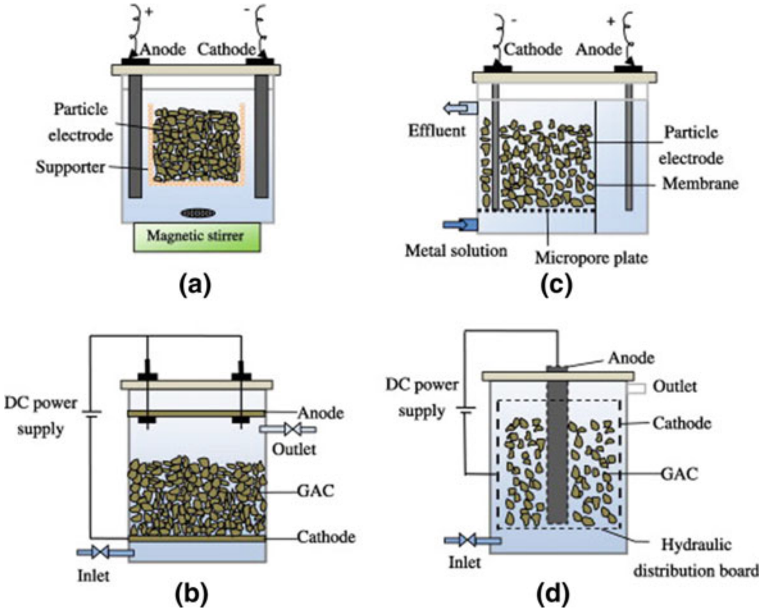

Fig. 7.5 Some typical structure of 3D electrode reactors (Zhang et al. 2013). Adapted from Zhang et al. (2013) and reproduced with permission through Elsevier

nitrate to elemental nitrogen. Other designs have also been executed where the anode is placed in the middle of the electrolysis chamber while the cathode is surrounded and fixed at the inner wall of the container (Zhou et al. 2009).

7.4.2.2 Fluidized Bed 3D-EC Reactor

Since fluidization offers a high mass transfer rate and mixing rate inside the reactors. Also, due to its high interfacial area and uniformity in the temperature, the fluidized bed is highly popular for electrolysis, electrochemical metal recovery, and cathodic reduction activities (Kumar et al. 2008). Figure 7.5c shows a 3D-EC fluidized bed reactor for heavy metals removal, where cathode chamber is separated by a membrane. The particle electrodes are placed inside the cathode chamber to increase the space–time yield in reactor. In terms of performance, these reactors are less stable due to their non-uniform distribution of current. This problem is sorted by inserting additional contact rods to increase the interaction between the electrode feeder and CPEs (Coeuret 1980; Chen 2004; Hutin and Coeuret 1977). Figure 7.5d shows another type of fluidized bed reactor. Here, the anode is placed inside and middle of the camber, whereas the cathode is surrounded and fixed at the inner wall of the container. The GACs (CPEs) in fluidization mode are placed on a hydraulic distribution board in the space between anode and cathode, and their fluidization mode is maintained by using flow rate. The mineralization of 150 ppm was almost entirely achieved within only 30 min, and about 90% GAC regeneration was also achieved within only 1.5 h after completion of five consecutive cycles (Zhang et al. 2013; Zhou and Lei 2006a, 2006b).

7.4.3 *Electrode Connections and Their Polarity*

If more than two electrodes are used in the electrochemical process (especially in electrocoagulation process), the electrode connections or arrangement pattern and inside the cell may also affect the system performance. Many investigations have discussed that there are mainly three most important electrode connections observed such as monopolar parallel, monopolar series, and bipolar parallel, as displayed in Fig. 7.6.

7.4.3.1 Parallel Connections of Monopolar Electrodes (MP-P)

As shown in Fig. 7.6a, anodes and cathodes are placed and connected parallelly inside the cell. The applied current is divided between all the electrodes of the chamber which is also correlated to the resistance of the individual cells. Therefore, as compared to series connection, very less potential difference is required.

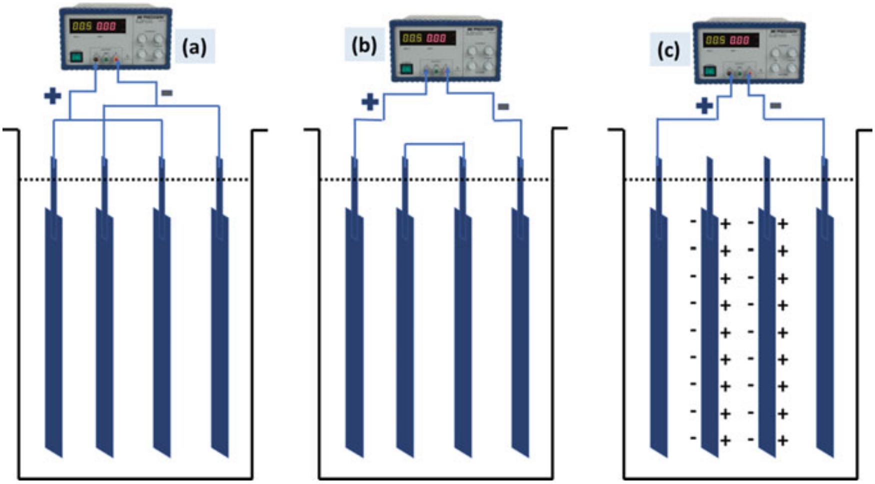

Fig. 7.6 **a** MP-P system, **b** MP-S system, and **c** BP-S system. Adapted and modified from Kobya et al. (2007)

7.4.3.2 Series Connections of Monopolar Electrodes (MP-S)

In this type of connection, each electrode couple is internally connected to each other with the wire as shown in Fig. 7.6b. Due to the sum up of cell voltage, a greater potential difference is needed for a given current.

7.4.3.3 Parallel Connections of Bipolar Electrodes (BP-S)

As shown in Fig. 7.6c, under this configuration only the outer electrodes are connected to the power supply. The electrodes placed between the driver or main electrodes do not have any electrical connection. Here, the extreme end electrodes are known as monopolar, whereas the internal electrodes are known as bipolar electrodes. This type of electrode connection is very cost-effective and easy during operation (Kobya et al. 2007).

7.4.4 Reactor Operation Mode

The reactor operation mode basically depends upon the various operating conditions as described above. Out of them, the reactor operation mode is extremely important and depends upon the reaction time and initial concentration of pollutants. Moreover, the stability of the treatment is also extremely correlated to the operation mode of the reactors. These are basically three types: (1) Batch mode, (2) continuous mode, and (3) semi-batch mode. Since, Many industrial operations continuously generate a large amount of wastewater, which is then treated through available treatment facilities. After its treatment, this treated water is again utilized in various applications either inside the plant or outside the plant. Hence, this process is continuous; therefore, the continuous mode of operation is very popular among other operation modes.

7.5 Treatment of Persistent Organic Pollutants in Different Types of Wastewater Through Electrochemical Oxidation Technology

Persistent pollutants or persistent organic pollutants are highly toxic in nature and remain in their original form for a long period of time. Many conventional treatment technologies have been employed for their treatment in aqueous media. But most of these techniques have some limitations in terms of removal efficiency, cost, treatment time generation of secondary sludge or pollutants, etc. Among them electrochemical technologies are a better option in order to treat a long range of pollutants. Recently, they got so much attention in the abatement of persistent pollutants from different wastewater due to their unusual flexibilities, number of possibilities of process modifications, easy operation, and eco-friendly nature. Some recent works based on electrochemical methods for the treatment of persistent pollutants available in different types of synthetic and real wastewater medium have been enlisted in Table 7.2.

7.5.1 Treatment of Coke-Oven Wastewater

Coke-oven wastewater usually generates during coal making process or coking process. These processes include coal gas purification, by-product recovery activities, coal washing and crushing, etc. During these processes, a huge amount of persistent organic and inorganic pollutants such as phenols, aniline, ammonium, cyanide, thiocyanate, polycyclic aromatic hydrocarbons (PAHs), several heterocyclic compounds containing nitrogen and sulfur, etc., are generated. Most of these pollutants are toxic, persistent, and have long-term negative environmental impacts. Moreover, they are highly resistant to conventional biological treatment methods (Ken and Sinha 2021; He et al. 2013).

Many studies focused on coking wastewater treatment through original and modified electrochemical methods. In our earlier work, the degradation and mineralization of synthetic coke-oven wastewater were achieved through electrochemical oxidation using Ti/RuO_2 as anode and graphite as a cathode. The simultaneous removal of COD, TOC, phenol, ammonia, and cyanide was achieved. The degradation efficiencies for COD, TOC, phenol, cyanide, and ammonia were attained as 90.13%, 85%, 99.34%, 96.23%, and 94.43%, respectively, within the optimum conditions (pH = 8.0, NaCl = 1.6 g/L, CD = 24 mA/cm^2, H_2O_2 = 0.030 M, reaction time = 180 min, 25 ^{0}C temperature and d = 1 cm electrode gap) (Ken and Sinha 2021).

Brillas et al. achieved the significant degradation of aniline and 4-chloroaniline in alkaline conditions using AO and AO-H_2O_2 techniques when PbO_2 was taken as anode and graphite or carbon-PTFE O_2-diffusion electrode was taken as a cathode. Authors have also tested several electrolytes (such as NaOH, Na_2CO_3, and Na_2CO_3 with $NaHCO_3$) to maintain the conductivity of the medium and lastly achieved almost similar results (Brillas et al. 1995). In a study, Na_2SO_4 supported 100 ppm aniline wastewater was treated separately using AO-H_2O_2, EF, and PEF-UVA processes in acidic conditions (pH = 3) while taking Pt as anode and a carbon-PTFE O_2-diffusion electrode as a cathode. On the basis of these results, it was seen that mineralization of aniline through different electrochemical approaches was achieved in order of PEF-UVA > EF > AO-H_2O_2 > AO. Additionally, a higher current density was helpful for faster aniline removal in case of in AO-H_2O_2 and PEF-UVA methods. Nitrobenzene derivative or benzoquinone imine, benzoquinone, hydroquinone, nitrobenzene, phenol and 1,2,4-benzenetriol were found as intermediates (Brillas et al. 1998; Moreira et al. 2017).

Pimentel and his team revealed the degradation of phenols (31 or 99 ppm) through the electro-fenton method at pH = 3 with synthetic or laboratory-prepared wastewater in an undivided cell containing Pt as anode and CF as a cathode. In this method,

Table 7.2 Some recent studies reported on treatment of different types of synthetic and real wastewaters through electrochemical oxidation technology. Adapted from Särkkä et al. (2015) and reproduced with permission

Matrix	Pollutant	Electrodes	Removal efficiency	Current density (mA/cm^2)	References
Synthetic dye wastewater	COD	Graphite	96.47%	69.23	Yue et al. (2014)
Synthetic dye wastewater	Color	Ti–Pt/β-PbO$_2$, BDD	100%	10–70	Ma et al. (2009)
Synthetic dye wastewater	Color	BDD	100%	4–50	Andrade et al. (2009)
Synthetic dye wastewater	Color	Ti/SnO$_2$–Sb/PbO$_2$	100%	5–40	Abdessamad et al. (2015)
Olive mill wastewater	COD, color	Ti/TiRuO$_2$	100%	60	Panizza et al. (2006)
Olive mill wastewater	Color, phenols	Ti/IrO$_2$	100%	50	Chatzisymeon et al. (2009)
Synthetic wastewater	Paracetamol	BDD	N 98% of TOC decay	33–150	Saad et al. (2016)
Tannery wastewater	COD, ammonia, Cr, sulfides	Ti/Pt–Ir, Ti/PbO$_2$, Ti/PdO–Co3O4, Ti/RhOx–TiO2	Satisfactory with all anodes	20 and 40	Szpyrkowicz et al. (2005)
Pulp bleaching effluent	Pentachlorophenol	Graphite	100%	6	Miwa et al. (2006)
Paper mill effluent	Organic material: COD	Lead	N 96%	2.2–11	Guinea et al. (2010)
Dye wastewater	Anthraquinone dye	BDD	100%	30	Brillas and Martínez-Huitle (2011)
Synthetic wastewater	Phenol	Ti/SnO$_2$–Sb, Ti/RuO$_2$, Pt	100%	20	Li et al. (2005)
Coking wastewater	Organic pollutants (TOC)	BDD	Almost 100%	20–60	He et al. (2013)
Synthetic wastewater	2,4-dichlorophenol	Ti-based oxide electrode	Almost 100%	−1.5 to 1.5 V	Chu et al. (2010)
Domestic wastewater	Sulfide	Ta/Ir, Ru/Ir, Pt/Ir, SnO$_2$, PbO$_2$	77–85%	10	Pikaar et al. (2011)
Synthetic wastewater	Ketoprofen	BDD and Pt	100%	4.4, 8.9 and 13.3	Muruganthan et al. (2010)

(continued)

Table 7.2 (continued)

Matrix	Pollutant	Electrodes	Removal efficiency	Current density (mA/cm^2)	References
Synthetic wastewater	1,4-dioxane	BDD	N 95%	5, 15 and 25	Choi et al. (2010)
Synthetic wastewater	4,6-dinitro-*o*-cresol	BDD	100%	33–150	Flox et al. (2005)
Synthetic wastewater	Chlorpyrifos	BDD	100%	15 and 30	Robles-Molina et al. (2012)
Citric acid wastewater	Organic pollutants	Ti/RuO_2–IrO_2	Almost 100%	9 V	Li et al. (2013)
Synthetic wastewater	Atrazine	BDD	Up to 94%	100	Borràs et al. (2010)
Paper mill wastewater	COD, resin acids	MMO, BDD			Eskelinen et al. (2010)
Paper mill wastewater	Sulfide	MMO	Up to 100%	14.3–42.9	Särkkä et al. (2009)
Synthetic wastewater	Methyl orange dye	MMO, BDD		30 and 50	Zhou et al. (2011)
Synthetic wastewater	Rhodamine B	BDD	100%	60 and 120	Araújo et al. (2015)
Synthetic wastewater	Amoxicillin	Carbon-felt, carbon-fiber, carbon–graphite, platinum, lead dioxide, DSA (Ti/RuO_2–IrO_2) and BDD	100% (with BDD)	20.83, 12.50 and 4.60	Sopaj et al. (2015)
Wastewater	Caprolactam	Carbon	COD removal 18%	7.9 V	Gedam et al. (2014)
Industrial wastewater	1,4-dioxane	BDD	COD removal 98%	12	Barndõk et al. (2014)

different metal catalysts such as Fe^{2+}, Co^{2+}, Mn^{2+}, and Cu^{2+} were also examined in order to increase the degradation and mineralization of phenols. It was seen that 5.6 ppm of Fe^{2+} was the optimum dose for best phenol removal. However, similar results were obtained in case of 5.9 mg of Co^{2+} dose. It was noticed that mineralization was slower than iron, whereas in case of Mn^{2+} and Cu^{2+} degradation efficiencies were significantly less. Also, hydroquinone, catechol, and p-benzoquinone were identified as the main intermediates.

Flox and his team conducted an electrochemical study using BDD or PbO_2 as anode separately and observed the significant degradation and mineralization of ortho-, meta-, para- derivatives of cresol in an undivided cell at $pH = 4$, where zirconium (Zr) was taken as cathode. Instead of PbO_2, the mineralization of cresols was much faster through BDD anode, whereas the degradation was almost same in both cases. 2-methylhydroquinone and 2-methyl-p-benzoquinone were recognized as intermediates during electrooxidation (Pimentel et al. 2008). In 2009, Zhu et al. revealed the degradation of coke-oven wastewater through electrochemical method, almost complete degradation was achieved of all the organic matter while BDD was taken as anode. The comparative results were also produced by taking other inactive anodes like SnO_2 and PbO_2. It was seen that BDD anode achieved substantially higher removal efficiency than SnO_2 and PbO_2 electrodes with 40% less energy consumption when current density (CD) = 20–60 mA/cm^2, pH = 3–11, and temperature = 20–60 °C were the reaction conditions (Zhu et al. 2009; Garcia-Segura et al. 2018a). In a study, electrochemical degradation of cyanide was achieved, more than 90% of cyanide was converted to cyanate and then CO_2 with the help of hydrogen peroxide species generated through RVC cathode. The platinum was taken here as anode and reticulated vitreous carbon (RVC) was applied as cathode. The copper ions with hydrogen peroxide was also tested for the improvement of electrocatalysis. The cell was undivided, and 0.1 mol L^{-1} of NaOH aqueous solution was filled inside the reaction chamber (Martínez-Huitle and Panizza 2018). In a study, Ozyonar et al. treated coke-oven wastewater using electrocoagulation (EC) and electrochemical peroxidation (ECP) processes in terms of COD, TOC phenol, cyanide and thiocyanate removal. The removal efficiency for COD, TOC phenol, cyanide and thiocyanate via electrocoagulation were achieved as 26%, 20%, 9%, 9.2%, and 8.2%, respectively, whereas in case of electrochemical peroxidation these removal efficiencies were 92.0%, 90.0%, 97.6%, 90.0%, and 93.6%, respectively. The optimum conditions for ECP process were established as pH 3, 200 mA/cm^2 current density, and 10 g/L of initial H_2O_2 concentration. Additionally, the operation costs for EC and ECP processes were also estimated as 1.46 €/m^3 and 5.64 €/m^3, revealing that ECP was more effective and costly over EC method (Ozyonar 2016). Zhang et al. (2013) electrochemically treated biologically pretreated coking wastewater in terms of COD and ammonical nitrogen. The 3D-electrochemical reactor involved Ti/RuO_2-IrO_2 as anode, stainless steel as cathode, coke powder packed between the electrodes used as 3D particle electrodes. The optimum conditions were achieved as 1 cm electrode gap, 20 mA/cm2 current density, and four pairs of electrodes connected alternatively. A total of 12 types of organic pollutants were fully removed, whereas the removal efficiencies for 11 organics were observed in the range of 13.3 to 70.3% within only 60 min of reaction (Zhang et al. 2013).

7.5.2 Treatment of Other Synthetic Wastewaters

7.5.2.1 Wastewater Containing Dyes

Synthetic dyes are widely used as coloring agents in various industries like food, pulp and paper, leather, pharmaceutical, cosmetics, inks, and textile industries. The high contents of these synthetic dyes are continuously discharging into the natural water bodies or rivers from these industries. Out of them, azo dyes are the most commercial dyes, which hold about 70% of the synthetic dye market. Because of their persistent nature, they are highly dangerous to living organisms (Moreira et al. 2017; Zollinger 1989; Forgacs et al. 2004). The big matter of concern is that they have shown excellent resistance to their treatment using conventional methods. The majority of work has been focused on the treatment of single matrix while few studies have focused on the removal of the complex matrix of dye (Rosales et al. 2009). Moreira and his team utilized SPEF, PEF-UVA, EF and AO-H_2O_2 methods for the treatment of one-liter solution of 290 mg Sunset Yellow FCF dye and observed that about 93%, 84%, 60%, and 29% of DOC was removed through SPEF, PEF-UVA, EF, and AO-H_2O_2 method, respectively, within only 150 min of reaction (Moreira et al. 2013). Solano et al. conducted an investigation for the treatment of 181 mg Congo Red dye water using BDD as anode and carbon-PTFE air-diffusion as a cathode, in which about 99%, 92%, and 39% of DOC were removed via PEF-UVA, EF, and AO-H_2O_2 methods, respectively, within only 360 min of reaction time. During this study, the optimum conditions were found to be pH 3.0, a temperature of 25 °C, and a current density of 100 mA/cm^2(Solano et al. 2015). Several studies have conveyed contradictory results in the field of dye removal and decolorization technology. It was seen that some investigators have established the supremacy of SPEF and PEF-UVA-method over EF method (Thiam et al. 2015) while in other studies the results of these three methods were found quite similar (Moreira et al. 2017; Ruiz et al. 2011).

7.5.2.2 Wastewater Containing Pesticides

Pesticides include bactericides, fungicides, herbicides, insecticides, antimicrobials, rodenticides, and other constituents or chemicals which are generally used to control pests. Agricultural activities and various manufacturing industries are basically the main sources of their origin and mixing in aqueous media. Due to their persistent nature, they are highly dangerous to living beings and the environment. Moreover, they have high resistance to biodegradation as well as to other conventional methods (Damalas and Eleftherohorinos 2011). A degradation study done by Abdessalem et al. through AO-H_2O_2 and EF processes has shown the treatment trends of three pesticides in order of chlorotoluron > carbofuran > bentazon (Abdessalem et al. 2010a, 2010b). In a study, Boye et al. treated 4-chlorophenoxyacetic acid (4-CPA) pesticide and attained 98%, 60%, 28%, and 25% of removal efficiency for different DOC concentration within only 180 min of time while the initial concentration of 4-CPA was 194 ppm (Boye et al. 2002). In another investigation, Flox et al. achieved 80% and 67% mineralization efficiency for mecoprop pesticide within 100 min of reaction through SPEF and PEF-UVA methods, respectively, when pesticide concentration was 100 ppm, $pH = 3.0$, temperature = 25 °C, CD = 50 $mA\ cm^{-2}$, BDD and carbon-PTFE air-diffusion electrodes were anode and cathode. In terms of pesticide removal, it was observed that SPEF, PEF-UVA, and EF methods are typically achieved similar outcomes and these outcomes were also found better than AO-H_2O_2 and AO methods. This depicted that in the bulk of the medium the degradation of the parental compound was outstanding through •OH species. On the other hand, many other investigators (Dhaouadi and Adhoum 2009; Borràs et al. 2013; Garza-Campos et al. 2014) have observed the better capacity of light-assisted EAOPs as compared to EF process for pesticide treatment suggesting the involvement of photoreduction reactions (Rodrigo et al. 2014) under operating conditions. Additionally, many publications have also pointed out that the removal efficiencies for pesticidal removal at lower concentration were far better than the higher initial concentration.

7.5.2.3 Wastewater Containing Pharmaceuticals

Chemical compounds or drugs which hold antibiotics, antipyretics, analgesics, anti-inflammatories, antimicrobials and hormonal properties are fundamentally referred to as pharmaceuticals. The original form of these compounds and their bioactive derivatives are substantially entered into the aqueous or soil media in the ppb to ppt range. The presence of even this trace concentration of pharmaceuticals makes them highly persistent to the environment and living beings. The manufacturing industries and hospitals are the main sources of their pollution. Since they are highly resistant to biological processes, hence easily escape almost intact from conventional treatment methods (Jones et al. 2005; Kümmerer 2001, 2009).

Most of the investigators have worked on drug concentration ranging from 2.0 to 2390 ppm in their studies. Ferrag-Siagh et al. achieved mineralization of tetracycline antibiotic drug via a combination of electro-fenton with the biological treatment process. It was seen that at the end of day 5, the biodegradability (BOD_5/COD ratio) of wastewater was increased from 0.02 to 0.56 within only 6 h of electro-fenton reaction. The activated sludge used in this EF process raised the mineralization efficiency of the drug by 28% as compared to the simple electrochemical oxidation process (Ferrag-Siagh et al. 2013). Many studies stated the involvement of dimensionally stable anodes (DSAs) in the significant treatment and mineralization of several pharmaceutical compounds such as salicylic acid, trimethoprim, ibuprofen, and chloramphenicol (Skoumal et al. 2009; Moreira et al. 2014; Garcia-Segura et al. 2014). Among them, BDD and platinum electrodes are extensively utilized as anode materials due to their higher redox potentials. Also, the substantial superiority of BDD over platinum electrodes have revealed by earlier literatures. Sires et al. revealed the degradation of chlorophene drug through electro-fenton process while taking BDD and Pt as anode separately and carbon-PTFE O2-diffusion electrode or a CF as a cathode. It was noteworthy that for a shorter period of time platinum electrode was dominating, whereas for longer electrolysis, the BDD electrode was found to be dominating in terms of mineralization performance (Moreira et al. 2017; Solano et al. 2015; Garcia-Segura et al. 2014).

7.6 Conclusion and Future Recommendations

In the past few decades, scientists have been focused extensively on the use of electrochemical oxidation technology for wastewater treatment. Due to their excellent degradation and mineralization performances, they are extensively beneficial for the treatment of a wide variety of contaminates and persistent organic pollutants from different type of wastewater. Operating conditions are highly important for a seamless run of any electrochemical treatment method, these operational parameters are extensively discussed in this chapter in a very elaborative manner. Moreover, the authors have also explained several possible modifications in the reactor designs, such as synthesis and fabrication of working electrodes, operation mode, catalytic particle electrodes, connections of electrodes, etc. These modifications are already executed or are being executed to make an outstanding electrochemical process. The selection, synthesis, and working of driver electrodes, developments of CPEs, are the main uncovered domains of the electrochemical oxidation field which needed further investigations for better outcomes. In addition to this, various electrocatalysts also need to be studied. In this book, chapter authors have also shown the applicability of different modified versions of electrochemical reactors for the treatment of different types of synthetic or real wastewaters. However, various Hybridge or combined electrochemical methods also have been discussed in order to get better reactor performances. It was noticed that most of the progress in electrochemical technology is only achieved at the laboratory scale. Most of the studies have been conducted only on laboratory-prepared wastewater (mainly, single matrix). Pilot scale studies using real wastewater are needed to be done. Moreover, the synthesis of novel electrodes and their treatment working mechanisms also need to be understood for the development of significant and cost-effective electrochemical oxidation technology for wastewater treatment.

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Chapter 8
Advanced Treatment Methods for the Emerging Contaminants: An Insight into the Removal of Anticancer Drugs

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Abstract Emerging contaminants (ECs) are unregulated chemical substances that on account of their persistent nature and high toxicity can cause inimical impact on the ecosystem. ECs occurred as a mixture of complex compounds where an undesirable synergy between them obviate their proper detection and remediation in the environment. Compounds like pharmaceuticals, personal care products, and polyfluoroalkyl substances comprised the major category of ECs. The surge in cancer incidence and chemotherapy treatment has enhanced the application of anticancer drugs (ACDs) which contributed to the existing problem of pharmaceutical pollution. ACDs being one of the major emerging contaminants are frequently detected in surface water, municipal wastewater, and pharmaceutical effluent that substantially causes genotoxic and mutagenic effects on the aquatic environment. Several remediation techniques were reported on the removal of pharmaceutical compounds such as anti-inflammatory, analgesic, and endocrine disruptors however very few studies documented the degradation mechanism of anticancer drugs. Hence, this chapter elucidates the occurrence of ACDs and their major route in the environment. In addition to this, the current treatment technology like ozonation, electrochemical treatment, and membrane bioreactor, employed for the removal of ACDs are also discussed.

Keywords Advanced treatment methods · Anticancer drugs · Emerging contaminants

8.1 Introduction

Emerging contaminants (ECs) are those chemical substances which occur either naturally or anthropogenically and subsists for a long period in the environment (Sauvé

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and Desrosiers 2014; Galindo-Miranda et al. 2019). ECs slowly seek into the environment and trigger negative impacts on human health. Pharmaceuticals compounds are considered as a significant group of ECs, which are frequently detected in various water matrices and can potentially affect the environment (Fent et al. 2006; Marsalek 2008; Feier et al. 2017; Gojkovic et al. 2019). In aquatic environment, pharmaceuticals remain biologically active and resists degradation (Aherne and Briggs 1989; Chen et al. 2002; Cleuvers 2004). Nevertheless, so far research on the fate and removal of anticancer drugs (ACDs) has received very less attention. The surge in cancer patients leads to the increase in the consumption of chemotherapy drugs which become a matter of concern, since these drugs never metabolize completely and ultimately reaches into the water which enhance the water pollution load (Trombini et al. 2016; Gonçalves et al. 2022). The function of the ACDs is to intervene with the cancer cell to prevent the DNA replication (Załęska-Radziwiłł et al. 2011). Hence, these drugs can cause mutations at low level without even killing the cancer cells (O'Keefe 2011). This book chapter compiles the latest updates on the advanced treatment methods applied on the removal anticancer drugs.

8.2 Sources, and Fate of Anticancer in Environment

The fate of cytostatic in environment mainly depends on the factors like dose, category consumption, and excretion rate of drugs from in and outpatients. Hospitals particularly focused on the tumour treatment are also recognized as the alleged source of cytostatic in the environment. As a matter of fact, the rate of excretion is considered as the main source of chemotherapy drugs in the environment. (O'Keefe 2011), detected ACDs in urine (40%), bile (45%), and faeces (50%) samples and advocated that certain amount of unmetabolized ACDs passed through the outpatients to the municipal wastewater. Moreover, effluents from pharmaceutical industries also recognized as a potential source of ACDs which could reach to the aquatic environment (Mahnik et al. 2006; Lenz et al. 2007; Zhang et al. 2013). Kosjek and Heath (2011) stated that most of the ACDs have high solubility which pertains to their high mobility in water, and they possibly pass from the wastewater treatment plant (WWTP) effluent to the surface water. Roberts and Thomas (2006) reported the concentration of tamoxifen up to 694 ng L^{-1} in the wastewater effluent of Tyne catchment in UK. Azuma et al. (2015) detected different ACDs (cyclophosphamide, tamoxifen, doxifluridine, capecitabine, and bicalutamide) in the Yodo river and effluents of sewage treatment plant (STP) of Japan. The concentration of the ACDs were measured up to 55 ng L^{-1} in river and up to 316 ng L^{-1} in STP effluent. The above studies confirmed that apart from hospital effluent, ACDs were also detected in the wastewater effluent which suggests the incapability of the convention methods in removing refractory compounds. Further the occurrence of different ACDs is presented in Table 8.1.

Table 8.1 Most detected anticancer drugs in environment

Drugs	Concentration	Matrix	References
Cyclophosphamide	6–146 10–20; 64 2–43; 20	Hospital effluent Surface water WWTP -effluent	Steger-Hartmann et al. (1996), Steger-Hartmann et al. (1997) Ternes (1998), Moldovan (2006) Negreira et al. (2014) Cristóvão et al. (2021)
Cytarabine	9.9 1.3	WWTP -effluent Surface water	Jureczko and Kalka (2020)
5-fluorouracil	5–124,000	Hospital effluent	Mahnik et al. (2004), Kovalova et al. (2009)
Gemcitabine	0.9–38	Hospital effluent	Kovalova et al. (2009)
Tamoxifen	0.2–8 110–147;143–694	Hospital effluent WWTP-effluent	Liu et al. (2010), Roberts and Thomas (2006), Negreira et al. (2014)
Procarbazine	< 5	Hospital effluent	Yin et al. (2010)
Ifosamide	30–1914 2–27; 30–40	Hospital effluent WWTP-effluent	Kümmerer et al. (1997) Negreira et al. 2014), Cristóvão et al. (2021), Catastini et al. (2008)
Doxorubicin	0.1–10	Hospital effluent	Mahnik et al. (2006), Yin et al. (2010), Mahnik et al. (2007)
	2.7	WWTP-effluent	Negreira et al. (2014)

8.3 Toxicity and Effect of Anticancer Drugs on the Environment

Anticancer drugs are designed to kill the cancer cells by modifying the cell DNA structure. However, upon reaching the aquatic environment, the ACDs interfere with the cells of non-target biota and alter their molecular pathways (Kiffmeyer et al. 1998; Nussbaumer et al. 2011; Russo et al. 2020). The solubility factor is also considered as an important aspect of ACDs in environment which determines the presence of ACDs in water. Most of the ACDs are hydrophilic in nature with negative log Kow value. This blend of low Kow values and high solubility factor leads to the high mobility of ACDs in water (Meylan et al. 1999). Previous studies on the ecotoxicity of the ACDs suggests the potential toxicity of these drugs on the aquatic organisms. (Fonseca et al. 2018) conducted an exposure study of the cyclophosphamide on the ragworm *Nereis diversicolor*. The ragworm was exposed with the drug having concentration of 0.5 µg/L for fourteen days and damaged the DNA of the organisms completely. Liu et al. (2019), reported that cyclophosphamide not only affect the cell DNA but can also inhibit the activity of lactate dehydrogenase enzyme of the non-target organisms. The authors conducted an exposure study of cyclophosphamide with 320 µg/L concentration on the *Megalobrama amblycephala* for 24 h. The applied dose of the drug results in the elevated levels of peripheral blood leukocytes in the blunt snout bream. ACDs can also induce histopathological modifications in kidney and liver of the aquatic organisms such as zebrafish (Kovács et al. 2015).

8.4 Treatment Techniques for Anticancer Drugs

Anticancer drugs (ACDs) considered as an emerging pollutant in water system and concerns are raised towards this category. Wastewater treatment plant play a crucial role in eliminating such persistent pollutant. However, the conventional processes, viz. adsorption, coagulation, and biodegradation lack complete removal of such compounds. Early studies reported on ACDs degradation were mostly devoted on the photocatalytic and UV-based treatment system.

8.4.1 Biological Treatment

8.4.1.1 Membrane Bioreactor (MBR)

Membrane bioreactor is recently explored as an effective treatment process for the removal of emerging pollutants. In MBR, activated sludge process is combined with the membrane filtration. (Delgado et al. 2009) studied the microbial behaviour of cyclophosphamide (CPH) and its major metabolite in a membrane bioreactor. The reactor run for 70 days along with a control without the drug. The chemical stress caused by CPH might obstruct the rate of sludge production where the energy consumption diverted towards the adaptive response instead of growth. This reflects the toxicity and low biodegradability of cytostatic drugs. In recent years advancement made in membrane technology improve the removal of refractory compounds. (Wang et al. 2018) employed forward osmosis method to enhance the removal efficacy of anaerobic membrane reactor. The anaerobic MBR-FO reactor was applied to eliminate a group of eight ACDs including cyclophosphamide, doxorubicin, and tamoxifen from wastewater. For the concentration of 100 ng/L, 95–97% of drug removed from the wastewater. Such elevated rate of drug removal suggests the high rejection capacity of the FO-MBR. It was also observed that molecular weight and surface charge of the ACDs mainly influenced the rejection capacity of the membrane. However, surge in volatile fatty acids implies the toxicity of ACDs towards the microbes. (Cristóvão et al. 2022), explored the potential of nanofiltration in removing ACDs namely cyclophosphamide, ifosamide, capecitabine, paclitaxel, and etoposide) in domestic wastewater at pilot scale. The removal efficiency of the applied system was maximized through operational parameters, viz. permeate flux, and recovery rates. The applied method results in 96% of rejection with 6 bar of pressure and 73% of recovery rate. Additionally, the samples did not induce any immobilization effect on the *Daphnia magna* species.

8.4.1.2 Fungi-Based Treatment

Besides membrane reactor, fungi-based degradation counts as a non-conventional biological method for the remediation of pharmaceuticals (Ferrando-Climent et al. 2015; Pereira et al. 2020). The enzyme associated with fungi species mainly participate in the degradation process. (Jureczko et al. 2021), used white rot fungi (WRF) for the attenuation of cytostatic drugs, viz. bleomycin and vincristine from conventional wastewater plant. The authors employed five species of WRTF namely *Trametes versicolor and Pleurotus ostreatus* which often used for the pharmaceutical removal. The degradation study was run over a period of 9 days that gives 95% of drug removal efficiency. Their study revealed that laccase and cytochrome P450 were the main enzymes which facilitates the extracellular oxidation and intracellular degradation. However, by-products formed by the parent compound was found as toxic to the fungal strains. Similarly, Yadav et al. (2022) also stated the potential of the WRF in the degradation of anticancer drugs. Their study evaluated three strains of WRF, viz. *Ganoderma lucidum, Trametes versicolor,* and *Phanerochaete chrysosporium*) on the removal of etoposide and cyclophosphamide. The *G.lucidum* strain has shown the highest removal of etoposide (99%) after six days of the treatment. However, only 71% of the cyclophosphamide was removed after treatment.

8.4.2 Advanced Oxidation Process

Advanced oxidation process is the chemical treatment method extensively used fort recalcitrant compounds. In this process factors like heat, catalyst, and light usually applied alone or in a combination to generate reactive oxygen species namely radicals. The high redox potential of these radicals significantly breaks the complex structure of hazardous compounds into non-toxic by-products rather than just a physical transformation (Khan et al. 2016; Zhao et al. 2019). A brief description of the types of AOP is given in Fig. 8.1 and the treatment techniques for the ACDs removal is represented in Table 8.2.

8.4.2.1 Photocatalysis

Photocatalysis is one of the significant AOPs which is widely applied in the wastewater treatment (Hasanpour and Hatami 2020; Sundar and Kanmani 2020). The main reaction in a photocatalytic process is initiated when a photon is absorbed (hν) in the presence of an incident light and generate electron–hole pairs on the surface of the catalyst. The electron (eCB^-) and holes ($h\nu_B$) thus produced are oxidizing and reducing species, respectively (Zhu and Zhou 2019). The electrons react with the dissolved oxygen and produce superoxide radicals (Eqs. 8.1 and 8.2). On the contrary, water molecules react with the generated holes and produce hydroxyl radicals as the oxidants (Eqs. 8.3–8.4) (Byrne et al. 2018; Wang et al. 2019; Motamedi

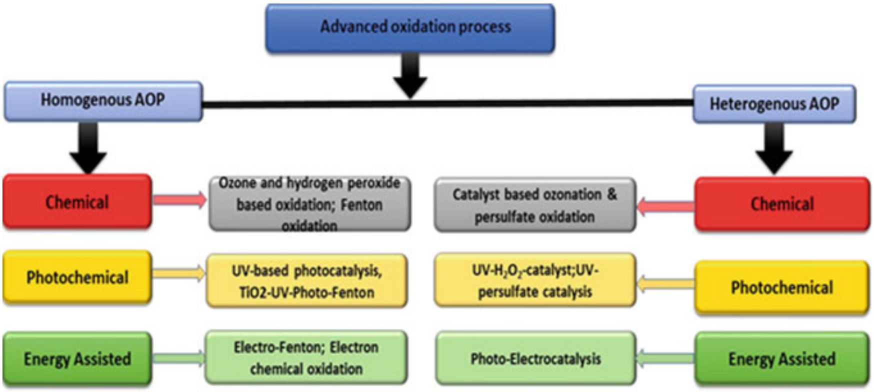

Fig. 8.1 Classification of different AOPs. Adapted and modified from Kim et al. (2022)

Table 8.2 Treatment methods applied on anticancer drugs

Target compound	Process	Matrix	Removal (%)	References
Cyclophosphamide Ifosfamide	Biological	–	59	Česen et al. (2015)
Irinotecan, Ifosfamide Cyclophosphamide Capecitabine	Ozonation	Hospital effluent	97	Ferre-Aracil et al. (2016)
Cyclophosphamide	Photocatalysis	Wastewater	69	Ofiarska et al. 2016)
Ifosfamide, Irinotecan Cyclophosphamide Capecitabine	Ozonation	Hospital effluent	97	Ferre-Aracil et al. (2016)
16 Anticancer drugs	Biological and photodegradation	Ultrapure water	50–90	Franquet-Griell et al. (2016)
Chlorambucil Cyclophosphamide Ifosfamide Decarbazine Tamoxifen Methotrexate	Ozonation	Wastewater	20–70	Li et al. (2016)
Cyclophosphamide	Membrane bioreactor	Wastewater	60	Seira et al. (2016)
Cyclophosphamide	Electrochemical oxidation	Ultrapure water	65–77	Siedlecka et al. (2018)
Doxorubicin	Electrochemical oxidation	Ultrapure water	85–100	Garcia et al. (2020)

et al. 2022).

$$\text{Photocatalyst} + \text{hv} \rightarrow \text{h}_{\text{VB}^+} + \text{e}_{\text{CB}^-} \tag{8.1}$$

$$\text{e}_{\text{CB}^-} + \text{O}_2 \rightarrow \text{O}_{2^\cdot} \tag{8.2}$$

$$\text{h}_{\text{VB}^+} + \text{H}_2\text{O} \rightarrow {}^{\cdot}\text{OH} + \text{H}^+ \tag{8.3}$$

$$\text{H}_2\text{O}_2 + \text{e}_{\text{CB}^-} \rightarrow {}^{\cdot}\text{OH} + \text{OH}^- \tag{8.4}$$

To understand more about the fate and degradation of ACDs, Franquet-Griell et al. (2016) studied the behaviour of 16 ACDs from hospital and wastewater effluent through different treatment process (hydrolysis, aerobic biodegradation, and UV-C photolysis). During hydrolysis process the chemotherapy drugs like doxorubicin, melphalan, and chlorambucil which were stable at pH 4–7 having high dielectric constant removed completely (95%) from the system. While nine drugs out of 16 like cytarabine, etoposide, and cyclophosphamide showed only 50% removal. Later in biodegradation process most the compounds were found to be refractory to the applied process, which suggests process like advanced oxidation was required for further degradation. Lastly, photolysis was applied which gives > 90% of removal, although compounds having chlorine such as cyclophosphamide and ifosfamide still remain that were later removed in a combined UV-H_2O_2 system. At last, the ACDs removal were simulated in surface water by solar photocatalysis. It was observed that most of the drugs circumvents sun's radiation which reflect the stability of such drugs in the environment. The high toxicity of ACDs towards biological system leads to the addition of advanced treatment, hence in later research mostly photocatalysis and advanced oxidation process was applied.

Authors of Ofiarska et al. (2016) reported degradation of two ACDs namely ifosfamide and cyclophosphamide by photocatalysis using TiO_2 and Pt-doped TiO_2 catalyst. It was observed that when undoped TiO_2 was used the removal occurred in the bulk solution while in case of Pt-doped TiO_2, the removal occurred on the surface of the catalyst as well. The addition of platinum at the catalyst surface increased the electron or hole separation that further promote accumulation of the $^{\cdot}OH$ radicals at the TiO_2 surface. Apart from TiO_2, oxyhalides of bismuth was also used as photocatalyst in the degradation study of the anticancer drug (Wilczewska et al. 2021). It was established that halogen atom intersects the layer of BiO_2 which facilitate the electric field that eventually enhanced the conduction band of the semiconductor. Unlike other photocatalyst, BiO_2 generate superoxide radicals $^{\cdot}O_2^-$ as the main oxidant no matter what light source was used during the photodegradation process. When used for the degradation of 5-FLU, it shows 95% of removal efficiency with 90 min of reaction time.

8.4.2.2 Ozonation

Ozonation process has been significantly applied in the treatment of organic contaminants. Ozone is a strong oxidant which can be generated through pure oxygen by means of different methods like chemical, photocatalytic, and electric discharge (corona) (Joseph et al. 2021; Gorito et al. 2021). Ferre-Aracil et al. (2016) employed ozonation to a hospital wastewater effluent contained with cytostatic drugs. With ozone gas concentration of 43 g m^3 about 97% of the target drugs were eliminated. The key factor of their research was the economic assessment and development of a prediction model to study the behaviour of the ozone reactor. The applied model helps to determine the rate kinetics, total dissolved organic concentration along with chemical ozone demand. These factors later applied to evaluate the cost of the reactor.

8.4.2.3 Electrochemical Advanced Oxidation Processes (EAOPs)

Electrochemical advanced oxidation is associated with the in-situ generation oxidants like $^\bullet$OH and H_2O_2 without adding chemicals as compared to usual AOPs. The mechanism behind the production of oxidant species is driven by the current supply (j) supplied across the anode and cathode that eventually reduce or oxidize the organic components into biodegradable compounds. Further section defines the different types of EAOPs.

Direct Oxidation

When the target compound oxidized at the electrode surface by means of direct electron transfer at anode then it is called as direct oxidation (Eq. 8.5). The direct oxidation depends upon two factors (i) diffusion process where the organic pollutant diffused through the electrolyte bulk solution to the anode surface and (ii) electrocatalytic property of the anode where interaction between the electrons and organic matter depends on the anode oxidation potential (Panizza and Cerisola 2009).

$$R \rightarrow +P + e^- \tag{8.5}$$

Indirect Oxidation

Indirect oxidation occurs when intermediate oxidant products generate at the interface of solution or at the anode surface in the presence of the external voltage (Eqs. 8.6 and 8.7) (Cavalcanti et al. 2013; Nidheesh et al. 2018). Whereas the generation of $^{\cdot}$OH radicals in bulk through water electrolysis is knows as indirect electrode surface oxidation. Here the anode material plays a vital role in forming the oxidant species (Eq. 8.8) (Sánchez et al. 2013) (Paiva Barreto et al. 2015).

$$2H_2O \rightarrow H_2O_2 + 2H^+ + 2e^- \tag{8.6}$$

$$3H_2O \rightarrow O_3 + 6H^+ + 6e^- \tag{8.7}$$

$$M + H_2O \rightarrow M(^{\cdot}OH) + H^+ + e^- \tag{8.8}$$

Based on the formation of $^{\cdot}$OH radical, oxidation mechanism of an electrochemical cell can be determined. The $^{\cdot}$OH radicals thus formed get adsorbed at the anode surface either physically or chemically. When a chemical bond is established between the oxygen atom of $^{\bullet}$OH molecules and anode surface then the radicals are chemically adsorbed (Eq. 8.9) (Panizza and Cerisola 2009; Brillas and Sirés 2015). Anodes like platinum, ruthenium, and graphite produce such radicals and they are known as active anode. On the other hand, radicals formed without any involvement of chemical bond form physiorbed radicals. These types of radicals are formed by electrodes such as boron diamond and are often called as inactive anodes (Escalona-Durán et al. 2020; Malpass and Jesus Motheo 2021). Furthermore, the reactivity of the anode also depends upon the oxygen evolution potential. The OEP of the non-active anode is less as compared to active anode thereby it shows higher reactivity towards organic compound. Moreover, oxidation of electrolytic solution also gives oxidizing radicals like Cl2, H2S2O8, and $HClO^-$ that are not as strong as $^{\bullet}$OH radicals but can remain for a long time of duration in the system and diffused at the same time in the reaction medium (Eqs. 8.10–8.12) (Neodo et al. 2012; Chanikya et al. 2021).

$$M(^{\cdot}OH) \rightarrow MO + H^+ + e^- \tag{8.9}$$

$$M(^{\cdot}OH) + Cl^- \rightarrow M(HClO) \tag{8.10}$$

$$2Cl^- \rightarrow Cl_{2(aq)} + 2e^- \tag{8.11}$$

$$HClO \rightarrow H^+ + ClO^- \tag{8.12}$$

The structure of cytostatic drugs is complex having purine or pyrimidine rings and are mostly non-biodegradable, hence restrict the performance of conventional wastewater treatment plants. Only few studies were reported on removal of CSTs through electrochemical process. (Siedlecka et al. 2018), removed five cytostatic drugs from aqueous solution through BDD electrode. Their study suggested that compound having more electron donor sites such as cyclophosphamide were more resistant to hydroxyl free radical attack. Though, use of BDD at pilot scale could increase the cost of the electrochemical reactor. Use of inactive anodes like graphite might solve this problem as this electrode is inexpensive and widely used for organic pollutant removal. Graphite in presence of sodium chloride as an electrolyte, generate chlorine oxidants and was reported to eliminate 90% of cytarabine from aqueous solution (Sivodia and Sinha 2020). The presence of anions in solution matrix also affects the degradation process, as anions like nitrite inhibit the oxidation process, while Cl^- ions accelerate the oxidation rate (Xu et al. 2020). The application of ECPs probably enhanced the biodegradability of such complex compounds.

8.5 Conclusions and Future Prospectus

Anticancer drugs as a group of pharmaceutical compounds become a matter of concern due to increase in the consumption rate, their endurance towards the conventional treatment methods (coagulation, filtration, and biodegradation) and carcinogenic effects on eukaryotic organisms. Besides, the ubiquitous occurrence of anticancer drugs in different water matrix such as surface water, groundwater, and wastewater effluent also reflect the resilience of ACDs against the applied treatment methods because of which they can easily seek into the environment. The chapter gives an insight on the ongoing remediation techniques of ACDs. Cyclophosphamide is the most studied compound of all ACDs because of its high consumption rate and low degradability. Oxidation process is the most effective technique which completely degrade the refractory compounds in a short span of time. The membrane technology also shown effective removal of various ACDs such as cyclophosphamide, capecitabine, and ifosamide, however higher removal efficiency was achieved only after combining other removal techniques. The number of studies reported on biodegradation of ACDs is limited and only white rot fungi has shown an effective degradation of the anticancer drugs. Also, toxicity study of the degradation by-products can also give more insights on the fate of ACDs after treatment. Lastly, removal of anticancer drugs in real water matrix should be explored to comprehend the implementation of the current methods at pilot scale.

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Chapter 9
Occurrence of Quinoline in the Environment and Its Advanced Treatment Technologies

Parmita Chawley, Alok Kumar Suman, and Sheeja Jagadevan

Abstract Quinoline is a nitrogen-containing heterocyclic compound that occurs widely in industrial wastewater originating from pharmaceutical, textile, coking coal and coal gasification industries. Despite its usefulness as a raw material in these industries, quinoline and its derivative compounds cause severe health problems such as damaging central nervous system. Moreover, due to steric hindrance of its bicyclic fused structure, it is difficult to degrade naturally. Various physical and chemical methods such as adsorption, UV catalysis and photocatalytic degradation by metal oxide nanocomposites have been employed for quinoline degradation. These methods typically suffer from poor performance and obstruct regeneration of the process for continuous operation. Apart from these conventional treatment methods, advanced treatment technologies such as catalytic ozonation, advanced oxidation process and hybrid treatment technologies where biological biodegradation is followed by advanced treatment processes are gaining popularity in recent years. These methods have been found to be more effective in terms of a faster rate of degradation, offer complete degradation and are known to produce lesser by products rendering the industrial wastewater for discharge into the environment. This chapter discusses various advanced treatment technologies employed in the past decade for degradation/ treatment of quinoline.

Keywords Quinoline · Aerobic treatment · Nitrification · Anaerobic treatment · Hybrid treatment · Biological wastes

9.1 Introduction

Quinoline was discovered in 1842 by Charles Gerhardt as a result of drastic decomposition of quinine and cinchonine (Manske 1942). It was then found in coal tar

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by Hoogewerff and van Dorp in 1885. It has been also found in petroleum distillates. In addition, natural occurrence of quinoline derivatives has been found in *Cinchona ledgeriana* plant extracts (Cheng et al. 2013). Newer discoveries report existence of quinoline derivatives as alkaloids in several other plant extracts such as *Quisqualis indica, Camptotheca acuminata* and *Dictamnus angustifolius* (Rout et al. 2021; Nguyen et al. 2021; Jian-Bo et al. 2014). These are produced in plant alkaloids as secondary metabolites, and they are nitrogenous heterocyclic derivatives of amino acids formed by transamination process (Aniszewski 2007). Quinoline alkaloid derived from the bark of above-mentioned plants have been used in the manufacture of various drugs (Fig. 9.1). Animal sources of quinoline come from Peruvian stick insect *Oreophoetes peruana* (Attygalle et al. 2021). This insect secretes quinoline as a defence mechanism when they are agitated and fed with L-tryptophan amino acid. These natural sources of quinoline in the environment become cheap source of raw material for manufacture of dyes, chemical preservatives, pharmaceuticals and several other purposes (Lam et al. 2012; Ali et al. 2021; Lilienkampf et al. 2009). Anthropogenically, it has been detected in very high concentrations (above 3000 μg/L) in groundwater of tar-contaminated field sites, coal gasification wastewater, coal tar and shale oil (Neuwoehner et al. 2009; Shi et al. 2019; Panaitescu and Predeanu 2007; Cui et al. 2021). Despite several uses of quinoline, it is regarded as an endocrine interferon, causing irritation to the respiratory system, liver injury and carcinogenesis (Hirao et al. 1976; La Voie et al. 1988). Moreover, one of its derivative—mefloquine as drug—has been found to be neurotoxic in nature (Nevin 2014). Therefore, owing to its toxic nature, it is imperative to discuss about its degradation methods. This chapter discusses about the various applications of quinoline, its physicochemical properties and different treatment options, i.e. physical, chemical, biological and hybrid treatment methods.

9.2 Applications of Quinoline

Quinoline is used in the manufacture of dyes (Lam et al. 2012) which is used in textile industries. Quinoline and its derivatives such as isoquinoline and methylquinoline (Fig. 9.1) have been found in clothing textiles, and it is a possible source of human exposure (Dik et al. 2014). It has been used as a component of creosote which is used as preservative of wood sample (Ali et al. 2021). Creosote preservatives are used to protect timber elements that require very long shelf life and they are persistent in chemically treated woods at their end-of-life (Dias et al. 2022). They are also used in pharmaceutical industries in the manufacture of medicinal compounds (Lilienkampf et al. 2009). It is used in the manufacture of anti-malaria, anti-cancer, anti-inflammatory, anti-fungal, anti-leishmania, anti-tuberculosis, anti-microbial and anti-HIV drugs and also for the treatment of arthritis (Vandekerckhove and D'hooghe 2015; Musiol 2017; Ambatkar and Khedekar 2019; Musiol et al. 2010; Razzaghi-Asl et al. 2020; Alcaraz et al. 2022; Kaushik et al. 2022). Recent discovery reports quinoline-based derivative as potent molecular probe for detection of nitric oxide

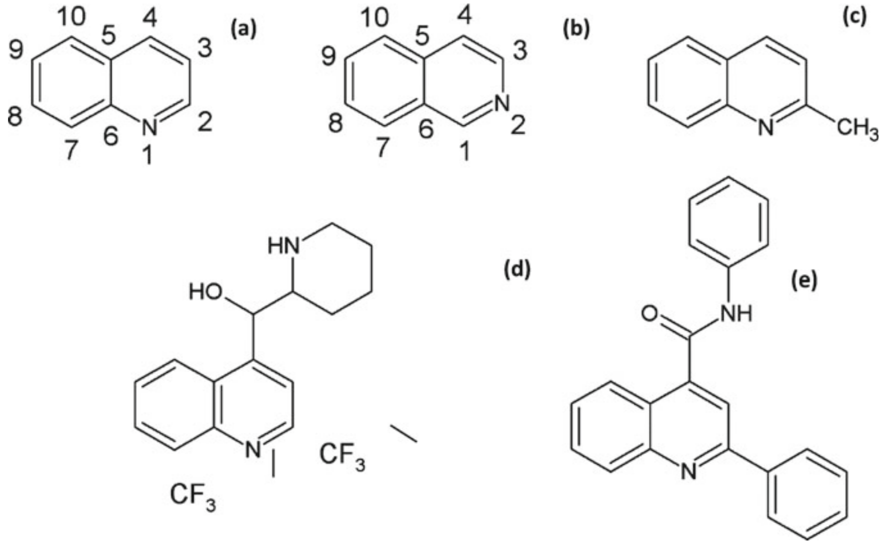

Fig. 9.1 Quinoline **a** and its derivatives **b** isoquinoline **c** methylquinoline **d** mefloquine (anti-malarial agent) **e** quinoline 4-carboxamide (anti-cancer agent)

which is a signalling molecule in COVID-19 and various immune, vascular and nervous disorders (Xing et al. 2022). It has also been used as fluorescent probe for detection of lead which finds its application in food industry for toxicity of lead ions in milk and packeted foods (Velmurugan et al. 2021). Additionally, it acts as a sensing molecule for H_2O_2, thiophenol and sulphite, which are found in living cells, manufacture of pharmaceuticals and food preservatives, respectively (Li et al. 2022a, b; Wu et al. 2021).

9.3 Physical and Chemical Nature of Quinoline

It is a colourless hygroscopic liquid, sparingly soluble in cold water and easily soluble in hot water. Furthermore, its solubility in water is pH dependent, at acidic pH (pH 2) solubility at 20 °C is 5 g/L (Nedoloujko and Kiwi 1997). It is miscible with organic solvents at ambient temperature. Quinoline exhibits a density of 1.093 $g\ mol^{-1}$, melting point of -15 °C and boiling point of 238 °C.

Quinoline is a heterocycle with two fused six-membered rings. It is also called benzo[b]pyridine or 1-azanaphthalene. It contains a nitrogenous aromatic heterocyclic ring with its common chemical reactions being nucleophilic and electrophilic substitution in nature than hydrogenation reactions, homolytic substitution and oxidation reactions (Ajani et al. 2022; Jones 1977). In the presence of acids, it can form a salt and shows similar reactions to that of benzene and pyridine. Quinoline is weakly alkaline (pKa = 4.85 at 20 °C) and exists mainly in the form of cations in aqueous solution (Cui et al. 2020). It shows self-associative property by forming dimer or trimer in aqueous solution with self-association constant of 8.8×10^3 K_a/L mol^{-1} (Latypov et al. 2005). It exhibits log K_{OW} (octanol/water partition coefficient) of 2.14 (Burgos and Pisutpaisal 2006). Octanol/water partition coefficient K_{ow} represents the ratio of concentrations of a compound between water-saturated octanoic phase and an octanol-saturated aqueous phase. Higher the value, more the bioaccumulation capacity of the compound (Zhang et al. 2022). Higher Log K_{ow} value also indicates its lower solubility in water. The hydrophobicity of the compound therefore inhibits its access to hydrophilic enzymatic sites. The bicyclic fused ring structure with dense electron density at N-atom of pyridine hinders electrophilic substitution reaction in the benzene ring (Tuo et al. 2012). Thus, it becomes a refractory compound for degradation.

9.4 Physical Treatment Methods

9.4.1 Thermal Decomposition

Thermal degradation of nitro-, acetylamide-, hydrogen-, substituted quinoline compounds has been observed at temperatures above 160 °C (Lizarraga et al. 2005). However, the chain length, degree of unsaturation and nature of substituent determines the temperature of degradation of substituted quinoline compounds. In thermal degradation process, compounds melt and decompose which is accompanied by superficial fusion.

9.4.2 Adsorption

Physical adsorption methods only transfer the contaminant from liquid phase to solid phase and do not degrade the pollutant. As a result, hazardous contaminants persist in the environment. Moreover, poor desorption and regeneration of the adsorbent create obstacles in its recyclability. Therefore, recent developments in adsorbents have been explored using carbon nanospheres because it imparts stable physical and chemical properties, large specific surface area, abundant porous structure, outstanding electrical conductivity and excellent biocompatibility (Cui et al. 2020). For better adsorption properties, magnetic carbon nanospheres have been used for removal of quinoline which follow chemical nature of adsorption (Cui et al. 2020). Magnetic carbon nanosphere has been prepared by KOH activation and nitric acid acidification which increases large number of pore structures and introduces oxygen-containing functional groups. These functional groups act as active sites which bind quinoline through acid–base interaction. The quinoline removal performance efficiency of

Table 9.1 Adsorption of quinoline by various adsorbents

S. no.	Adsorbent	Quinoline adsorption capacity	References
1	Activated carbon from coconut shell (*Elaeis guineensis*)	56.6 mg g^{-1}	Oliveira Ferreira et al. (2019)
2	Magnetic carbon nanospheres	297.21 mg g^{-1}	Cui et al. (2020)
3	Quartz and kaolinite sand	20 mM	Okhrimenko et al. (2021)
4	Granular activated carbon (GAC) and bagasse fly ash (BFA)	77.82 mg g^{-1}	Rameshraja et al. (2012)
5	Bamboo charcoal	17.7 mg g^{-1}	Liao et al. (2013)
6	Metal–organic frameworks MIL-101(Cr)	64.69 mg g^{-1}	Wang et al. (2013)
7	Sulfonic acid-functionalized resins	2.5 mM g^{-1}	Sun et al. (2022)

chemically treated magnetic carbon nanospheres has been reported to be enhanced by threefold than non-chemically treated nanospheres. Various adsorbents and their adsorption capacities have been listed in Table 9.1.

9.4.3 Gamma Irradiation

Gamma irradiation uses a similar process as that of employing advanced oxidation process (AOPs) which generate ·OH radicals. In contrast to AOPs where powerful chemical agents are used to produce reactive oxygen species, ionizing radiation employs radioactivity source such as ^{60}Co or ^{137}Cs for gamma irradiation and electron accelerator to produce ·OH radicals. ·OH radicals act as an electrophile and react readily with molecules of higher electron density. Quinoline, having an electron-dense nitrogen atom, causes faster degradation rate with ·OH radicals. Owing to the higher electron affinity of Gamma radiation using ^{60}Co has been employed to degrade quinoline completely into CO_2 and ammonium (Chu et al. 2018). Its efficiency has been found to be enhanced by addition of TiO_2 nanoparticle in the medium. TiO_2 nanoparticles have been believed to generate conduction band electron e- and valence band holes H^+ and subsequently induce the formation of ·OH radicals (Zacheis et al. 2001).

9.5 Chemical Methods of Degradation of Quinoline

9.5.1 Catalytic Ozonation

Ozone is highly water soluble and has high reduction potential of −2.07 V which mediates the oxidation of organic compounds (Jin et al. 2023). Therefore, it is used in the treatment of wastewater containing organic pollutants. Catalytic ozonation process involves generation of non-selective oxidizing hydroxyl radicals through ozone decomposition by use of catalysts. This method is divided into homogeneous and heterogeneous catalytic ozonation. The former involves metal ion catalysis whereas later involves oxides of metal present in bulk such as nanosheets or on carrier support system such as ceramic membrane (Jin et al. 2023).

Catalytic ozonation using MgO nanowires has been suitably used in biologically pre-treated quinoline-rich coal gasification wastewater (Zhu et al. 2017). Complete degradation of quinoline by sole ozonation releases small molecular organic acids which lower the pH of the solution (Liu et al. 2022). This drawback is eliminated by using $NiFe_2O_4$/sepiolite catalytic ozonation which shifts the pH towards alkalinity and facilitates ozone decomposition to generate reactive oxygen species (Liu et al. 2022). Another form of heterogeneous catalysis was performed by Wang et al. (2022) where disilicate-modified nZVI has been employed for quinoline removal. This novel material carried –[Si–O–Fe]–OH groups on its surface which facilitated adsorption and enhances catalytic decomposition of O_3 on the solid–liquid interface. Quinoline removal efficiency of 91.9% has been achieved by this system within 60 min time.

These catalytic ozonation methods are laid back by the stringent alkaline pH range which determines surface properties of catalyst, dissociation constants (pKa) and the generation of active radicals (Zhu et al. 2017). In addition, this method suffers from recycling of the catalytic process and also stability of the catalyst is of prime importance.

9.5.2 Catalytic Wet Peroxide Oxidation

Catalytic wet peroxide oxidation belongs to advanced oxidation processes (AOPs) which have been recognized as highly efficient and environmental-friendly techniques for the degradation of toxic organic pollutants from industrial effluent (Oturan and Aaron 2014). These techniques rely on the use of powerful oxidizing hydroxyl radicals (·OH) which are generated through different modes of operation (Moreira et al. 2017). Among them, catalytic wet peroxide oxidation (CWPO) is a propitious option because of its ability to completely degrade the pollutants into CO_2, N_2 and inorganic ions under benign operating conditions (temperature (<373 K) and atmospheric pressure) (Ribeiro et al. 2016).

Catalytic wet peroxide oxidation is one of the simplest process of quinoline degradation where wastewater containing quinoline is mixed with strong oxidizing agent—hydrogen peroxide (H_2O_2) and catalysts (such as CuO that have been doped with Ce or copper impregnated over modified zeolite) (Jiao et al. 2022; Singh et al. 2018). These catalysts aid release of hydroxyl radicals from H_2O_2 in aqueous solution. Since the OH radical has a strong electrophilic nature and a high redox potential ($E0 = 2.80$ V), it helps break down organic molecules largely through electrophilic addition reactions. It targets the electron-dense nitrogen atom of quinoline heterocyclic ring which is vulnerable to electrophilic addition reaction. The decomposition of H_2O_2 into ·OH radical and perhydroxyl radical ($HO\cdot_2$) occurs by cyclic oxidation–reduction of Cu^+ and Cu^{2+} species which act as catalyst (Singh et al. 2018). The schematic diagram of the mechanism is depicted in Fig. 9.2. The reaction mechanism is described below:

$$Cu^{2+} + H_2O_2 \rightarrow Cu^+ + H^+ + HO_2 \tag{9.1}$$

$$Cu^+ + H_2O_2 \rightarrow Cu^{2+} + HO\cdot + OH^- \tag{9.2}$$

$$Cu^{2+} + HO_2\cdot \rightarrow Cu^+ + H^+ + O_2 \tag{9.3}$$

$$H_2O_2 + HO\cdot \rightarrow HO_2\cdot + H_2O \tag{9.4}$$

$$\text{Quinoline} + HO\cdot \rightarrow CO_2 + H_2O + \text{intermediates} \tag{9.5}$$

Photodecomposition of H_2O_2 has improved the above-discussed technique. Quinoline breakdown is accelerated by peroxide oxidation in the presence of UV light at 366 nm because it allows for the faster production of oxidizing radicals (Nedoloujko and Kiwi 1997). It is further improved by photocatalytic Fenton oxidation in which ferric ions assist decomposition of hydrogen peroxide to generate ·OH radicals when exposed to UV light.

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2\cdot + H^+ \tag{9.6}$$

$$HO_2\cdot + e^- \rightarrow OH^- + 0.5\ O_2 \tag{9.7}$$

$$\cdot OH + e^- \rightarrow OH^- \tag{9.8}$$

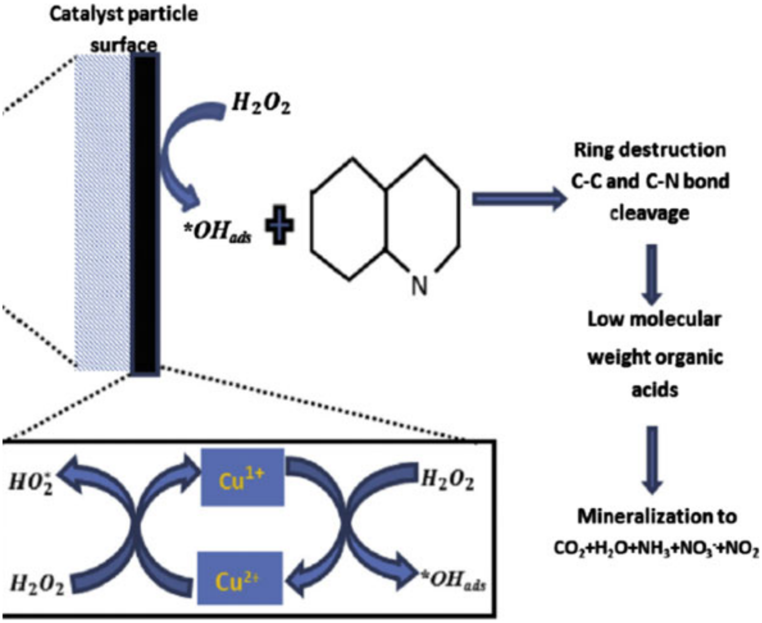

Fig. 9.2 Catalytic wet peroxide oxidation mechanism of quinoline degradation (Singh et al. 2018)

9.5.3 *Photocatalysis*

Titanium oxide (TiO_2) is commonly known as anatase, when added as suspension to aqueous solution, and if exposed to UV light, it absorbs light below $\lambda = 385$ nm leading to the production of $OH^\bullet$ on the surface. Hydroxide radicals thus generated without requiring strong oxidizing agent such as H_2O_2 participate in degradation of organic compounds. Jing et al. (2012) used photocatalysis ($\lambda = 365$ nm) with suspended TiO_2 to degrade quinoline. The removal of quinoline reached 91.5% under the optimized experimental conditions (initial quinoline concentration 0.55 mmol/L, TiO_2 dosage 1.5 g/L and pH 6.06). Photocatalytic generation of OH radicals has been found to be further improved by using polyaniline (PANI)/TiO_2 nanocomposites which can absorb both UV and visible light ($\lambda = 190$–800 nm) in contrast to pure TiO_2 suspension which absorbs only UV light ($\lambda < 385$ nm). Such composites have been used to degrade quinoline yellow dye which is a quinoline derivative (Salem et al. 2009).

9.5.4 Supercritical Water Oxidation

Water at conditions of pressure $P = 22.1$ MPa and temperature $T = 374.15$ °C presents as gas-like transport properties and liquid-like solvent characteristics, and this has been called as supercritical water. At such high temperature and pressure, it is characterized by high dielectric constant and ionic constant (Ogunsola 2000). It has been known to dissolve several non-volatile organic and inorganic chemical species and convert hazardous organic compounds to less hazardous compounds such as carbon dioxide and water. Oxidation of recalcitrant organic compounds in supercritical water releases heat as energy which is stored in them; hence, preheating temperature and pressure are critical points of consideration. Quinoline degradation by supercritical water oxidation follows the path of quinoline liquid → secondary products → volatile compounds → gaseous end products (Ren et al. 2019). Formation of degradation intermediates as hydroxyl quinoline must have been initiated by ionic reaction involving H^+ and OH^- ions. Hydrogenation by H^+ causes the heterocyclic ring to be saturated which is followed by hydrogenolysis of C–N bonds. Hydrogenolysis first opens the hetero-ring and then covers the resultant aliphatic and aromatic amine intermediates to hydrocarbons and ammonia (Moreira et al. 2017). Table 9.2 enlists various physical and chemical methods with its advantages and disadvantages.

Table 9.2 Various physical and chemical methods with its advantages and disadvantages

S. no.	Methods	Maximum quinoline removal efficiency (%)	Advantage	Disadvantage	References
1	UV photolysis for accelerated quinoline biodegradation and mineralization	9	Significantly improves the biomass growth kinetics and maximum specific growth rate	Increase in initial concentration of quinoline increases the time required for quinoline removal	Yan et al. (2013)
2	Activated carbon chemically modified with H_2SO_4	67.08	The H_2SO_4 treatment increases the polarity of the surfaces of the adsorbent, resulting in an improvement in removal efficiency	Surface area and pore volume of the adsorbent reduces due to oxidation of sulphuric acid	Oliveira Ferreira et al. (2019)

(continued)

Table 9.2 (continued)

S. no.	Methods	Maximum quinoline removal efficiency (%)	Advantage	Disadvantage	References
3	Graphite oxide and Activated carbon	–	Act as a promising adsorbent for selective removal of quinoline from liquid hydrocarbon streams	Effective regeneration of the adsorbent is largely dependent on the polarity of solvent	Feng et al. (2015)
4	Fe_2O_3/Biochar	99	The addition of Fe_2O_3 nanoparticles increases the active adsorption sites on biochar surface, which can promote the removal of quinoline	There is no appreciable increase in adsorption capacity	Xu et al. (2018)
5	Coke powder with inorganic anions	93.31	Addition of K^+ and Ca^{2+} ion increases the adsorption efficiency from 84.9% to 92.02% and 93.31%, respectively	–	Wang et al. (2020)
6	Catalytic ozonation using disilicate-modified nZVI	91.9	Compared to the nZVI, the Si-nZVI displayed satisfactory catalytic stability and benign reusability as well	Self-aggregation and rapid passivation of nZVI are the problems associated with the process	Wang et al. (2022)
7	Methylcellulose /tannic acid complex	60	Maximum adsorption capacity of 460.92 mg/g quinoline was recorded with facile separation, excellent adsorbent regeneration and reusability	Tedious method	Abebe and Kim (2022)
8	Bagasse fly ash	84	The value of $\Delta G°$ was found to be negative at all temperatures indicating the spontaneity of adsorptive treatment	Very poor desorption for quinoline was observed with alkali and water in comparison with the strong acids	Rameshraja et al. (2012)

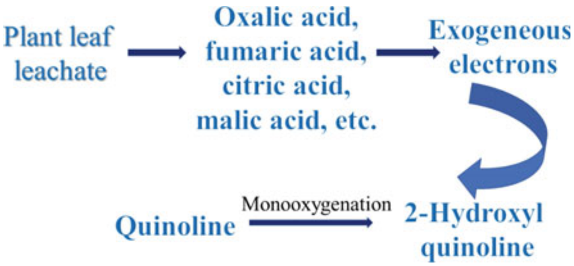

Fig. 9.3 Schematic diagram of degradation of quinoline by biological waste

9.6 Biological Methods of Degradation

9.6.1 Biological Wastes

Fallen plant leaves have proven good solution to quinoline degradation. This has been accompanied by using plant leaf (*Platycladus orientalis* and *Ginkgo Biloba*) leachate which is a source of organic acids such as oxalic acid, fumaric acid, malic acid and citric acid (Xiong et al. 2012). These organic acids provide electron donors which accelerate the degradation process. They act as a source of exogenous electron donor which aid monooxygenation reaction for quinoline degradation (Fig. 9.3) (Lu et al. 2019; Xu et al. 2017).

9.6.2 Aerobic Degradation of Quinoline

Aerobic biodegradation of quinoline has been investigated in several bacteria (Table 9.3). In all cases, 2-hydroxyquinoline occurs as the first intermediate product of degradation. Thereafter, further degradation is divided into two pathways: (a) the 5,6-dihydroxy-2(1H) quinolinone pathway and (b) the 8-hydroxycoumarin pathway (Zhu et al. 2008). Quinoline degradation by bacteria has been observed by production of pink, yellow and brown coloured pigments in the culture medium which appear one after another. These pigments could be related to different metabolites produced at different phases of bacterial growth. (Lin and Jianlong 2010). *Rhodococcus* sp. Q1 has been found to produce green pigment during log phase growth on quinoline which later turns greenish brown during the stationary phase (O'Loughlin et al. 1996). Similarly, *Rhodococcus* sp. QL2 produced pink pigment followed by brownish red pigment during quinoline degradation (Zhu et al. 2008).

Generally, microorganisms which carry out biodegradation of toxic organic compounds bear the potential to use a broad range of substrate among aromatic compounds such as pyridine, indole, phenol, benzene, naphthalene and several others as the sole carbon source. Therefore, bacteria which have been found to degrade quinoline have been found to be capable of degrading other xenobiotic organic compounds. For example, *Achromobacter* sp. DN-06 is capable of degrading dual

Table 9.3 Aerobic degradation of quinoline by bacteria

S. no.	Species	Isolated from	Concentration of quinoline degraded	Time (h)	Degradation products	References
1	*Pseudomonas putida*	Activated sludge of municipal wastewater treatment plant	500 mg/L	3	2-hydroxyquinoline, 2,8-dihydroxyquinoline and 8-hydroxycoumarin	Lin and Jianlong (2010)
2	*Rhodococcus ruber*	Activated sludge	1 mM	26		Zhu et al. (2021)
3	*Bacillus tropicus*, *Bacillus aquimaris* and *Rhodococcus ruber mixed culture*		1 mM	20		Zhu et al. (2021)
4	*Bacillus sp.* Q2	Petroleum contaminated soil	300 mg/L	48	2(1*H*)-quinolinone and 8-hydroxycoumarin	Tuo et al. (2012)
5	*Achromobacter* sp. DN-06	Activated sludge of coking wastewater treatment plant	100 mg/L	32	2,8-dihydroxyquinoline	Zhao et al. (2014)
6	*Pseudomonas sp. BW003*	Activated sludge of coking wastewater treatment plant	200 mg/L	4	NH_3-N	Bai et al. (2009)
7	*Burkholderia pickettii*	Activated sludge of coking wastewater treatment plant	500 mg/L	6.5	2-hydroxyquinoline	Jianlong et al. (2002)
8	*Pseudomonas* sp. Q1	Anode of microbial fuel cell	500 mg/L	15		Zhang et al. (2012)
9	*Rhodococcus* sp. QL2	Activated sludge of coking wastewater treatment plant	120 mg/L	7	2-hydroxyquinoline, 2,6-dihydroxyquinoline and 8-hydroxycoumarin	Zhu et al. (2008)

substrate—quinoline and m-cresol simultaneously (Zhao et al. 2014). Under dual substrate conditions, degradation rate of individual compounds becomes slower and this kind of substrate uptake is described by non-competitive inhibition which is described by the Michaelis Menten equation:

$$V_o = \frac{\alpha V_{\max} S}{K_m + S} \tag{9.9}$$

$$\alpha = \frac{1}{1 + S_I / K_I} \tag{9.10}$$

where $V_{\max}$ is the maximum reaction velocity, S is the concentration of organic pollutant 1, S_{I} is the concentration of organic pollutant 2 (inhibitor), K_{m} is the Michaelis–Menten constant and K_{I} is the inhibitory constant.

In such systems, quinoline competes with *m*-cresol for the same enzyme sites. However, the formed enzyme–quinoline complex could not generate its end-product and thus fail to release the combined enzyme for the initial biocatalytic reaction. Moreover, the specific enzyme for *m*-cresol degradation presented in the system has a high affinity for quinoline. The inhibition by m-cresol could be relieved by increasing the concentration of quinoline in such systems. Similar degradation capability has been studied in *Rhodococcus ruber* which has been fed with quinoline and pyridine together (Zhu et al. 2021). Conversely, two bacterial species—*Bacillus tropicus* and *Rhodococcus ruber*—have been studied to synergistically degrade quinoline.

Amongst eukaryotic degraders, fungi have been well known for quinoline removal efficiency. Filamentous fungus *Cunninghamella elegans* IM 1785/21Gp have been found to degrade quinoline up to 200 mg/L which has been accomplished by the formation of quinoline degradation metabolites—2-hydroxyquinoline and 3-hydroxyquinoline (Felczak et al. 2016). Quinoline exposure to *C. elegans* IM 1785/21Gp led to changes in the membrane fatty acid and phospholipid composition. Owing to the presence of stress compound, quinoline, membrane fatty acid profile shifted from saturated fatty acids towards more of unsaturated fatty acid content. Similarly, another microscopic fungus *Curvularia lunata* IM 4417 has shown quinoline-degrading ability with change in membrane fatty acid profile (Felczak et al. 2081). White rot fungus, *Pleurotus ostratus*, as a strain is capable of growing in the presence of quinoline and removing the pollutant at a concentration of 250 mg L^{-1} within 15 days (Zhang et al. 2007).

9.6.3 Anaerobic Biodegradation of Quinoline

Anaerobic degradation of quinoline has been previously reported to be facilitated by sulphate-reducing, nitrate-reducing and methanogenic bacteria (Licht et al. 1997; Li et al. 2001; Gao et al. 2020). In anaerobic biotransformation pathways, dehydrogenase enzymes serve as a counterpart to oxygenases (catalysing O_2-dependent hydroxylation) and they use water as a source of oxygen atom for the aromatic ring hydroxylation reactions (Dermer and Fuchs 2012). Hydroxylation of the aromatic ring is an essential process in the metabolism of the heterocyclic compounds. The steric requirements of the enzyme involved in the hydroxylation reaction might favour substitution at C-2 position next to the heteroatom of aromatic ring further destabilizing the ring structure. In contrast to aerobic biodegradation, in anaerobic process N(1) = C(2) double bond is first broken followed by addition of an ion of H^+ in the place of N(1) and then -CH_3 is added in the place of C(2), leading to the formation of 2-Methylquinoline (Shi et al. 2019). This is followed by ring opening and formation of short chain olefins and NH_3-N. Anaerobic degradation is mainly promoted by iron-reducing bacteria which degrade aromatic compound. In order to change Fe (III) to Fe(II), these bacteria go through a cyclic redox reaction, these bacteria undergo cyclic redox reaction to convert Fe(III) to Fe(II) and which produces OH radical (Huang et al. 2020) that degrades quinolines (Huang et al. 2020). Therefore, addition of ferric ion in the form of Fe_3O_4 attached to the surface of carrier such as polyurethane help to encourage biofilm growth of anaerobic bacteria which can facilitate degradation of organics such as quinoline. The use of polyurethane carrier provides hydrophilic surface bearing cationic groups on its surface which help firm attachment of microorganisms to its surface. Several other carriers such as powdered activated carbon and biochar have also been employed (Li et al. 2019).

Organic compounds are used as electron donor and nitrate/nitrite are used as electron acceptor under anoxic condition. Denitrifying microorganisms are one such system which can anaerobically use quinoline as carbon substrate. In denitrifying systems, quinoline degradation has been achieved when it has been used as a sole carbon source in the presence of 80 mg/L nitrate which is entirely converted into nitrogen gas (Li et al. 2001). Denitrifying microcosms have been reported to produce 2(1H)-quinolinone as degradation product of quinoline when they consume nitrate as electron accepter (Li et al. 2010). It has been discovered that the addition of zero-valent iron (ZVI) nanoparticles further degrades 2(1H)-quinolinone build-up caused by anaerobic degradation (Xu et al. 2020). ZVI has been postulated to enhance degradation of organic compound such as quinoline in two ways. Firstly, ZVI is oxidized to Fe^{2+} using water as an oxidant in anaerobic circumstances with extremely little dissolved oxygen content.

$$Fe^0 + 2H_2O \leftarrow H_2 + Fe^{2+} + 2OH^- \tag{9.11}$$

Alternatively, it also acts as electron donor to promote hydrogen-consuming microorganisms, such as methanogenic and denitrifying bacteria.

9.7 Hybrid Methods for Degradation of Quinoline

Hybrid methods involve combination of both physicochemical processes with biological treatment methods (Table 9.4). Fe_3O_4 nanoparticles have been known to enhance enzymatic activity for quinoline degradation but are laid by drawback of reuse of the material. Therefore, functionality of these nanoparticles has been improved by supporting over bamboo carbon which provides large effective surface area, a high porosity, strong adsorption ability and physicochemical stabilization. It then becomes a good carrier for immobilization of bacteria which effectively carries out degradation activity in the presence of Fe_3O_4. As compared with freely suspended cells, immobilized cells over bamboo carbon show better quinoline removal efficiency with significant improvement (Zhuang et al. 2015). Moreover, the immobilization provides better tolerance to environmental factors such as pH and temperature (Zhuang et al. 2015).

Conventional anaerobic treatment systems have been found to remove quinoline at lower concentration (50 mg/L) in a very time-consuming (30 days) manner (Wang et al. 2017). To this score, microbial electrolysis cell (MEC) coupled with anaerobic digestion has resulted in efficient quinoline removal. Additionally, this hybrid system results in renewable energy recovery in the form of biogas along with quinoline degradation. Biogas has been reported to be produced as a result of growth of mixotrophic microorganisms such as methanogens, ammonia-oxidizing archaea and other anaerobes in the electrochemical cell. Coupling of both processes leads to increase in

Table 9.4 Hybrid methods of quinoline removal

S. no.	Species	Physicochemical pre-treatment	Quinoline degraded	Time (h)	Degradation products	References
1	*Streptomyces* sp. N01	Fe_3O_4 nanoparticles were loaded on bamboo carbon (BC) as a carrier for immobilization of bacteria	400 mg/L	16	–	Zhuang et al. (2015)
2	Quinoline degrading mixed culture bacteria	Fe(III)-rich nontronite clay mineral (anaerobic process)	100 mg/L	12 days	8-hydroxycoumarin, mono- and di-methylated mono-hydroxyl quinoline, mono- di-, tri- and tetra-hydroxylated quinolone, methylated hydroxyl quinolone	Huang et al. (2020)
3	Quinoline degrading mixed culture bacteria	Montmorillonite clay-coated soil containing quinoline-degrading bacteria	–	–	2-hydroxyquinoline	McBride et al. (1992)
4	Anaerobic mixed culture	Microbial electrolysis cell coupled with anaerobic digestion	400 mg/L	120	2-hydroxyquinoline and 8-hydroxycoumarin	Gao et al. (2020)

removal efficiency (90%) in lesser time (120 h) with the application of 1 V current in contrast to sole anaerobic digestion as discussed above (Gao et al. 2020). Moreover, this coupling effect of biodegradation and electrochemical reaction stimulates and enhances the growth and activity of electrochemically active microorganisms which allows higher range of quinoline, i.e. 400 mg/L to be degraded.

9.8 Conclusion

Quinoline, which is a N-heterocyclic compound, is commonly used in various industrial processes. As a result, quinoline and its derivative have been widely found in environment and exert its toxic effects on organisms from various trophic levels. Although several methods have been employed for efficient removal of quinoline, complete mineralization of quinoline leads to the accumulation of NH_3-N, which is again a problem. Therefore, quinoline removal strategies should be coupled with elimination of ammonia from the wastewater. To overcome this problem, biological methods such as combination of nitrification and denitrification could provide a good solution to quinoline removal. Furthermore, pre-treatment of wastewater, optimization of operation conditions and novel coupling processes in hybrid methods are necessary to improve efficiency of contaminant removal. Better understanding of environmental parameters and biochemical reactions between microorganisms and organic intermediates could pave way to more efficient treatment technologies.

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Part IV

Removal of Persistent Metals from Water Systems

Chapter 10
Strategies to Enhance Selective Biosorption-Based Remediation and Recovery of Persistent Metal Pollutants

Ankur Singh, Saumya Anand, and Vipin Kumar

Abstract Heavy metals are almost ubiquitous, owing to their persistent nature in the environment. In the past few decades, a significant rise in concentrations of these metals due to anthropogenic activities has been reported in a variety of environmental samples, which has led to an increase in health hazards to both plants and animals including human beings. A variety of strategies have been reported for the remediation of these pollutants; however, bio-sorption remains one of the most prominent due to its good efficiency accompanied by economic feasibility. A wide range of biological materials have been experimented with, and significantly new strategies to improve their adsorption capacity are reported. In the recent past, technological advances have also facilitated the improvisation that has enhanced the selective adsorption capacities of biosorbents. Since selective adsorption paves the path for the economic recovery of these metals, these strategies have emerged as a center of interest for several industries. This book chapter focuses on the strategies that can be used to enhance the sorption capacity and selective nature of the bio-sorbents. A brief review of the processes, approaches, mechanisms, and mathematical models will be presented accompanied by a future course of further research in the field.

Keywords Selective sorption · Biosorption · Heavy metals · Activated bio-sorbents · Metal recovery

10.1 Introduction to Persistent Toxic Metals: Environmental Concerns vs Economical Value

Metals have remained a major contributor to human civilizational and industrial progress throughout history. However, with progressing expansion of industrial manufacturing and utilization, they have emerged as a major cause of environmental

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concern due to improper management. A huge amount of metal is released into the environment every day in form of wastewater, industrial effluent, and solid waste. The recovery of metal from solid waste is easier; however, the recovery from wastewater is extremely challenging due to a lack of economic methods. As a result, this portion is lost into the environment, where it is responsible for damage to flora and fauna. This loss is significant not only due to the sheer quantity but also due to the precious, semiprecious, and economical cost of the elements.

The anthropogenic sources of heavy metals in the environment include exhaust gas from automobiles, smelting factories of metals like copper and zinc, pesticide and insecticides industries manufacturing chemicals, burning of fossil fuels, paint industries, household product industry, cosmetic industry, etc. (Masindi and Muedi 2018). These sources ultimately release the pollutants into the environment, which are either washed away to water bodies or wastewater discharged. The wastewater generated from households and industries consists of a wide variety of metals that have economic value and are useful in our day-to-day life. These metals can belong to the group of macro-nutrients (Co, Fe) and micro-nutrient (Cu, Ni, Cr, Fe, Mn, Mo), highly toxic elements (Hg, Cd, Pb, Ag, Au, Pd, Bi, As, Pt, Se, Sn, Zn), precious elements (Au, Ag, Pt, Pd, Ru), and radionucleotides (U, Th, Ce, Pr) (Selvi et al. 2019). Depending on the intrinsic properties, they might be useful nutrients or may have chronic toxicity in living organisms due to their ability to accumulate in biomass (Jaishankar et al. 2014). The heavy metals tend to accumulate in organisms as one moves up in the food pyramid; thus, organisms at the apex are likely to experience more toxic effects than the ones at the lower level (Garai et al. 2021). Human beings are the apex predators of the ecosystem; thus, they are exposed to a heavy dosage of heavy metals through dietary intake. The metals are well known to target critical organs such as kidneys, lungs, brain, liver, and skin, leading to various kinds of ailments including organ failure, neuropathies, cancer, ulcer, etc. (Mahurpawar 2015; Engwa et al. 2019). Thus, remediation and the prevention of further contamination of the environment from these toxic metals are of high priority for several governmental agencies.

The removal of heavy metals is possible through various chemical, physical, and biological methods or by a combination of the two or more methods through technological advancements. Figure 10.1 represents the important sources of toxic persistent metal and the methods that can be employed for their recovery from wastewater.

10.2 Toxic Metal Remediations and Recovery Approaches

The removal of heavy metals is possible through various chemical, physical, and biological methods or by a combination of the two or more methods through technological advancements. Figure 10.1 represents the important sources of toxic persistent metal and the methods that can be employed for their recovery from wastewater.

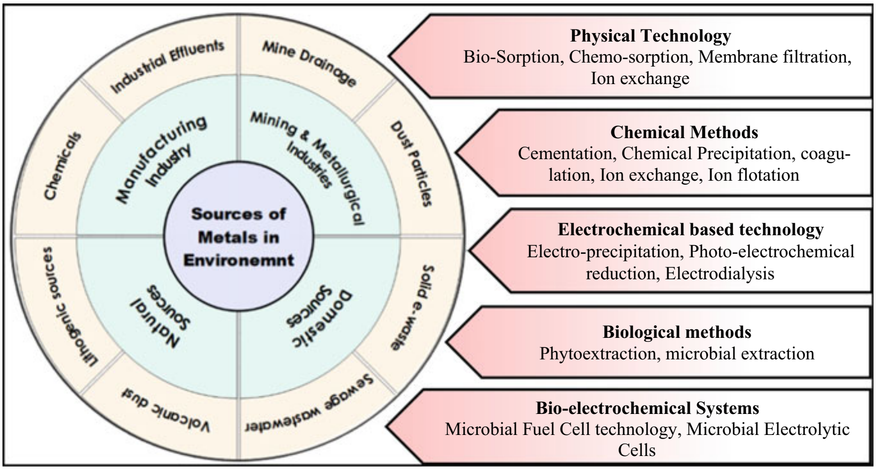

Fig. 10.1 Various sources of persistent metals in the environment and the widely used technological methods for their recovery

10.2.1 Chemical Approach

The chemical approach includes the process mechanisms which rely on the reactivity of the ions with other materials, leading to phase transfer from dissolved form to solid form. This includes.

Cementation:

The process of cementation involves the precipitation of dissolved metals as sponge metals by contacting them with specific meatal power or scrapes and filaments (Kazakova et al. 2020). In this method, automatic deposition of metallic ions on the surface of the other metal, the substrate, occurs due to favorable thermodynamics (Jeon et al. 2020). For example, iron is often used as a substrate metal for the cementation of copper from wastewater (Jhajharia et al. 2016) and zinc dust is used for the removal of gold and silver from cyanide solutions containing a mixture of several metals (Yakornov et al. 2018).

Chemical precipitation:

This includes the removal of soluble ions by changing the chemical composition or properties of the water, which results in the phase transfer of metals to an insoluble form, either in elemental form or as a reaction product. The chemical change in composition can be brought about by the change in pH. For example, increasing pH to 9 -10 precipitates metal ions to elemental solid form. Alternatively, the precipitation can be done in form of metal hydroxides, sulfides, carbonates (Krishnan et al. 2021), or using other chemicals.

Ion exchange:

This method includes a reversible chemical reaction that occurs by the exchange of ions of similar charges from a solid surface with ions in the liquid media. This is commonly employed in chemical industries, where the solid media consist of special high-capacity ionic resins. For example, uranium is recovered from its ore at high rates using resins (Amphlett et al. 2020). In another case, graphene oxide impregnated with Fe3O4 was used as an ion-exchange surface for the recovery of Cu+2, Pb+2, and Cd+2 (Hur et al. 2015).

Ion flotation:

This process involves the use of surfactants or collectors for negative charges, that are opposite to that of positive charges on the metal ions. The binders react with metals and can be separated by bubbling air through the water (Taseidifar et al. 2019). The collected froth can then be used to recover the metal ions. This process is commonly used in the mineral processing industry. The ion flotation method is also classified as dissolved-air flotation (DAF), dispersed-air flotation, electro-flotation, vacuum-air flotation, and biological flotation (Chang et al. 2019), depending on the specific process.

10.2.2 Biological Approaches

The process that relies on the properties of biological agents such as plants, microbes, or some organic material can be classified as the biological approach for metal recovery.

Phyto-extraction:

This process involves the use of specialized plants called hyperaccumulators. These plants extract metals from the environment and concentrate them in their vegetative parts, as a strategy to avoid metal toxication (Sytar et al. 2021). This strategy is convenient for remediation of soil contaminated by toxic metals, where other methods of removal can be highly costly (Yu et al. 2022). The commonly used hyperaccumulator plants used include Helianthus, Crassula, Solanum, Clerodendrum, Brassica, Arabidopsis, Thlaspi, Sedum, Opuntia, Phyllanthus, Pteris, Rinorea, etc. (Rajput et al. 2021).

Bio-extraction method:

The method of using microorganisms for the extraction of metals from water or solid residue can be classified as the bio-extraction method. This usually encompasses the process of bioleaching and bioremediation. The former is more suitable as a process for extraction of metals from solids such as waste scrapes or minerals (Yin et al. 2021), while the latter is usually deployed for the treatment of wastewater.

The process of bioleaching uses specialized microbes such as the acidophilic sulfur-oxidizing bacteria for achieving low pH, a condition suitable for the dissolution of metals to their ionic form (Hong and Valix 2014).

Bio-electro-chemical systems:

This method involves the usage of the combined effect of chemical potential gradient generated by microbes and the membrane technology for the reduction of the ionic metals to a solid form. The cathodic deposition of the metal ions is possible by accepting the electrons generated from the electrogenic microbes in the anodic chamber (Kumar et al. 2021). The reduction of the metal is the function of the potential difference generated at the electrodes. Hence, removal of metals such as Zn, Cd, U, and Pb with lower reduction is possible with microbial fuel cell configuration, while metals with higher reduction potential such as Hg, Pd, Ag Cr, and Co can be done by supplying small voltage in microbial electrolytic cell configuration (Wang et al. 2022a).

10.2.3 Physical Approach

Membrane methods:

The process of filtration involves the use of membranes of different pore sizes to separate ions with the difference in their hydrated radius. The membrane method is also suitable for the separation of a wide range of organic contaminants from inorganic contaminants. Depending on the size of the pore, the filtration of the specific metal ion is possible (Batouti et al. 2021). For example, ultrafiltration is used for filtering ions of size 5 to 20 nm and molecular weight from 1000 to 100,000 Da. The structural modification of the membrane can significantly impact the selectivity of the system (Ye et al. 2019). The membrane technology allows rapid treatment; however, it has its problem of the high cost of and biofouling.

Adsorption:

The process of adsorption can be defined as the attachment of one mobile ion or molecule onto a relatively stable surface, which is usually solid. Depending on the nature of the interaction between the molecules and surface, adsorption is often classified as physisorption and chemisorption. The type of interaction in the former is van der Waals forces; in the latter, the chemical reactions dominate. Physisorption is one of the most popularly used methods for the recovery of heavy metals from the water due to several advantages over other processes (Table 10.1). The process of adsorption and its selective nature has been discussed in further sections.

Table 10.1 Advantages and disadvantages of different methods of metal recovery from wastewater

Method	Advantages	Disadvantages
Cementation	• Low cost, low energy consumption • Recovery of metals in pure metallic form, ease of control • The simplicity of operation and high efficiency	• Its excess sacrificial metal consumption • Requires post-treatment to remove high concentrations of iron and aluminum ions • Cost of the maintenance
Chemical precipitation	• Low pH conditions and efficient for copper removal • Low detention time requirements • Carbonate sludge has better filtration characteristics	• The process faces larger than stoichiometric reagent consumption • Large quantity of sludge generation • Ineffective at low ionic concentration
Ion exchange	• Low costs • Minimal energy is required • Regenerate chemicals are not expensive	• Adsorption of organics • Bacterial contamination • Organic contamination from the resin
Ion flotation	• Drives it more widely for industrial utilization • Highly selective and not hindered by complexing agents	• Very high initial capital cost • Energy costs for operation
Phyto-extraction	• Cost-effective • Effective for low concentration extraction • Efficient in soil	• Slow rate, spanning from months to years • Requires supporting technology from final recovery
Bio-extraction	• Low cost • Low carbon footprint • Suitable for mining purpose as well	• Adsorption capacity a subject of chemical properties of water • Growth stage of cells affects results

(continued)

Table 10.1 (continued)

Method	Advantages	Disadvantages
Bio-electro-chemical	• Energy efficient, low minimal energy requirement • Simultaneous treatment of organics in wastewater • Ecofriendly dual-purpose technology • Metal obtained ad deposits on electrode	• Technology at developmental stage • Scaling up is challenging • Initial cost and maintenance cost for reactor
Membrane technology	• Small space requirement • Low solid waste generation • Simple, rapid, and efficient, even at high concentrations	• Investment costs are often too high for small and medium industries • High energy requirements • Limited flow rates
Adsorption	• Wide range of commercial products and a wide variety of target contaminants • Fast kinetics hence ow time requirement • Can be cost-effective and low-cost sorbents	• Regeneration can be expensive • Requirement for several types of adsorbents

After Kikuchi and Tanaka (2012), Hemdan et al. (2022) and Krishnan et al. (2021)

10.2.4 Selective Adsorption and Isotherms

Adsorption can be defined as the process in which a mobile fluid forms a condensed phase (absorbate) over a substrate (absorbent) due to inter-molecular interactions between the two types of molecules. This leads to the development of monolayer or multilayer deposition of absorbate on the surface of the absorbent, at the solid–liquid interface. Depending on the properties of the sorbent, the phenomenon can be used for the efficient removal of the organic as well as inorganic components from the wastewater (Dev et al. 2022). The process and capacity of adsorption for material are subject to various parameters that can affect the interphase interaction between the molecules. These factors include the surface area of the absorbent, the porosity of the absorbent, pH of the medium, contact time given for adsorption, the temperature of the surrounding, absorbent dose, and concentration of the absorbate in the medium, and the presence of the interfering ions in the solution. Thus, optimization of these factors is considered important for the development of any adsorbent.

The process of adsorption, in general, is governed by the physical forces of interaction; for example, an adsorbent with an abundance of positively charged functional groups will attract anions more efficiently than any other cation and vice versa. Since heavy metals are mostly present as cations in the wastewater, a negatively charged adsorbent is preferred for their removal and recovery. If a sample contains multiple cations, which is usually the case, one might expect that adsorption for all cations occurs in the proportion of their relative abundance. However, this is not the case in real absorbents. It has been observed that one cation is adsorbed more on the sorbent that the other cations, even though they were present in equal amounts. This phenomenon of the metal ions getting preferentially adsorbed over other metal ions can be termed selective adsorption (Dev et al. 2022).

Selective adsorption is governed by the type of inter-molecular interactions between the adsorbate and adsorbent, which essentially depend on the types and degree of functional groups present on the adsorbent. The chemical properties and reactivity of the functional group will govern the type of interaction between the metal ions and the adsorbent. For example, the process can be governed by: (a) electrostatic force of attraction, (b) diffusion, (c) coordination, (d) chemical bonding, (e) ion exchange, (f) acid–base interaction, or (g) reduction (Chang et al. 2021). Several mechanisms may be involved simultaneously in the adsorption; however, the dominance of one over the other can significantly affect the selectivity of the adsorbent. The factors governing the selectivity of the adsorbent for heavy metal adsorption will also depend on the thermodynamics of the interactions, subject to other limitations. For example, an interaction will always proceed to reduce the Gibbs free energy of the system (Al-Senani and Al-Fawzan 2018); however, the pore size of the adsorbent may prevent the adsorption of ions that reduces the system's energy to the least value (des Ligneris et al. 2020). Similarly, in general a smaller or divalent cation is preferentially adsorbed (Valisko et al. 2007), however, in the case of competition between a divalent ion of larger size and a monovalent ion of smaller size a competitive situation arises. In such cases of lower surface charges, the electrostatic advantage of the divalent ions dominates, whereas at higher surface charges the entropic advantage of the small ions dominates (Valisko et al. 2007). The selective adsorption can be better understood better with (Hard-soft-acid–base) HSAB theory and Density function theory, which are beyond the scope of this concise chapter.

The theorems explain the phenomenon of adsorption began with a simpler version like that of Brunauer–Emmett–Teller (BET) and Langmuir but after the 1950s the complexity of the theory increased. Now, the focus of the theoretical system shifted from just single-layer or multilayer adsorption to inter-molecular interactions of adsorbate, localized, and mobile-localized adsorption and phase transitions in the adsorbed layers (Dąbrowski 2001). Several adjustments and developments have been made for the explanation of adsorption. An overview of these equations can be found in Table 10.2. However, there remain deviations in experimental isotherms, from the predictions made by the theoretical approaches, especially in the case of smaller and high-pressure zones (Dąbrowski 2001).

10.3 Adsorbents for Metal Remediation and Recovery

A wide range of adsorption materials has been reported that can be used for the recovery of metal ions from wastewater. These materials must have some important properties to be considered good sorbents, and these include (a) ease to recycle, (b) selectivity in adsorption, (c) large specific surface area, (d) nontoxic nature, and (e) a simple energy-efficient process of production. Adsorbent materials can be

Table 10.2 Different adsorption isotherms used for describing the phenomenon of physical adsorption of metals on different adsorbents

S. no.	Adsorption isotherms	Equation	Governing factors	References
1.	Langmuir isotherm equation [Two parameter isotherm, for monolayer adsorption, at homogeneous site]	$Q_\mathrm{e} = Q^\mathrm{e}_\mathrm{th}\frac{K_\mathrm{eq}C_\mathrm{e}}{1+K_\mathrm{eq}C_\mathrm{e}}$	• Q_e = absorption capacity by weight at equilibrium • Q^e_th = theoretical maximum adsorption capacity by weight • K_eq = equilibrium constant of adsorption reaction • C_e = concentration of adsorbate at equilibrium	Singh et al. (2021), Kargi and Cikla (2006), Tunali et al. (2006)
2.	Freundlich isotherm equation [Two parameter isotherm, for multilayer adsorption, at heterogeneous site]	$\mathrm{Q_e = k_F C_e^{1/nF}}$	• Q_e = absorption capacity by weight at equilibrium • C_e = concentration of adsorbate at equilibrium K_F and n_F = Freundlich constant	Kargi and Cikla (2006), Tunali et al. (2006)
3.	Sips isotherm equation [Three-parametric isotherm for monolayer adsorption]	$Q_e = Q^e_\mathrm{th}\frac{K_\mathrm{eq}C_e^{n_s}}{1+K_\mathrm{eq}C_e^{n_s}}$	• Q_e = absorption capacity by weight at equilibrium • K_eq = equilibrium constant of adsorption reaction • C_e = concentration of adsorbate at equilibrium n_s = Sips constant	Kumar and Porkodi (2006)
4.	Redlich–Peterson isotherm equation [amends inaccuracies of Langmuir and Freundlich isotherm]	$Q_\mathrm{e} = K_\mathrm{rp}\frac{C_\mathrm{e}}{1+\alpha_\mathrm{rp}C_\mathrm{e}^\beta}$	• Q_e = absorption capacity by weight at equilibrium • C_e = concentration of adsorbate at equilibrium K_rp and α_rp = Redlich–Peterson constant	Preetha and Viruthagiri (2005)

(continued)

Table 10.2 (continued)

S. no.	Adsorption isotherms	Equation	Governing factors	References
5.	Khan isotherm equation [For localized monolayer model]	$Q_e = Q_{\max} \frac{b_T C_e}{\left[1+(b_T C_e)^{\frac{1}{n_T}}\right]^{n_T}}$	• Q_e = absorption capacity by weight at equilibrium • C_e = concentration of adsorbate at equilibrium b_T and n_T = constant	Khan et al. (1997)
6.	Radke–Prausnitz isotherm equation [For high concentration of adsorbate, an extended form of Freundlich isotherm]	$Q_e = a_R b_R \frac{C_e^{\alpha_R}}{K_R + C_e^{\alpha_R - 1}}$	• Q_e = absorption capacity by weight at equilibrium • C_e = concentration of adsorbate at equilibrium a_R, α_R, b_R = constant	Vijayaraghavan et al. (2006)
7.	Dubinin–Radushkevich isotherm equation [Adsorption mechanism with Gaussian energy distribution onto heterogeneous surfaces]	$Q_e = Q_{\mathrm{DR}} \exp\left(-K_{\mathrm{DR}^{\varepsilon^2}}\right)$	• Q_e = absorption capacity by weight at equilibrium • Q_{DR} = Dubinin–Radushkevich constant	Vijayaraghavan et al. (2006)
8.	Dubinin–Radushkevich isotherm equation [Two parameter isotherm for chemi-adsorbption]	$Q_e = Q_{\mathrm{DR}} \exp\left(-K_{\mathrm{DR}^{\varepsilon^2}}\right)$	• Q_e = absorption capacity by weight at equilibrium • Q_{DR} = Dubinin–Radushkevich constant	Tunali et al. (2006), Vijayaraghavan et al. (2006)
9.	Frumkin isotherm equation [Considers interactions between adsorbate molecules]	$\frac{\theta}{1-\theta} \exp(-f\theta) = K_F C_e$	• C_e = concentration of adsorbate at equilibrium • θ = coverage degree of adsorbent surface	Başar (2006)

(continued)

Table 10.2 (continued)

S. no.	Adsorption isotherms	Equation	Governing factors	References
10.	Flory–Huggins isotherm equation [Degree of surface coverage characteristics of the adsorbate on the adsorbent]	$\frac{\theta}{n_{\text{FH}}(1-\theta)^{n_{\text{FH}}}}\exp(-2n_{\text{FH}}\alpha_{\text{FH}}\theta)\theta$ $= K_{\text{FH}}C_e$	• K_{FH} = Flory–Huggins isotherm constant • C_e = concentration of adsorbate at equilibrium n_{FH} = constant α_{FH} = effective constant	Jnr and Spiff (2005)
11.	BET isotherm equation {For multilayer adsorption]	$Q_e = \frac{BCQ^0}{(C_s-C_e)[(1+(B-1)C_e)/C_s]}$	• Q_e = absorption capacity by weight at equilibrium • Q^0 = amount of solute adsorbed per unit weight of adsorbent • C_e = concentration of adsorbate at equilibrium B = constant C_s = saturation concentration of the solute	Preetha and Viruthagiri (2005)
12.	Temkin isotherm equation [Assumes multilayer adsorption, considers interactions between the adsorbent and the adsorbate]	$Q_e = \frac{\text{RT}}{b_t}\text{In}(a_tC_e)$	• Q_e = absorption capacity by weight at equilibrium • R = gas constant • T = absolute temperature • b_t = constant related to the heat adsorption • a_t = Tempkin isotherm constant	Vijayaraghavan et al. (2006)
Adsorption kinetics				
13.	Pseudo-first-order equation	$\frac{\text{d}Q_t}{\text{d}t} = k_1^{'}(Q_e - Q_t)$	• Q_t = the amount of adsorbate adsorbed at time *t* • Q_e = its value at equilibrium $k_1^{'}$ = constant	Febrianto et al. (2009)

(continued)

Table 10.2 (continued)

S. no.	Adsorption isotherms	Equation	Governing factors	References
14.	Pseudo-second-order equation	$\frac{\mathrm{d}Q_t}{\mathrm{d}t} = k_2^{'}(Q_e - Q_t)$	$Q_t =$ the amount of adsorbate adsorbed at time t • $Q_e =$ its value at equilibrium $k_2^{'} =$ constant	Lu et al. (2020)

systematically classified in several ways for study. For example, pore density and size are crucial parameters for the classification of adsorbents. According to the IUPAC depending on the size of pores, they can be microporous (pore diameter < 2 nm), mesoporous (pore diameter between 2 and 50 nm), and macro-porous (pore diameter > 100 nm) (Costa et al. 2020). However, for convenience, we have considered the grounds of relevance in advancements for categorization. Therefore, adsorbents are categorized as conventional sorbents, advanced nano sorbents, and emerging low-cost sorbents.

10.3.1 Conventional Sorbent

The conventional sorbents consist of three categories of sorbents including conventional carbonized materials, ion-exchange resins, and metal–organic framework structures. They make up the pioneer wors in the fields of adsorption.

Carbonized materials:

Derivatives of carbon and carbon in their raw form are one of the most prominent adsorbents used for the adsorption of a wide range of pollutants including heavy metals. This property of carbon results from the structural characteristics of the molecules that give a large surface area, which can be easily modified with different functional groups. The most common carbon sorbent is carbonized materials. The process of carbonization refers to the conversion of a substance into carbon, and it is also referred to as charring or pyrolysis. This is often achieved by heating the designated substance in a controlled inert environment in the temperature range of 200–900 °C, subject to the type of material being carbonized. Depending on the rate of temperature increase, the process can be fast (rate of heating > 2 °C/s) or slow (rate of heating < 2 °C/s). However, both processes intend to increase the percentage of carbon in the material. If the carbonization is done for a biologically derived material, the product is called biochar.

A wide range of materials has been carbonized to derive char including lignocellulosic biomass (Qin et al. 2022), wood (Kim et al. 2020), and rubber tires (Shahrokhi-Shahraki et al. 2021), etc. In some cases, the biochar might be activated with help of oxidizing agents to produce highly active sites on the char. The activation can be done either before charring or after charring by increasing temperature in the presence of oxidizers such as CO_2, steam, air, or their mixture (Ani et al. 2020). A generalized procedure for the development of carbonized biochar has been given in Fig. 10.2.

Ion exchange resin:

The process of ion exchange is a reversible phenomenon that involves the exchange of similarly charged ions between the resin matrix (solid phase) and the bulk solution (aqueous phase). The nature of the resin depends on the abundance of charges on the resin, which come from the functional groups in the resins. These functional groups can be strongly basic groups like sulfonic acid, weakly acidic like carboxylic acid

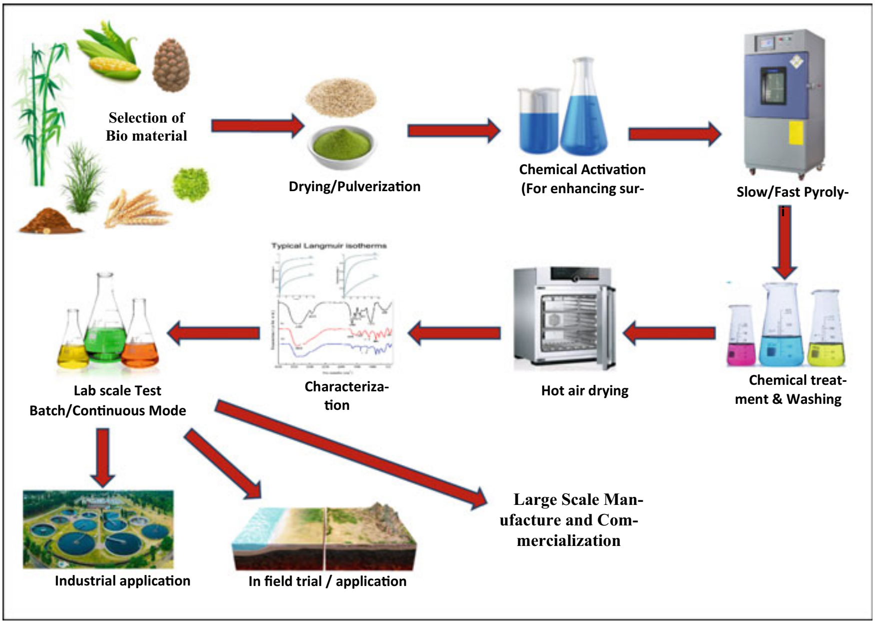

Fig. 10.2 Outflow of the general process for developing carbonized adsorbent materials for the sorption and recovery of heavy metals from the liquid media

groups, strongly basic groups like quaternary amino groups, and weakly basic groups like tertiary amino groups (Botelho Junior et al. 2019). Thus, resins can be acidic, basic, or chelating. Depending on the functional group, the mechanism of action of the resin also changes. For the separation of metal ions from the wastewater, the resins are made into contact with the bulk solution, and metal ions exchange or chelate spontaneously on the resin. After the fixed contact time, the resin can be separated from the bulk solution and eluted for recovery of the metal ions. The process of elution refers to the reinstatement of the original resin ions and their regeneration. The eluting solution varies from acid to basic or other chelating liquid, depending on the nature of the resin.

Bhavna et al. (2010) used m-Cresol-based Chelating Resin for selective adsorption of heavy metals from surrounding and their separation during desorption (Bhavna et al. 2010). Similarly, Nekouei et al. (2019) developed a macro-porous ion-exchange resin for selective adsorption and separation of metal ions (Nekouei et al. 2019). Gámez et al. (2019) used cation exchange resin Purogold MTA 5011 for the separation of Au and Ag by thiosulfate elusion from e-waste leachate (Gámez et al. 2019). They also achieved recovery by electrodeposition of 82% for Au and 94% for Ag recovery on the cathode surface.

10.3.2 Advance Nano Sorbents

The prominent use of nanomaterial in a variety of applications has revolutionized several fields and adsorption is not an exception. The use of nano-derived sorbents has a larger surface area to volume ratio compared to other materials used as sorbents, which imparts them with higher efficiency and a faster rate of adsorption of metal ions (Sadegh et al. 2017). The most commonly used nanomaterials for heavy metal adsorption include carbon nanotubes, graphene, activated nano carbons, manganese oxide, ferric oxide, titanium oxide, magnesium oxide, and zinc oxide nano particles.

Graphene:

This carbon-based material consists of thin or few layers of carbon atoms arranged in a typical poly hexagonal arrangement like graphite. The material is known to have excellent adsorption capacity, especially for cationic pollutants like heavy metals. This property can be attributed to the abundance of pie-electrons on the surface that attract the positively charged molecules. The van der Waals forces are enhanced with the $\pi - \pi$ stacking and interactions with the pollutants (Sadegh et al. 2017). Graphene is a relatively less stable material; however, the stability can be enhanced by modifications. The chemical properties of graphene can also be easily modified for making it efficient for a wide range of adsorbates. This can be achieved by chemical modifications that involve oxidation to form reduced graphene oxide. These graphene oxide nanosheets are known to have excellent adsorption capacity and are also more economical compared to carbon nanotubes (Sadegh et al. 2017).

Carbon nanotubes:

These are one-dimensional (diameter of 1 nm to few nm), nanoscale variants of the carbon material that can be used for heavy metal recovery. The unique dimension of the material imparts it with a very high surface area (Ouni et al. 2019). The carbon nanotubes can be functionalized with different groups to enhance adsorption capacity. Since carbon is nontoxic material, it can be easily applied in the purification of water including drinking water. The mechanism of sorption for the carbon nanotubes involves electrochemical potential, surface trapping, and ion-exchange process (Baby et al. 2019).

Organic polymers:

This group of nanomaterials consists of organic polymeric substances chemically synthesized or functionalized for adsorption. The two most common polymers used for adsorption are nano-cellulose and nano-chitosan. These polymers have an abundance of negatively charged functional groups such as –NH2, –COOH, and –OH that help in adsorption through electrostatic force, complexation, ion exchange, and reduction (Chang et al. 2021). However, these materials have a lower surface area compared to the carbon nanomaterials; thus, composite materials with inorganic particles are often prepared for the enhanced adsorption capacity.

Metal oxide nanoparticles:

The metal oxide nanoparticles are known for their characteristic adsorption photocatalytic properties. Thus, they are used in the treatment of wastewater. The most commonly used metal oxide nanoparticles include TiO_2, Fe_3O_4, ZrO_2, etc. The iron oxide nanoparticles are magnetic; thus, they can be easily separated from the bulk solution. However, these nanoparticles suffer from the disadvantage of the tendency to aggregate over time in the water (Chang et al. 2021). Thus, their stabilization is achieved by linking them to organic polymers, giving rise to a composite material.

Metal–organic frameworks:

These materials are also called porous coordination polymers due to their perforated structures and resemblance with the polymers, besides the rigidity of the inorganic materials and the flexibility of the organic materials (Kitagawa 2014). These materials are three-dimensional self-assembled clusters of metal ions and organic linker molecules, which are often multidentate ligands. The metal–organic frameworks have several advantages over other adsorbents. For example, they have an enormous surface area along with high porosity that helps in adsorption by mechanisms including diffusion. The BET surface area of these composites is considered to be maximum and can reach up to 14,600 m^2g^{-1} (Chang et al. 2021; Kinik et al. 2021). Another advantage is the adjustable pore size by changing the size of the linker molecules, and this can provide selectivity to the adsorption phenomenon by restricting the diffusion of ions based on size. For example, Chen et al. (2018) developed polypyrrole/TiO_2 composite for achieving high selective adsorption for $Zn^{2+} > Pb^{2+} \gg Cu^{2+}$ in a ternary ion system (Chen et al. 2018). These composites can be further chemically modified for specific purposes.

10.3.3 Organic Bio-sorbent

In recent past few years, the use of biological methods for solving environmental concerns has become more popular. The use of microbes including unicellular organisms like bacteria and microalgal cells (Al-Dhabi and Arasu 2022), and multicellular organisms including macroalgae (He and Chen 2014), and fungi mycelium (Wang and Cui 2017) for heavy metal removal has increased significantly. The bio-sorbent materials can also include biomass derived from plant parts (Ugwu and Agunwamba 2020) or polysaccharides from microbes (Blaga et al. 2021). The microbes may also be used in immobilized forms such as in alginate beads for metal adsorption (Velkova et al. 2018).

The mechanism involved in the removal of heavy metals includes both the process of adsorption as well as absorption and the uptake of the metal ions by the live cells of the microbes. However, the process of biotransformation and biomineralization may also contribute to the overall process of the remediation procedure (Ayangbenro and

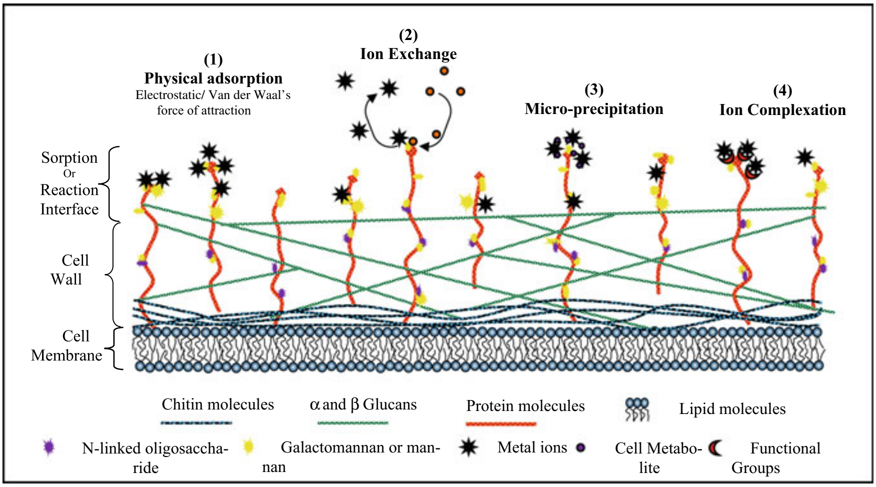

Fig. 10.3 Possible mechanism of interaction between biomass present in biosensor and bulk solution during the pre-concentration step. One or more processes can simultaneously affect the degree of sorption of the cations on the cell wall

Babalola 2017). The process of bioaccumulation, biotransformation, or biomineralization is the active attempt of microbes to reduce the toxicity created by the metal ions in the surrounding. This involves of ATP-driven mechanism of active transport and the kinetics of transformation by the enzymes and proteins.

The mechanism of adsorption on other hand can be seen as a passive strategy of microbes to reduce toxicity for themselves. The microbial cell wall contains active fictional groups that can be involved in metal adsorption. The abundance of the negative charge from groups such as carbonyl and amines widely present in the biomolecules can be a site of attraction for the metal ions. The capacity of a microbe to attract ions will depend on the type and distribution of the functional groups in the cell wall. For example, fungal microbes have more diverse groups and higher density on their cell wall and generally attract more ions on the surface than the bacterial cell; however, the total remediation potential may vary subject to the other mechanisms involved. The mechanisms involved in the adsorption of metal ions on the fungal biomass have been schematically represented in Fig. 10.3.

10.3.4 Low-Cost Sorbents for Heavy Metal Removal and Recovery

The manufacturing, synthesis, or preparation of chemical sorbents can be an expensive task. Even though they can be regenerated and reused, the recycling can only be done a limited number of times, after which removal efficiency gradually declines.

Thus, the need for extremely low-cost sorbent is desirable for large-scale remediation applications. These low-cost sorbents also have a low carbon footprint. In the past decade, several low-cost sorbents have been explored for their potential for the removal of a variety of pollutants including heavy metals. The materials that are considered waste can be easily used as a sorbent for metal recovery. For example, Wang et al. (2022b) used the sugarcane bagasse for sequential recovery of Cu(II), Cr(III), and Zn(II) metal ions electroplating sludge leachate (Wang et al. 2022b). Agriculture waste can be an alternative sorbent material due to its abundance and easy availability (Tsade et al. 2020). Material like low-cost bio-sorbent from spent seedcake of Calophyllum inophyllum (Adenuga et al. 2019), industrial solid waste (Soliman and Moustafa 2020), cement brick waste (Mokokwe and Letshwenyo 2022), phosphor-gypsum (Es-Said et al. 2020), fly ash, and bottom ash derived from the wood pellet-based thermal power plant (Park et al. 2020), pine cones (Amar et al. 2021), groundnut shell (Bayuo et al. 2019), cactus material (Amari et al. 2019), human hair (Zhang et al. 2020), eggshell (Sankaran et al. 2020), dry leaves (Anastopoulos et al. 2019), etc. All these materials are mostly rich in lignin or cellulosic material that has a high negative charge on their surface that have the electrostatic force of attraction for the cationic heavy metals.

10.4 Strategies to Enhance Selective Sorption

The selectivity of a sorbent can be regulated by various parameters depending on the material. A material of biological origin can be subjected to chemical modification or modified using genetic engineering tools for selectivity, whereas materials like graphene and metal–organic frameworks can be structured and engineered for selective adsorption.

10.4.1 Chemical Functionalization of Sorbent

The presence of the functional group, its type, and density on the surface is one of the most important factors that contribute to the adsorption by the electrostatic force of attraction. Thus, adding functional groups to the sorbent not only enhances the adsorption capacity but also imparts selectivity due to the preferred attraction for different ions by different groups. The functional groups can be easily introduced on sorbents by chemical modification. The disulfide or the thiol group can enhance the selectivity of polymeric sorbent for copper and cadmium in presence of calcium (Ko et al. 2017). Disulfide was used as a linker molecule for the monomers, resulting in a polymer that has an adsorption rate 10 times higher than activated carbon. Huang et al. (2020) used phosphoric acid to modify cellulose-rich sugarcane bagasse for developing adsorbents. They observed that the phosphate group promoted the adsorption of lead ions on the surface. Similarly, hydrazine-modified alginate polymers were found to have excellent selectivity for mercury compared to any other metal (Shi et al. 2022). The pretreatment process for the biosorbents like microbes with a specific chemical to introduce desired functional group can also be seen as a strategy to improve the selectivity of the sorbent by increasing the density of the specific functional group (Yang et al. 2015).

10.4.2 Regulation of the Structures

The structures of a sorbent material can be more easily controlled when it is synthesized from a bottom-to-top approach synthesis, like in the case of carbon nanotubes, graphene nanosheets, and metal–organic frameworks. A graphene oxide material if regulated for fold structure (three-dimensional structures) and pore size control can significantly enhance the adsorption capacity and ability to filter out selected metal ions in the adsorption process (Kong et al. 2021). Such material can be easily applied for water filtration application. Wang et al. (2021) found that the structuring of carbon nanotubes into a magnetic absorbent with a multiwalled layer can enhance the selectivity of the material for the removal of Cu and Cd. Sometimes unique structures can be responsible for imparting selective nature to the materials. For example, Bashir et al. (2020) developed dumbbell- and flower-shaped potato starch phosphate polymer for selective adsorption of Zn(II) (Bashir et al. 2020). The metal–organic framework structure can be regulated by changing the length of the polymeric chain or the connecting ligand. This controls the porosity and the ability of the composite to adsorb certain metals over others (Wang et al. 2019).

10.4.3 Genetically Engineered Microbes

The microbes used as bio-sorbent can be engineered for responding to selected metals for bioaccumulation. Since the cellular ports responsible for the inlet of the metal ions being protein are regulated by the genetic material of the organism, the manipulation of the microbial RNA can be used for the regulation of metal ion uptake. In nature, the ports of the cell membrane are mostly nonselective; however, the structural modifications in the protein can alter their selectivity for metal ions. These proteins include metallothioneins, phytochelatins, and other short peptide molecules (Yang et al. 2015). Similarly, the surface proteins of the outer membrane of bacteria can be engineered for having a functional group with a higher charge density (Li and Tao 2015). For example, Valls et al. (2000) engineered outer membrane proteins of Pseudomonas Putida to enhance selective adsorption of mercury cadmium (Valls et al. 2000).

10.5 Desorption and Recovery

As discussed, earlier regeneration and reusability are considered to be essential properties of any successful sorbent use in the field. The regeneration of the adsorbent directly contributes to the economic value of the material and is considered highly desirable for the field application of sorbents. Thus, the procedure and treatment for regeneration or desorption are considered an important stage. The use of chemicals for regeneration, economical cost, and time taken in regeneration is some of the important considerable parameters for any sorbent. There are several methods of desorption that fall under the different categories of chemical treatment discussed below.

10.5.1 Chemical Regeneration

The nature of the reagent used for regeneration will depend on the type of the adsorbent. However, acids including HCl, H_2SO_4, HNO_3, HCOOH, and CH_3COOH are some of the most commonly used desorbing reagents besides the alkalis or the chelating agents (Chatterjee and Abraham 2019). The use of the alkaline solution of sodium hydroxide and sodium bicarbonate is most common for biological sorbents like microbes and cells and some low-cost materials like egg shells (Dev et al. 2022). The use of acid or base relies on the phenomenon of phase transformation in the metallic ions, subject to the change in the external pH of the medium. Another mechanism that may be involved in the desorption process can be changing the ionic strength of the surroundings or using scavenging molecules. In some cases, salt like sodium nitrate and calcium chloride may be used for changing ionic strength or chelating reagents like ethylenediamine-tetra-chloroacetic acid (EDTA) and [S, S]-ethylenediamine-di-succinic acid (EDDS) can be useful for changing adsorbed metal to soluble form again.

10.5.2 Thermal Regeneration

This method of adsorbent regeneration is widely applied for the recovery of mercury from the adsorbent. At higher temperatures, mercury volatilization occurs, which is followed by oxidation (Kuang et al. 2008). The method used for increasing temperature may be physically heating or the use of microwave irradiation. The thermogravimetric analysis can be an important study in determining the effect of temperature on mercury metal desorption.

10.5.3 Electrochemical Regeneration

There are several types of electrochemical recovery such as anodic regeneration, cathodic regeneration, combined regeneration, electro-Fenton regeneration, dielectric barrier discharge plasma regeneration, and peroxide regeneration. (Zhou et al. 2021). Heavy metal regeneration is done by cathodic regeneration. This process involves the desorption induced by the changes in the electrical field. It is most commonly applied to carbon-based materials that have considerable conductivity. On application of negative charge to the sorbent by electrodes, the metal ions are transferred back to the bulk solution (desorbed from the surface), and this may be accompanied by the reduction of the metal from their ionic form to the elemental form. This method of regeneration has the advantage of no requirement for chemicals in the process (Zhou et al. 2021). The method is also known to have a high degree of desorption efficiency and is commonly used in industries (Yasri and Gunasekaran 2017).

10.5.4 Ultrasonication for Regeneration

This process exposes the loaded adsorbent to ultrasonic sound for accelerating desorption. The mechanism involved in the process is the hydrodynamic and thermal effect created due to the sound waves. The ultrasonic sound generates cavitation bubbles in the medium which collapses, releasing energy that increases the localized temperature and pressure, initiating the desorption (Chatterjee and Abraham 2019). Thus, the increase in the intensity of ultrasound increases the rate of recovery. The combination of ultrasonication with other chemical treatments can enhance the process of recovery of materials such as agro waste bio-sorbent (Hegazi 2013).

10.6 Conclusions

This chapter has reviewed the currently available mechanisms for recovery of metals, both of toxic and precious nature from the wastewater samples. A detailed comparison of the advantages and disadvantages of these methods has been presented. The current research in the field of metal removal and recovery leans toward the adsorption-based methods, probably due to the promise of the highly economical and ecofriendly nature of the method. The review of various adsorbents suggests that engineering and chemical methods of synthesizing biosorbents have given us some excellent materials useful for the adsorption of specific heavy metals. However, the materials can be costly and not practically applicable for large-scale field applications of removal. In such conditions, low-cost materials of biological origin or cellulosic or chitosan origin can be helpful. We have also discussed how strategies of structural, chemical, and genetic engineering can impart selectivity to sorbents. But further research still needs to focus on improving the selectivity of the low-cost sorbent.

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Chapter 11
Bioelectrochemical Systems for Advanced Treatment and Recovery of Persistent Metals in the Water System: Mechanism, Opportunities, and Challenges

Nishant Pandey, Ankur Singh, and Vipin Kumar

Abstract Despite extremely low concentrations in the earth's crust, heavy metals are recognized as one of the biggest causes of water resource contamination. The persistent nature of these metals accompanied by their cytotoxicity leads to their accumulation and gradual increase in chronic toxicity in higher aquatic organisms. Our crucial dependence on these elements in day-to-day life leaves us with no choice but to prevent the entrance of these metal ions into the environment by treatment of anthropogenic discharges. The process of treatment is slow and requires extra capital investments; hence, the pursuit of economical and sustainable methods is always on. In the past few decades, the field of the bioelectrochemical system has flourished and successfully demonstrated that not only does it have the potential to treat a variety of contaminants but also acts as a source of green energy, courtesy to the electrogenic microbes. This book chapter explores the advances in the field of bioelectrochemical systems for the removal of metallic ions from different water media, with special reference to the mechanisms involved in the process. The current, persisting challenges in the field will be reviewed along with possible opportunities and approaches to enhance the treatment efficiencies of the system, making it more economical and sustainable.

Keywords Bioelectrochemical systems · Electrogenic microbes · Heavy metals · Cathodic reduction

11.1 Introduction

Metal extraction is a chief requirement for infrastructure development that remains the backbone of the economic development of any country. Metals are mainly

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consumed in the production of various electrical appliances, construction frameworks, and other engineering goods. The metal processing industries during different procedures generate waste, which is metalliferous and can contaminate the nearby soil and water source if not properly managed. Modern human society is facing environmental pollution as a major challenge due to rapid industrialization and urbanization. Among the pollutants, in the environment, heavy metals are considered an important agent as they have the property of being persistent in the environment and are also considered toxic at deficient concentrations. The bio-accumulative nature of these metals develops a hazardous impact on the flora and fauna present in the surroundings (Ali et al. 2019). The major sources of dispersion of these persistent pollutants come from the transport, effluents from the industries, organic wastes, and power generation (Mahurpawar 2015), which are rich in heavy metals like Arsenic (As), cadmium (Cd), mercury (Hg), copper (Cu), and chromium (Cr). These metals are mainly discharged by the industries in the form of wastewater into the natural streams. However, if this wastewater is subjected to advanced technologies for treatment, the metals can be recovered, recycled, and reused as a resource in the industries.

The various methods that can be used in metal recovery from industrial wastewater include the chemical treatment method, biological sorption method, electrochemical method, and physical methods (Shrestha et al. 2021). Some of these methods like chemical treatment can be expensive, for example, electrochemical and chemical treatment while others can be time taking like biological treatment methods. In the recent past decade, bioelectrochemical systems (BES) have emerged as a promising technology to overcome these drawbacks. The BES are considered as hybrid technology of biological systems with the electrochemical system. These systems are considered energy efficient and ecofriendly due to their capability of generation of electricity (microbial fuel cell configuration) or require very low amount of voltage supply (microbial electrolytic cells.) (Singh and Kumar 2022). Both of these configurations are used for metal recovery depending on the reduction potential of the metals. The BES systems are capable of metal recovery along with the generation of energy (Tao et al. 2014) and other resources like hydrogen (Luo et al. 2014) from waste-containing organics. This chapter focuses on the discussions involving different types and application of the BES, the mechanisms involved in various processes, and the advances in the metal recovery systems and their construction.

11.2 Bioelectrochemical Systems: A Gift of Exo-electrogenic Microbes

BES are advanced technology of the recent development that produces electric power with the help of microorganisms by harvesting the chemical energy from bio-organic material and has also expanded its application to wastewater treatment. Apart from this, BES can also be used for efficient and clean production of fuels and high-value

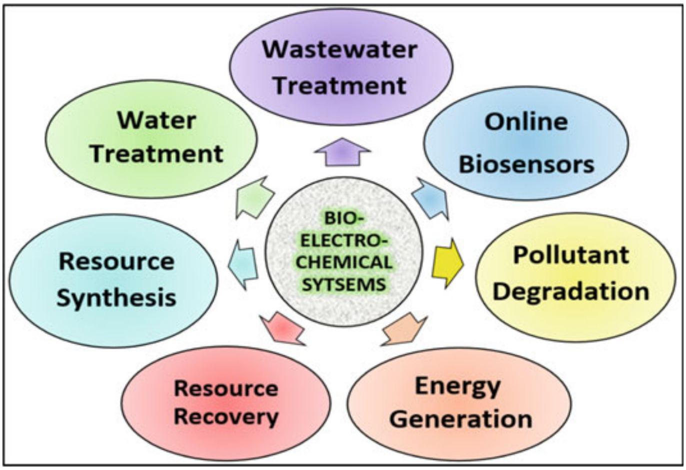

Fig. 11.1 Multi-faced application of bioelectrochemical system for environmental and energy application

chemicals using microorganisms, making them a sustainable innovation. BES find various applications in tackling various environmental challenges (Fig. 11.1). The discovery of exo-electrogenic microbes has made the BES possible.

While looking into its historical background, Galvani in 1789 used a biological medium to produce electricity. The frog muscles, which were in contact with copper and zinc wires, got twitched (Galvani 1954). This phenomenon was considered the beginning of the production of energy by the biological medium (Cohen 1931) by making use of microorganism electrode reduction was reported by M.C. Potter in 1911. It is an integration of the microbial system, electrochemistry, biotechnology, and material science. The mechanism of these electrochemical systems is the creation of potential difference by the redox potentials of an oxidation reaction at the anode and a reduction reaction at the cathode, which is the driving force for the flow of electrons from low potential to high potential. Electric current is measured through the flow of electrons in the external circuit. The degradation of organic substrates by the microbes leads to the production of protons in an anodic chamber. The protons are needed to be transported to the cathode chamber via a cation exchange membrane to avoid acidification of the anode compartment. It is considered a sustainable and renewable technology with a multidisciplinary approach. In comparison with the conventional electrochemical system, the operating conditions for BES are mild and simple. Conventional systems require precious metals as a catalyst, while BES operations rarely need them. BES have emerged as a bioreactor for the efficient removal of toxic pollutants and heavy metals such as Ni, Cu, and Cd from wastewater and can recover metal for reuse and recycling in industry. Cu in the waste stream can be recovered at the cathode in its metallic form, and the anode side will provide energy for the metal reduction by oxidizing the organic carbon (Heijne et al. 2010). Tandulkar et al. (2009) mentioned a similar mechanism for Cr (III) recovery. The soluble metal ion in the wastewater stream is converted into insoluble or less soluble oxide or metal complex by bacterial respiration.

11.2.1 Microbial Fuel Cells [MFCs]

MFCs are designed to derive electric current from organic matter by microbial oxidation using a solid electrode as an electron acceptor. The microbes are attached to the anode surface of MFCs and electrons are generated by the oxidation of organic matter, which are further transferred via an external circuit to the cathode compartment. The development of biofilms of electroactive bacteria on the anode compartment functions in the generation of electricity. The generation of electricity in MFC is directly proportional to the liberation of electrons by the exo-electrogens [microbes generating electricity] from the organic substrate through its oxidation. The stable reduction products are formed on the cathode surface by a reaction between electrons, protons, and oxidants. Bioanodes with mixed cultures of bacteria have witnessed higher and more stable currents rather than with pure culture. Different types of membranes are installed in between the anode and cathode chamber depending upon the pollutants which are to be degraded. The functional groups which are negatively charged are linked to the cation exchange membrane (CEM) that induces the transfer of cations. In an anion exchange membrane (AEM), anions are transported due to the presence of a positively charged functional group in the membrane (Dhar and Lee 2013).

11.2.2 Microbial Electrolysis Cells [MECs]

MECs use bacteria to convert chemical energy to electrical energy and electrolysis of water also occurs. Electron movement is accelerated from cathode to anode by the application of an external circuit. Apart from MFCs, the anaerobic condition is maintained in the cathode compartment, which facilitates the production of hydrogen. In comparison with MFCs, high voltage is observed in MECs due to the supply of additional voltage. In addition to this, the generation of hydrogen in MECs can initiate the biochemical production of other chemicals. Lu and Ren (2016) reported that the efficiency of the production of hydrogen in MECs is quite higher than the electrolysis of water and fermentation process (Lu and Ren 2016). In MECs, the pollutants are degraded by electrogenesis bacteria into electrons, protons, and carbon dioxide. The most used terminal electron acceptor in MFCs is oxygen while in MECs the electron acceptors are mainly protons in H_2- produced. Different types of MECs are introduced in the laboratory studied which include dual-chamber MECs, single-chamber MECs, multi-electrode MECs, and tubular MECs.

11.2.3 Microbial Electrosynthesis [MES]

MES is the emerging perspective of BES, which produces value-added products at the cathode by utilizing the reducing power generated at the anode by oxidation. Cathodic surface with attached biofilms produces value-added products by reducing the availability of terminal electron acceptors (Ivanov et al. 2010). The key component of MES is the biocathode where the presence of electrode oxidizing microbes helps in the formation of reduced value-added products such as ethanol and acetate. It is mainly an electrochemical cell that produces chemical compounds by electricity-driven CO_2 reduction and also uses microbes as a biocatalyst for the reduction/oxidation of other organic compounds. Depending on the selection of biocatalysts, the microbial electrosynthesis process can be highly specific. In organic products having covalent bonds, MES acts as an alternative process to capture electrical energy.

11.2.4 Enzymatic Fuel Cells [EFCs]

Enzymatic fuel cells [EFCs] facilitate specific reactions for various applications by making use of specific enzymes on the surface of the electrode that drives the catalytic oxidation of fuel. The use of highly selective enzymes at the cathode and anode eliminates the need for any membrane layer between the compartments of the cathode and anode. In comparison with conventional fuel cells, mild conditions (ambient temperature, neutral pH) are required for reactions to occur in EFCs due to specific enzyme presence. Cell voltage and currents combine to form the power output of the cell. Due to the production of catalysts of a wide range, these cells are highly versatile to oxidize or reduce different kinds of substrates under optimal conditions. EFCs are more profitable and advantageous in comparison with conventional noble metal catalysts. In regards to transition metal catalysts which are available in a limited number, biocatalysts are cost-effective and have long durability. Due to the wide utilization of biocatalysts in the complex fuel, they are more divergent in respect to conventional fuel cells, which have poor chemistry of fuels (Ivanov et al. 2010).

11.2.5 Microbial Solar Cells [MSCs]

MSCs entrap solar energy with the help of photoautotrophic microbes or higher plants, which are further used to perform electrode-driven reactions by utilizing electroactive bacteria. This biotechnological system is the combination of photosynthetic and electrochemically active microorganisms, which on reaction generates compounds like methane, hydrogen, ethanol, or electric current. Sunlight is used by photosynthetic organisms such as microalgae, cyanobacteria, or macroalgae to produce organic matter in an MSC that is further converted to electricity (Marshall et al. 2012). Schamphelaire et al. (2008) reported plant MFC which is a type of MSC, which uses its root to deliver organic matter in MFC to electrochemically active bacteria (Schamphelaire et al. 2008). MSC principles have been used in the treatment of algal blooms in the lake. The benefits of this system include CO_2 sequestration and the conversion of light to electricity directly.

11.3 Mechanism of BES

The most important compartment in a living system is the microbial electron transport chain because the main energy source of living microbial cells is obtained by oxidation of degradable organic substrates (Wesolowski et al. 2008). Katuri et al. (2012) stated that in BES, the process of electron transfer from living microorganisms toward electrodes is exploited or is considered as the diagnostic tool for rapid assessment of microbial activity (Katuri et al. 2012). Substrate present in the anode section is broken down by microbial species by the process of fermentation which produces electrons (e^-) and proton (H^+). The migration of proton ions occurs toward the cathode compartment via ion selective membrane. In the primary operation of BES, there is direct extracellular electron transfer [EET] from the cell to the acceptor or indirectly mediated by electron shuttles. Electron transfer from living cells to the electrode surface is mainly regulated by anodic respiration in the absence of oxygen, which is the final electron acceptor. The principal mechanism to operate BES is the combination of the interaction of microbes, anodic respiration, and intracellular redox reactions. The generation of electric current in the BES system is correlated with the number of viable microbial cells present in it. There are two important mechanisms of the physical transfer of biologically liberated electrons to the electrode surface, direct electron transfer and indirect electron transfer (Fig. 11.2b).

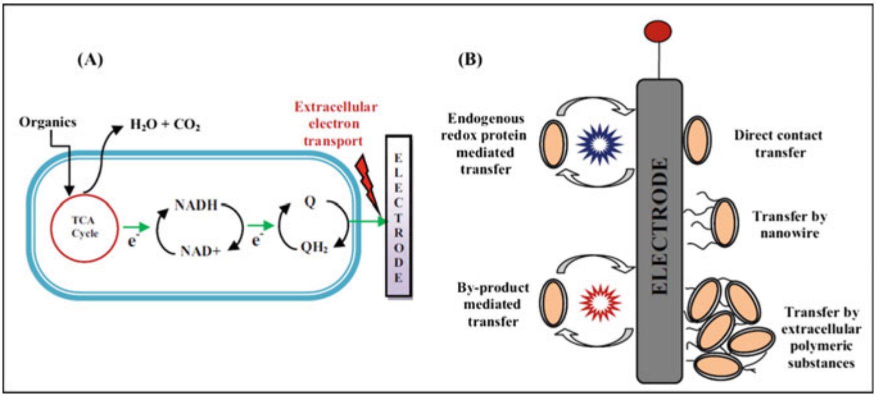

Fig. 11.2 Intracellular (**a**) and extracellular (**b**) electron transport mechanism in the exoelectrogenic microbes. With permission from Singh and Kumar (2022)

11.3.1 Direct Electron Transfer [DET]

Some of the microbial species, which are electroactive also known as exo-electrogens, can transfer electrons extracellularly to conductive materials directly without the help of mediators. Busalmen et al. (2008) stated that before the transfer of electrons to the electron acceptor surface (EET) the pathway for the transfer of electrons occurs from the c-type protein, which is an inner membrane protein to the periplasmic protein (Busalmen et al. 2008). The growth of microorganisms is encouraged by this process. During the process, before the transfer of electrons to the cathode there is the development of a biofilm on the surface of the electron acceptor electrode which provides extra energy. Choi and Sang stated that the transfer of electrons mainly arises from an area that has a low redox probability to an area of high redox probability (Choi and Sang 2016). Pirbadian et al. (2014) examined that in Shewanella oneidensis, bacterial nanowires were created to facilitate extracellular electron transfer (Pirbadian et al. 2014). Sure et al. (2016) indicated that nanowires include a different combination of outer membrane protein, periplasmic protein, and cytochromes of different types (Sure et al. 2016). Electron transfer was also seen by the electroactive metabolite secretion in the extracellular matrix (Wu et al. 2014). According to Yi et al. (2009), by applying selective pressure to exo-electrogenic microbes, the EET mechanism can be enhanced toward the anode by increasing the nanowires (Yi et al. 2009). In marine and freshwater sediments, cable bacteria are found, which are filamentous multicellular and can transfer electrons for a few centimeters distance (Bjerg et al. 2018).

11.3.2 Mediated Electron Transfer [MET]

Electrochemically inactive microorganisms, which are incapable of transferring electrons to the electrode surface directly, required exogenous electron shuttles to transfer electrons by a process called mediated electron transfer. Due to the hiding of electrochemically active groups, which are responsible for redox reactions within the prosthetic groups, the interaction between the surface of the electrode and the cell gets affected. Bacterial cells transfer the electrons to the redox mediator which leaves them in a reduced state and is transferred to the anode. Redox mediators are oxidized and can transfer electrons. According to Ieropoulos et al. (2005), the mediator can mediate electrons when they can easily cross the bacterial cell membrane, should be non-toxic to bacteria, and able to transport electrons by having positive redox potential (Ieropoulos et al. 2005). There are mainly two kinds of redox mediators: (1) endogenous (bacteria produce themselves); and (2) exogenous (compounds added externally). The groups of bacteria include species of *Streptococcus lactis*, *Proteus Vulgaris*, and *Escherichia coli.*

11.3.3 Reactions at Cathode and Anode

The disintegration of the substrate in the anode compartment by the action of microorganisms leads to the liberation of electrons. These electrons are transported via a transport chain from an electron donor of low potential to an electron acceptor of high potential to the cathode. The membrane-bound compounds catalyze the reaction and an ion gradient is developed around the membrane. In the anode compartment, there is the production of electrons and protons due to oxidation reaction. Equations (11.1) and (11.2) provide an example of the oxidative reaction of glucose and acetate at the anode.

$$\mathrm{CH_3COO^- + 4H_2O \rightarrow 2HCO_3^- + 9H^+ + 8e^-} \tag{11.1}$$

$$\mathrm{C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 24H^+ + 24e^-} \tag{11.2}$$

The reduction reaction occurs in the cathode compartment. Electrode present in the cathode acts as an electron acceptor. The proton generated in the anodic chamber is migrated to the cathode chamber via the proton exchange membrane. Equations (11.3) and (11.4) represent the reactions at the cathode.

$$\mathrm{4e^- + 4H^+ + O_2 \rightarrow 2H_2O} \tag{11.3}$$

$$\mathrm{2H^+ + 2e^- \rightarrow H_2} \tag{11.4}$$

Due to the generation of different charges between the cathode (+) and anode (−), the cell voltage is developed, which helps in electron flow. Equations (11.5) and (11.6) summarize the redox reactions occurring at the cathode and anode.

$$\mathrm{C_6H_{12}O_6 + 6H_2O = 6CO_2 + 24H^+ + 24e^-} \quad \text{Anode} \tag{11.5}$$

$$\mathrm{24H^+ + 24e^- + 6CO_2 = 12H_2O} \quad \text{Cathode} \tag{11.6}$$

11.3.4 Factors Affecting the Performance of BES

The components of BES such as cathode, anode, electrolyte, membrane material, the volume of the reactor, and spacing between the electrodes play an important role in the performance and maintaining its functioning. Ghangrekar and Shinde (2007) evaluated the performance of the membrane-less MFC (MLFC) and the effect of the distance of the electrode (Ghangrekar and Shinde 2007). The BOD removal in MLFC was found to be 87% and 10.13Mw/m^2 of maximum power density was observed after lowering the electrode spacing. According to Rinaldi et al. (2008), the limitations in a single unit of voltage and power could be overcome by stacking the MFC (Rinaldi et al. 2008). Electron donors also determine MFCs performance and their biodiversity (Chae et al. 2009). Zhang et al. (2009) stated that the separator is a key component as it reduces the distance between the electrodes in the MFC and enhances the generation of power (Zhang et al. 2009). The application of Graphene-modified stainless-steel mesh as an anode material increases the power output as it improves the ability of electron transfer and microbe adhesion on the anodic surface (Zhang et al. 2011). The sulfonated and porous uncharged membrane was used as an alternative to the nafion membrane (Kim et al. 2014), results indicate that the former membrane was having low internal resistance and high ion exchange capacity in comparison with Nafion. Corbella et al. (2016) analyzed fuel cell performance by positioning the cathode close to the water contact in constructed wetlands (Corbella et al. 2016). Cathodes were replaced by TiO_2 nanotubes, which were both amorphous and crystalline (Yahia et al. 2016) for the treatment of wastewater and production of bioelectricity. The performance of the MFCs was enhanced with maximum COD removal and power generation. Imran et al. (2019) modified the electrode surface by coating it with cerium. In comparison with the uncoated surface, the former showed lower internal resistance with better biofilm formation and 5.8 times more power density generation (Imran et al. 2019). Apart from this, the performance of MFC is mostly governed by the physical and chemical parameters such as materials of electrode and catalyst, the concentration of substrate, pH, design of the reactor, and temperature (Kondaveeti et al. 2018). Bhowmick et al. (2019) fabricated MFCs with a different load of Rhodium combined with activated carbon and used as a cathode catalyst (Bhowmick et al. 2019). The efficiency of the treatment of wastewater was observed to be enhanced.

11.4 Metal Recovery Using BES

Apart from the generation of bioelectricity and wastewater treatment, BES has also been used in the recovery of metals especially copper from the mining wastewater effluents. These heavy metals, which are present in very low concentrations, are removed effectively with BES and are considered as an alternative process that is economically viable. Li et al. (2017) studied the MFC-MEC for sustainable treatment and recovering heavy metals such as Cu, Cd, and Cr with a fixed initial concentration of 5 mg/l (Li et al. 2017). MEC showed complete recovery with the generation of electricity simultaneously. A hybrid system was designed by Tao et al. (2014) in which Cu (II) was reduced to Cu2O at the cathode, and recovery of Zn and Pb was done by electrolysis (Tao et al. 2014). Removal of Zn, Cu, and Pb was found to be 95.4%, 98.5%, and 98.1%, respectively. Reduction of copper occurs at the cathode using bioelectrochemical acetate oxidation at the anode. Other metals such as vanadium and chromium can be recovered from the wastewater containing these metals by using dual-chambered MFCs.

An osmotic microbial fuel cell was installed by Cao et al. (2021) for the removal of hexavalent chromium [Cr (VI)] and the production of energy (Cao et al. 2021). This fuel cell mainly removes contaminants through an oxidation–reduction reaction. At the initial pH of 2, about 97.6% of Cr (VI) reduction was observed with the power generation of 76.07 Mw/m^3. Luo et al. (2014) conducted an experiment to remove metal from acid mine drainage by utilizing the microbial electrolysis cell (MEC) (Luo et al. 2014). Under the condition of single and mixed metal conditions, Cu^{+2}, Ni^{+2} and Fe^{+2} were reported to be removed. In a single operation, the removal efficiency of Cu^{+2}, Ni^{+2} and Fe^{+2} was found in the range of 99.2 ± 0.1%, 97 ± 1.3%, and 97 ± 1.8%, respectively. In the observation of the mixed metal sample, the recovery reached the highest efficiency of 89%. A stacked Bioelectrochemical system model was constructed by Huang et al. (2017) for efficient recovery of W (VI) and Mo (VI) which includes a combination of microbial electrolysis cells (MECs) and microbial fuel cells (MFCs) (Huang et al. 2017). One MEC unit in the stacked system was connected serially with three parallel MFC units. The deposition of W and Mo was 27.6 ± 1.2% and 75.4 ± 2.1%, respectively. A high concentration of heavy toxic metals is usually present in smelting wastewater with a high degree of acidity. The treatment of smelting wastewater was conducted by Ai et al. (2020) by coupling a thermoelectric generator with BES. Efficient recovery of Cu^{+2}, Cd^{+2} and Co^{+2} occurred from the organic wastewater and about 99.97 ± 0.004% Cu^{+2} was recovered selectively from wastewater (Ai et al. 2020).

BES technology has been proven efficient in the reduction or degradation of various chemical constituents or heavy metals, which are of high health risk to human beings and the environment. The azo dyes, which are widely used in the textile, leather, and cosmetic industry, are a serious threat to the environment because of their toxicity. The available treatment technologies such as ozonation, photodegradation, and membrane process are quite expensive. BES employed to decolorize the dye has been successfully proven. Organochlorines are another set of pollutants in the environment. They are mainly organic compounds consisting of at least one chlorine atom. A major source of these compounds is bleaching agents, industrial chlorinated solvents, and pesticides. The removal of these chemicals by BES includes the anaerobic bacteria, which dechlorinate the chlorinated aliphatic hydrocarbons in groundwater by utilizing them as a terminal electron acceptor for microbial respiration. MFCs are shown to reduce Cr (VI) which is highly toxic to less toxic, less soluble Cr (III) at its cathode site by providing an acidic and anaerobic environment. This technique also provides a sustainable power supply.

11.4.1 Metal Recovery Using Fuel Cell Configuration

Fuel cell configuration produces electricity with the help of chemical reactions which are abiotic in the absence of any combustion process. With innovations in fuel cell research, the microbial fuel cell has emerged as a prominent and widely used technology in different application processes. The most sustainable use of MFC is the production of bioelectricity with the assistance of microbes (Santoro et al. 2017). In addition to electricity production, MFC is expanding its importance in the area of metal recovery. As some metals are considered as pollutant in the environment due to their toxic and bioaccumulate nature, remediation or treatment is a necessary step. Apart from their hazardous properties, they are also considered beneficial for any country's economy due to their applications in infrastructure and manufacturing goods. Researchers are applying this technique in the recovery of different metals from contaminated sites. Heijne et al. (2010) recovered copper with a removal efficiency of 99.88% from the waste streams (Heijne et al. 2010). Complete recovery was obtained of mixed Sn (II), Fe (II), and Cu (II) catholyte effluent (Song et al. 2019). MFC was developed to recover silver (Ag) metal from the wastewater containing silver ions with a recovery efficiency of 99.91% (Choi and Cui 2012). Removal of toxic metals V and Cr with reduction efficiency of 67.9 ± 3.1% and 75.4 ± 1.9%, respectively, was done by employing MFC from the wastewater containing Vanadium (Zhang et al. 2012). Coupling of Cr (VI)-MFC and Cd (II) was performed to recover Cd (Choi and Cui 2012). Lim et al. (2021) experimented with the removal and recovery of Zn from industrial wastewater (Lim et al. 2021). Results were promising as the removal efficiency of Zn from synthetic and industrial samples was noted to be 96%. Plant MFC which is considered as a cost-effective sustainable technology was employed in Cr-contaminated water. The removal efficiency was greater than 90% (Habibul et al. 2016). Single-chamber air–cathode MFC was developed to determine the removal efficiency of Cd and Zn. Individual treatment of Cd and Zn resulted in 90% and 97% recovery with simultaneous generation of high power (Abourached et al. 2014). Singh and Kaushik (2021) introduced inoculum from the wetland in both anode and cathode for the treatment of Ni and Cd. Biocathode use enhanced the metal removal from 30–70% (Singh and Kaushik 2021). Aiyer (2020) employed dual-chambered MFC for recovering Cu (II), V(V), and Cr (VI) into less toxic forms, i.e., Cu, V(IV), and Cr (III) (Aiyer 2020). Cao et al. (2021) introduced osmotic dual-chambered MFC for Cr recovery with a removal efficiency of 97.6% (Cao et al. 2021) (Fig. 11.3).

11.4.2 Metal Recovery Using Electrolytic Cell Configuration

A microbial electrolytic cell is a type of bioelectrochemical system, which requires an external power source for the generation of electrons to the electrode surface. In recent times, it has been preferred over MFCs not only for wastewater treatment but also for the generation of value-added products of high yield, recovery of metals, and coupling with another bioelectrochemical system to form a hybrid system. In terms of metal recovery, MECs are employed for enhanced recovery of metals from contaminated wastewater. Jiang et al. (2014) demonstrated the dual-chambered MEC for the recovery of Co (Jiang et al. 2014). The recovery was found to be in the range of 22.5 ± 0.1 to 43.2 ± 0.7%. Luo et al. (2014) employed MEC to recover Cu, Ni, and Fe from the acid mine drainage (Luo et al. 2014). The removal rate

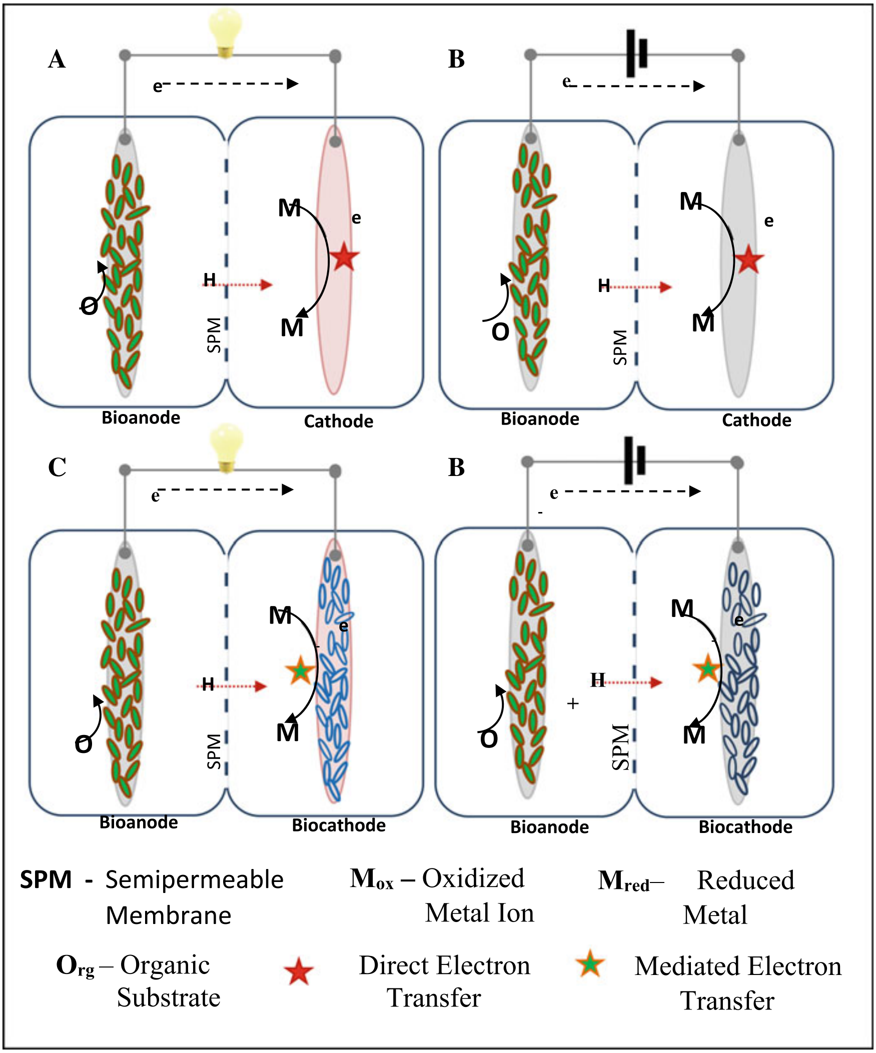

Fig. 11.3 Different configurations of the microbial electrochemical systems for recovery of metal ions: **a** and **c** are systems with microbial fuel cell configuration, **c** and **d** are systems with microbial electrolytic cell configuration. Metal recovery using electrolytic configuration

was obtained to be 89%. Recovery of Zn was conducted in a MEC using an acidic catholyte (Modin et al. 2017). MEC with biocathode was used to achieve enhanced removal of Cd from the contaminated sites (Chen et al. 2016). A hybrid system was constructed (Li et al. 2017) with a combination of the MFC-MEC system for the efficient recovery of Cr, Cu, and Cd. The recovery of these metals from the contaminated water was found to be Cr (81.6 ± 1.2%), Cu (73.8 ± 1.2%), and Cd (74.3 ± 1.4%). Another hybrid system was introduced with the combination of MEC coupled with thermoelectric generators for the treatment of Cu, Cd, and Co from the smelting wastewater which is highly acidic with high concentrations of toxic metals in it. Metal recovery efficiency of different fuel cell combinations is shown in Table 11.1. Waste heat was efficiently utilized with the help of these generators to recover these metals (Ai et al. 2020). Antimony (Sb) recovered from the dual-chambered MEC with a recovery efficiency of 96.3%. Hybrid systems are more preferred over individual cells as they are found promising in terms of multiple metals recovery with enhanced recovery rate. MFC-MEC was coupled to recover Cu, Ni, and Fe from the acid mine drainage. The recovery efficiency was found to be Cu (99.9%), Ni (77%), and Fe (60%) (Leon-Fernandez et al. 2021).

11.5 Emerging Challenges in BES

BES is considered as a recent innovative technology in the field of bioelectricity production, metal recovery, and treatment of wastewater. Despite its multidisciplinary approach, certain fields need further research to overcome certain challenges. Although BES has emerged as a sustainable and energy-efficient technology, it has mostly remained on a lab scale or as a demonstration project. According to Zhang et al. (2016), the initiatives to scale up the bioelectrochemical technologies were impacted negatively by the low efficiency of cell to reduce pollution and the rate of production was minimal (Zhang and Tremblay 2016). Cheng and Logan (2011) studied the role and efficiencies of different substrates employed in the application in BES and found variation in the output due to nutrient availability for the microbes (Cheng and Logan 2011). The use of enzyme-selective microbes in reducing the particular compound is another challenge. Shehzad et al. (2016) examined the use of landfill leachate and wastewater as a substrate in BES (Shehzad et al. 2016). These substrates are however toxic and are of high-risk factor to human health and the environment. Due to the low concentration of many metals in wastewater, metal recovery from leachate is quite challenging (Iskander et al. 2016). Electrode material used in BES should possess qualities such as large surface area, high conductivity, chemical stability, and mechanical strength. However, materials with such qualities as graphite and platinum are expensive and it limits the economic practice of the process. The performance of BES differs in terms of the application of different types of membranes due to their certain limitations. Nafion, a type of CEM, is permeable to oxygen and substrate (acetate), by which the performance of MFC could be affected (Chae et al. 2008). According to Harnisch et al. (2008) in MFCs due to large leakage, Bi-polar membrane is unable to prevent pH gradient and has poor performance among other ion exchange membranes (Harnisch et al. 2008). The study of BES involves the employment of various reactor configurations and different conditions to operate, which include electrode type, type of substrate, and pH adjustment making it difficult to evaluate the functions of the membrane (Yang et al. 2020). High complex pollutants such as monoaromatic compounds (MACs) are of great challenge to be degraded by BES (Li et al. 2020). High background nutrient concentrations

Table 11.1 Comparison of metal recovery efficiency of various bioelectrochemical systems

S. no.	Type of reactor	Metal recovered	Anode	Cathode	Membrane	Recovery efficiency	References
1.	Dual-chambered MFC	Cu, Zn, Pb	Graphite felts	Graphite plate	PEM	Zn (95.4%) Cu (98.5%) Pb (98.1%)	Tao et al. (2014)
2.	Dual-chambered MEC	Co	Graphite brush	Graphite felt	CME	22.5 ± 0.1–43.2 ± 0.7%	Jiang et al. (2014)
3.	Dual-chambered MEC	Cu, Ni, Fe	Graphite brush	Carbon cloth with Pt catalyst	BPM	89%	Luo et al. (2014)
4.	MFC-MEC hybrid system	Cr, Cu, Cd	Graphite felt	Carbon rod, titanium sheet	CME	Cr (81.6 ± 1.2%) Cu (73.8 ± 1.2%) Cd (74.3 ± 1.4%)	Li et al. (2017)
5.	Dual-chambered stacked MFC	W, Mo	Graphite felt	Stainless-steel sheets	CME	W (27.6 ± 1.2%) Mo (75.4 ± 2.1%)	Huang et al. (2017)
6.	BES-electrode position cell	Pb, Zn	Carbon brush	Graphite rod	AME	Pb (98.5 ± 1.4%) Zn (98.7 ± 0.7%)	Zhang et al. (2020)
7.	Dual-chambered MFC	Se	Graphite	Graphite	PME	73.6%	Sravan et al. (2020)
8.	Dual-chambered MFC	Cr	Graphite fiber brushes	Titanium wires	PEM, CEM, AEM	99.93 ± 0.63%	Yu et al. (2020)
9.	Dual-chambered osmotic MFC	Cr	Carbon cloth	Carbon cloth	Nafion	97.6%	Cao et al. (2021)
10.	MEC coupled with thermoelectric generator	Cu, Cd, Co	Carbon brush	Carbon cloth	AME	Cu (99.97 ± 0.004%)	Ai et al. (2020)
11.	Combination of MFC-MEC	Cu, Ni, Fe	Carbon felt	Copper electrode	BPM	Cu (99.9%) Ni (77%) Fe (60%)	Leon-Fernandez et al. (2021)

(continued)

Table 11.1 (continued)

S. no.	Type of reactor	Metal recovered	Anode	Cathode	Membrane	Recovery efficiency	References
12.	Dual-chambered MEC	Sb	Carbon felt	Carbon felt	PME	96.3%	Arulmani et al. (2021)

Abbreviations: AEM: Anion Exchange Membrane, PEM: Proton Exchange Membrane, CME: Cation Exchange Membrane, BPM: Bi-polar Membrane such as SO_4^{-2} and NO_3^- inhibit biological efficiency of MACs which further compete with anode for electron donors and reduce the generation of electricity by BES.

11.6 Conclusion

This book chapter has provided a brief review of an emerging technology, microbial electrochemical systems, and its principles of operations. We have discussed the scope of application of the BES technology for assisting various environmental solutions. However, the focus has remained on the metal recovery opportunities from wastewater from industrial wastewater. The use of microbial fuel cells and microbial electrolytic cells has been revived for their efficiencies for metal recovery of different metals from their dissolved ionic form in effluents. Apart from metal recovery, BES technology has been proven in the reduction or degradation of various chemical constituents. Organochlorines are set of pollutants in the environment. They are mainly organic compounds consisting at least one chlorine atom. Major source of these compounds is bleaching agents, industrial chlorinated solvents, and pesticides. The removal of these chemicals by BES includes the anaerobic bacteria which dechlorinate the chlorinated aliphatic hydrocarbons in groundwater by utilizing them as terminal electron acceptor for microbial respiration. (Li et al. 2020) introduced the microbial electrolysis desalination cell (MEDC) for nutrient recovery from municipal wastewater apart from removal of saline and organic matter. The BES technology is still an emerging technology and is most studied under laboratory conditions. However, some scale-ups have demonstrated the possible applicability of the system at a larger scale. The scaling-up of systems will have to face several challenges as discussed in the previous section, which will need rigorous studies and significant technological development in the field. Nevertheless, the BES remains a promising technology for tackling the problem of the energy crisis and simultaneously treatment of wastewater. The future perspective of BES includes the synthesis of different chemicals such as acetate, peroxide, and reduction of complex inorganic chemicals. The BES can be fabricated to enhance its power generation and improve its remediation ability.

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Chapter 12
Fate and Transport of Chromium Contaminant in Environment

Abhinav Raj and Alok Sinha

Abstract Chromium is a pervasive contaminant that is widely used in a number of industries. The two main form of chromium found in nature are Cr(III), or trivalent chromium, and Cr(VI), or hexavalent chromium, in which Cr(VI) is a carcinogen in nature. Human exposure to a chromium contaminant can come from both natural and industrial sources of chromium. Mathematical models are used to understand how biotic and abiotic reactions influence the fate and transport of chromium contamination. Models are created with the understanding that a variety of biochemical processes, including reduction/oxidation, sorption/desorption, precipitation/dissolution, and the formation of complex ions, as well as physical migration processes, like advection, dispersion, and diffusion, can directly or indirectly affect the fate of trace metals. In addition, chromium contamination can take place in air, water, and soil. So mathematical model will be applied for air, water, and soil combined as movement of contaminant in soil and water may be interrelated and also trace metals will follows the principle of fluid dynamic in water and air. A mathematical model consists of a set of differential equations that are known to regulate the pathway of trace metals. The reliability of predictions using the mathematical model depends on how well the model approximates the field situation. To simulate the flow path of the contaminant principally two types of mathematical models are used: the finite difference model and the finite element model. These mathematical models can be used to create a simulator program using C or Python. Several software programs exist such as ModFlow, SWAT Model, RockWorks, which can be used with GIS for a better simulation outcome.

Keywords Chromium contamination · Advection · Dispersion · Diffusion mathematical model · Finite difference model · Finite element model etc.

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12.1 Introduction

The rapid rate of industrialization and commercialization has led to the release of the enormous quantity of metal pollutants into the environment. Mining operations are a leading cause of heavy metal contamination by natural water (Moncur et al. 2005). These metals can adsorb in the soil surfaces, drain into rivers and lakes, and seep into ground water (Mulligan et al. 2001). Due to oxidation and reduction processes, mine's ore wastes produce acid mine drainage, which leach out significant amounts of heavy metals into the soil, which degrades the quality of surface and groundwater (Concas et al. 2006). Effluent from chromium mine and from various industries such as tannery, electroplating, dyes and paint, steel alloy, ferro-chrome and glass manufacturing, pulp and paper, and chemical industries are releasing huge amounts of chromium into the environment (Das and Mishra 2010; Jianlong 2009). Due to the solubility of chromium in water, chromium concentration increases in the water and due to the leaching of chromium, its concentration also increases in soil, thus easily ingested and accumulated in the bodies of plants and animals (Bio-accumulation) and keeps increasing higher in the tropic level of the ecosystem (Biomagnification) (Chattopadhyay et al. 2002; Ruus et al. 2005). Excessive releases of chromium to the environment have shown adverse effects on humans and plants/animals that affect the ecosystem. Additionally, chromium can impair the immune system, elevate blood pressure, damage the liver, and produce skin irritation, breathing difficulties, and liver damage. The World Health Organization (WHO) and the Bureau of Indian Standards (BIS) both specify that 0.05 mg/L is the maximum allowed for total Cr or Cr(VI) in drinking water.

There are two oxidation states of Cr that are typically present in the environment, i.e., trivalent and hexavalent chromium. Among these two, Cr(VI) is highly reactive and soluble in water. Cr(VI) can easily penetrate the living cells (Alloway 2012; Naz et al. 2016a, b). Chromite ore typically releases chromium in the form of Cr(III) into the surface and groundwater, but certain environmental factors, such as the presence of MnO_2, higher alkalinity ($pH > 7$) and high electrical conductivity, cause Cr(III) to change into Cr(VI) (Rai et al. 1989; Moran et al. 2015).

These mathematical models use various factors that govern the fate and transport of Cr(VI) in environmental media such as surface water, groundwater, soil, and atmosphere. While every medium has its characteristics, there are also many similarities. Due to weathering of chromium-containing ultramafic rocks, chromium leach into the soil that contaminates the surrounding surface and groundwater. Contaminated water from chromite mine quarries gets infiltrated into groundwater, raising the concentration of Cr(VI). Releasing the quarry's water into the surface water stream pollutes the surface water bodies (Dhal et al. 2011). According to local geological study, the weathering of chromite-containing ultramafic rocks is the major factor that affect the quality of the groundwater. In mines open-pit chromite extraction generates huge amounts of seepage water. These mine water containing Cr(VI) may adversely contaminate nearby water bodies if it is not treated (Nriagu and Nieboer 1988).

Chromium in air will eventually settle and end up in waters or soil. Chromium in soils adsorbs to soil particle and percolates to groundwater (Tokunaga et al. 2001). Chromium may adsorb on sediments and become immobile in water.

12.2 Chromium in Environment

Chromium has varieties of application in numbers industrial. They are widely used in leather processing and finishing (Nriagu and Nieboer 1988), for the production of refractory steel, electroplating cleaners, catalytic manufacturing, and chromic acid production. Hexavalent chromium(VI) compounds are used in industry for metal planting, cooling tower water treatment, hide tanning and, until recently, wood preservation. These anthropogenic activities have resulted in widespread contamination of chromium in the environment and increased its bio-availability and mobility (Kotaś and Stasicka 2000).

The leather industry is the main cause of the significant contribution of chromium to the biosphere, representing 40% of total industrial use (Barnhart 1997). In India, between 2000 and 32,000 tons of primary products are discharged into the environment each year from the tanning industries (Barnhart 1997).

Chromium may infiltrate natural streams through various processes, including the weathering of rocks that contain Cr, discharge from various industries and soil leaching. Cr may undergo sorption, desorption, oxidation, dissolution, reduction and precipitation in an aqueous environment (Kimbrough et al. 1999).

pH of the water affects Cr(III) solubilities in aqueous solutions. Cr(III) will precipitate at neutral to basic pH levels, but it will prefer to dissolve at acidic pH levels. Although divalent cations can cause the Cr(VI) chromate and dichromate forms to precipitate, they are very soluble in all pH ranges (Kimbrough et al. 1999).

Depending on the chemical composition of the rocks and sediments that form the soils, the concentration of Cr in those materials may vary widely (Kimbrough et al. 1999; Wang and Choi 2013). Chromium concentration in soil may rise primarily due to anthropogenic deposition, such as air deposition (Rosas et al. 1989), and the disposal of chromium-containing liquids and solid wastes, such as industrial slag, chromium plating baths, and chromium byproducts (Kimbrough et al. 1999). In most cases, Cr in the soil is a mixture of Cr(III) and (VI). Like an aquatic environment, Cr changes through reduction, sorption, oxidation, precipitation, and dissolution once in the soil or sediment (Kimbrough et al. 1999). Cr(III) can be converted to Cr(VI) due to the presence of oxidants in the ground (such as dissolved oxygen and MnO_2) (VI) (Fendorf and Zasoski 1992). Compared to MnO_2, Cr(III) oxidation by dissolved O_2 appears minimal. On the other hand, iron, vanadium, sulfides, and organic substances diminish the forms of Cr(VI) (Cary 1982). However, suppose the soil's reducing capacity is surpassed. In that case, Cr(VI) may continue to exist in the soil or sediment for years, mainly if the soil is sandy or contains little organic matter (López-Luna et al. 2009; Chandra et al. 1997). It was discovered that Cr(VI) was more mobile in the soil and caused higher toxicity on plant seeds of wheat, oat, and sorghum plants (López-Luna et al. 2009; Chandra et al. 1997).

About 60–70% of the chromium in the atmosphere is a result of human activity. The rest of the chromium comes from natural sources (Seigneur and Constantinou 1995). Chromium in the atmosphere results from industrial activities like electroplating, combustion of refuse and sludges, combustion from brick and thermal and cement industries, and combustion of fuel from vehicles (Nriagu and Nieboer 1988). Natural phenomena causing chromium in the atmosphere are volcanic eruptions, smoke from forest wildfires, erosion of soils and rocks, and airborne sea salt particles (Nriagu and Pacyna 1988). The majority of the atmospheric movement of chromium happens in the liquid and solid phases (i.e., droplets and particles) or, more generally, in the form of aerosols (Seigneur and Constantinou 1995). The size of the particles affects chromium transportation in the atmosphere. Large-sized particles typically deposit on the surface quickly, whereas small-sized particles travel a long distance and are generally deposited on the surface due to rain.

12.3 Physical Processes Affecting Chromium Contaminant Transport and Fate

There are two types of physical process by which chromium are carried in the fluids, bulk fluid movement from one site to another (advection), and random mixing within the fluids (diffusion and dispersion) (Zhang et al. 2016).

12.3.1 Advection

Advection refers to the transport of matter by the motion of a fluid (Fig. 12.1). The water will flow while carrying the chrome that has been dissolved in it. Likewise, the chromium molecules resident in the air will be transported as the air circulates. Advection is usually the most critical mode of transportation of contaminants into the environment. The primary cause of the widespread movement of chromium pollutants into the environment is advection transfer through water or air (Brusseau and Chorover 2019). The transport of the mass of contaminants via advection is proportional to the speed of movement of the fluid (Schumer et al. 2001). Consequently, to characterize the advective transport potential of chromium at a particular location, it is necessary to determine the direction and flow rate of the liquid at that location. Monitoring the flow of air through the atmosphere will help determine the flow of chromium contaminants through the air (Brusseau and Chorover 2019). The chromium contaminant is transported on a larger surface area if the air flow is high. Surface water flow direction and speed can be easily determined; for example, a

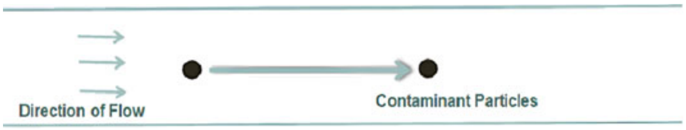

Fig. 12.1 Advection in stream flow

stream's direction is determined by the stream channel, and the water level determines its speed. On the other hand, it is much more complicated to characterize the direction and flow of the liquid in the groundwater (Schumer et al. 2001).

12.3.2 Diffusion

Diffusion describes the propagation of particles by random movements of regions with higher concentrations to regions with lower concentrations (Fig. 12.2). It can happen in air, in water, and even in contaminated soil. Diffusion is different from dispersion as diffusion involves the separation of particles from a larger structure, dispersion involves the uniform distribution of particles throughout a volume. Dispersion is a process without an enthalpy change, whereas diffusion is always an endothermic process (Rowe 1996; Shackelford and Daniel 1991).

The diffusion of chromium-like contaminants into the fluid is one of the major fields of formation for both natural and anthropogenic substances introduced into the aquatic environment. Proper methods for calculating the transport of biogenic components, dissolved gases and pollutants cannot be selected without a thorough understanding of the rules for contaminant diffusion in the fluid (Brusseau and Chorover 2019). Due to the more significant number of variables affecting a substance's dispersion, diffusion processes in fluids are exceedingly complex. Only by combining theoretical and experimental approaches can the regularities of compound diffusion in the fluid be studied more thoroughly (Shackelford and Daniel 1991).

The diffusive movement of a chromium in a gas, liquid or solid is governed by Fick's first law:

$$F = -\mathrm{Dr}\frac{\mathrm{d}C}{\mathrm{d}x} \tag{12.1}$$

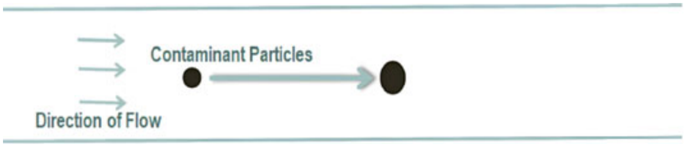

Fig. 12.2 Diffusion in a stream flow

"*F*" is the chromium contaminant mass flux. (i.e., mass transported per unit area per unit time).

"Dr" is the diffusion coefficient for the chromium in water, air or soil.

"*C*" is the concentration of the chromium at a particular position *x* and time.

$\mathrm{d}C/\mathrm{d}x$ is the concentration gradient (i.e., the change in concentration with position) and this gradient will be in negative as chromium moves from higher to lower.

Using this formula, we can calculate the amount of chromium transported in a unit area in a given time, if we know the change in concentration with position.

12.3.3 Dispersion

Dispersion is spreading or scattering the contaminant particle the central contaminant mass (Fig. 12.3). Dispersion results from local turbulence, movements that last less time than the time used to calculate the transportation average. Due to the dispersion in fluid, the size of the plume will increase. That is, the plume "grows" as it moves. This propagation is due to molecular scattering and the uneven flow field. It should be noted that spreading occurs in fluid systems only (Zhang et al. 2016).

Random motion of individual molecules results in molecular diffusion. Due to its kinetic energy, molecules vibrate and move. As the molecules move in random motion direction of the molecules is not defined. The end result of these various motions is that molecules will diffuse from zones with higher concentrations of molecules to regions with lower concentrations of molecules (Brusseau and Chorover 2019). We can observe the effect of diffusion when a drop of coloring dye is added to transparent water in a beaker. The contribution of molecular distribution of global transport and the spread of a contaminant is usually smaller on the subsoil. It has become particularly important in systems with minimal advection, such as clay units in the saturated subsurface (Schumer et al. 2001).

The major source of dispersion is the non-uniform drainage field. When a fluid moves in the environment, it doesn't move as a uniform body—instead, different sections of fluid move at different velocities. For example, when water flows into a river, the speed of the water is greater than that of a riverbank because of the friction of the water is elevated to the riverbank. The atmospheric dispersion is due to local variation in the flow direction. Dispersion in the subsoil occurs on a variety of spatial scales. For small scales (<1 m), dispersion is due to non-uniform flow through the medium porous pores and manifests in three main ways:

Fig. 12.3 Dispersion in a stream flow

1. In a single pore, fluid movement will be slower at the pore wall due to friction with the wall and faster at the center of the pore.
2. The larger pores have a faster flow of fluid than the smaller ones (a smaller portion of fluid is affected by friction in the bigger pores).
3. Less complex pore sequences reduce the time it takes for a molecule of fluid or contaminant to move from one area to another (less tortuous flow path).

On a large scale, the fluid moves faster in larger permeable soil like clay.

Consequently, advection rates differ for various parts of the fluid. Therefore, when a plume of dissolved contaminants moves, different portions of the plume move at different speeds. This results in the plume spreading or "growing" in the direction of movement. To see the dispersion process, consider marathon runners as an analogy. In marathon, in the beginning, all participants will be grouped into small groups at the point of departure. After the event starts, the runner will start to scatter in due time because some runners are faster than others. The leading and the slowest racers may be separated by a kilometer or more when the first runner crosses the finish line (Schumer et al. 2001).

Dispersion Transport Equation (Eq. 12.2) can be used to calculate the change in concentration of chromium with time.

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \tag{12.2}$$

"*C*" is the concentration of chromium concentration.

"*D*" is dispersion coefficient, (proportional to dispersivity and velocity).

12.3.4 Advection Dispersion Reaction

Generally, it is seen that advective movement of contaminant particle is superimposed by random dispersive displacement, whose magnitude is dependent on dispersivity and seepage velocity (Rowe 1996; Schumer et al. 2001). So, a common equation is made which is known as Advection Dispersion Equation. The Advection Dispersion Reaction (ADR) equation (Eq. 12.3) is frequently used to predict the transport of dissolved solutes in groundwater.

$$\frac{\partial C}{\partial t} = Dx\frac{\partial^2 C}{\partial x^2} + Dy\frac{\partial^2 C}{\partial x^2} + Dz\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} - \lambda \mathrm{RC} \tag{12.3}$$

where *C* is the concentration of chromium contaminant.

Dx, *Dy*, *Dz* are dispersion coefficients in the x, y and z directions. (Cartesian coordinate axes).

V is the adjective transport velocity (seepage velocity) in the *x* direction.

λ is an effective first order decay rate due to combined biotic and abiotic processes.

R is the linear, equilibrium retardation factor.

Here advection take place in x direction and dispersion of the contaminant particle take place in the y and z direction. As this equation deals in all three directions of plane many software is made which use this equation for the simulation of contaminant particle transport in the environment (Rowe 1996).

12.4 Mass Transfer

As we know, a chromium contaminant can be in the air, in water, or in combination with a solid phase. An important aspect of contaminant behavior is the transfer of pollutants from their original pages to other stages. Precipitation/Dissolution, sorption and general redox behavior of chromium are the main mechanisms involved in the transportation of chromium contaminants in the environment.

12.4.1 Precipitation/Dissolution Reactions of Chromium

Precipitation or dissolution reaction may occur in chromium compounds, which is governed by its solubility (Bodek et al. 1199; Stanin 2005). When Cr(III) is dissolved in water, it generally forms chromium hydroxides. The speed at which chromate, dichromatic anions, and these cations precipitate or dissolve are very variable and pH-dependent. The precipitation of Cr(III) in neutral water is enhanced by the precipitation of Cr(III) as its combination with iron hydroxide. This quick reaction kinetics make it a crucial factor in regulating solubility (Rai et al. 1987; Stanin and Pirnie 2004).

Chromate can, however, exist as the insoluble salt of different divalent cations. Considering that Cr(VI) frequently enters the environment through the dissolving of such chromate salts, understanding dissolution processes is crucial in environmental studies. Because they provide as a consistent source of chrome anions, some chromate salts, such $SrCrO_4$, are highly soluble and hence important to dissolve (Stanin 2005).

12.4.2 Sorption of Chromium

In soil Cr(III) get sorbed very quickly by clay minerals, and sand, which contain Fe and Mn (Stanin and Pirnie 2004; Bartlett and Kimble 1976; Dreiss 1986; Griffin et al. 1977; Rai and Zachara 1984; Schroeder and Lee 1975). Experimental results show that this sorption occurs quickly, with iron oxides and clay minerals absorbing 90% of the chromium in under 24 h (Stanin and Pirnie 2004). Additionally, the sorption of Cr(III) increases with rising pH (Griffin et al. 1977) (as clay surfaces become more negatively charged) and rising soil organic matter, content (Paya Perez 1988), whereas the adsorption of Cr(III) decreases in the presence of other inorganic cations or dissolved organic ligands.

Cr(III)'s partitioning ratios (Kd) were estimated very highly. The Kd sorption model, however, cannot be used to predict delay except for a certain concentration since sorption Cr(III) is not linear (Griffin et al. 1977). Due to its limited solubility, Cr(III) would similarly be mostly stationary above this pH (Griffin et al. 1977). Due to their higher solubility or decreased sorption as compared to the non-complex form of Cr, complexes are anticipated to improve the mobility of Cr(III) (III). The formation of complexes would likely improve the mobility of Cr(III) due to their reduced sorption or increased solubility compared to the non-complex form of Cr(III) (Davis and Olsen 1995).

Mn, Al, and Fe oxides and hydroxides, as well as clay minerals can sob chromate ions ($HCrO^{4-}$ and CrO^{4-}) (Stanin 2005; Griffin et al. 1977; James and Bartlett 1983; Musić 1986; Rai et al. 1989; Zachara et al. 1987). These minerals can typically occur in aquifers (Stumm et al. 1981). Aquifers contain high concentration of amorphous iron, which acts as an absorbent. Iron hydroxides significantly adsorb to Cr(VI) (James and Bartlett 1983). The Freundlich isotherm best fit for sorption (Naz et al. 2016b). However, it is seen that it exhibits the Langmuirean behavior at neutral pH and that its Kd decreases with concentration (Kimbrough et al. 1999).

12.4.3 Redox Behavior of Chromium in Environment

Redox reactions and redox conditions will control the conversion of Cr(III) to Cr(VI), including in the aquatic environment like groundwater (Stanin and Pirnie 2004; Richard and Bourg 1991). Eh–pH charts are often used to study the distribution of Cr(III) and Cr(VI) in aqueous solutions.

Redox reagent also plays an important role, which takes or supplies the necessary electrons, which is required for the redux transition of Cr(III) to Cr(VI) or Cr(VI) to Cr(III). Important redox couples (reducing agents/oxidation agents) in aquatic environments are: H_2O/O_2, Mn(II)/Mn(IV), NO_2/NO_3, Fe(II)/Fe (III); $S^{2-}/SO_4{}^{2-}$ and CH_4/CO_2 (Stanin 2005; Richard and Bourg 1991).

The capacity of the chemical agent to provide or absorb electrons controls the redox processes with chromium compound. Many times, common chemical agent is responsible for the chromium redox reaction (Kimbrough et al. 1999). The concentration of these chemical controls the redox processes of chromium. It is known that several oxidizing agents can convert Cr(III) to Cr(VI), but their concentration is so low that they become ineffective in the environment (i.e., groundwater). For example, ozone can convert Cr(III) to Cr(VI) (a reaction with $Eh = 0.87$ V) by oxidizing Cr(III), but the ozone concentration in the environment is usually insufficient to perform oxidation (Stanin and Pirnie 2004; Grohse et al. 1988). There are many reducing agents in the environment that have the potential to effectively reduce Cr(VI) to Cr(III) and are generally found at adequate levels. Despite being less favorable thermodynamically (a reaction with Eh, just 0.56 V), the reduction of Cr(VI) by Fe(II) is possible because iron concentrations are often adequate in the environment (Rai et al. 1989). Chromates occur as chronic acid (H_2CrO_4) and hydrogen chromate ($HCrO^{4-}$) at lower pH levels. When the concentration of $CrO4^{2-}$ is high, it will change into dichromate in the presence of reducing agents at low pH or high Eh. Chromates are poor oxidizers at high pH and are consequently more stable when their Eh values are lower. Due to the high solubility of Cr(VI) it may travel large distances in groundwater, but if the transported Cr(VI) encounters a region with low Eh, it may undergo reduction and precipitate as Cr(III). In the presence of organic matter, particularly at low pH, Cr(VI) can easily be reduced to Cr(III) (Bartlett and Kimble 1976; Bloomfield and Pruden 1980). Fe(II) and dissolved sulfides can reduce Cr(VI) (Schroeder and Lee 1975). Due to its low solubility, Cr(III) is rarely transferred through ground water at large distances. However, if the redox conditions change from reducing to oxidizing during transportation, Cr(III) can be converted to the more soluble Cr(VI). Manganese has been observed to oxidize Cr(III) to Cr(VI) under natural circumstances (Schroeder and Lee 1975; Bartlett and James 1979).

12.5 Mathematical Model (Finite Difference and Finite Element Method)

Finite difference methods are numerical approaches used in mathematics for approximative differential equations' solutions to approximative derived. Here we aim at finding solutions for differential equations, i.e., to identify a function (or a discrete approximation of these functions) that fulfills the boundary conditions along the edges of the domain and a specific relationship between different derivatives on a given region of space or time or both (Wang and Anderson 1995). Generally, the answer to this challenging problem cannot usually be found in an analytical formula. A finite difference approach works by substituting the approximate derivatives into the differential equation in place of the derivatives. Instead, the differential equation is replaced with a sizable algebraic system of equations that can be easily solved on a computer (Hossain and Yonge 1997).

Using the finite element method for groundwater issues is a recent development compared to the finite difference method. Each approach resulted in a set of algebraic equations where the unknowns are the heads assign to a finite number of nodes (Wang and Anderson 1995; Faust et al. 1989). Conceptual vision of a problem field approached by both methods is shown in Fig. 12.4 (Wang and Anderson 1995). The finite difference method is normally carried out with rectangular cells. The finite element method is carried out with a variety of elements, but the triangular element is a good starting point to describe the process. Triangular elements have 3 nodes, one at each corner. These nodes are used to locate unknown heads, that is, they are the points in the area of the problem at which the heads are computed. In addition, the head of each element is defined in terms of node values per base or interpolation functions. The head is defined in the whole field of the problem fragmentarily on the individual elements (Kobus 1993). An essential idea that separates the finite element method from the finite difference method is used interpolation functions to define potential in the issue area. The finite difference method automatically sets the head to the points. The definition of the head through the domain of the problem in the finite element method makes it possible to apply residual variational or weighted principles (Wang and Anderson 1995).

Finite element method emphasis on the method's adaptability for issues including irregular borders, diverse environments, or anisotropic environments. Finite differential programs can also explain these complications. However, the flexibility of the finite element method assists in the resolution of coupled issues, such as the transfer of contaminants, or issues with shifting boundaries, such as a fluctuating water table. The choice of method ultimately comes down to the user's comfort level with each strategy as well as the complexities of the problem (Faust and Mercer 1979).

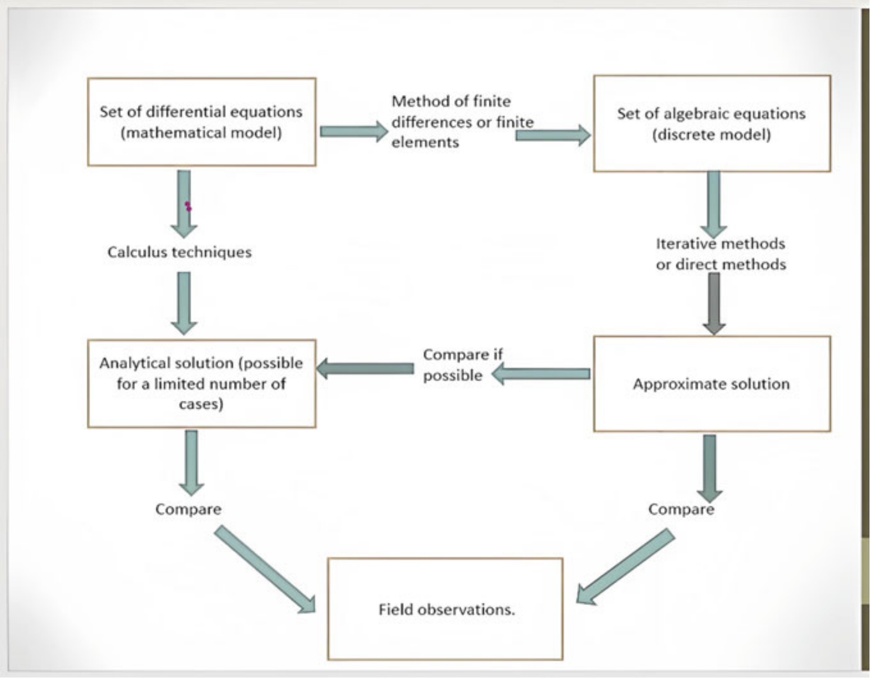

Fig. 12.4 Relationship between mathematical model, discrete algebraic model, analytical solution, approximate solution, and field observation. Adopted and modify from Wang and Anderson (1995)

12.5.1 MODFLOW Model

MODFLOW is one of the most comprehensive and user-friendly modeling software for practical applications in 3D groundwater flow and contaminant transport simulations (Loudyi et al. 2014). MODFLOW uses a partial differential equation (Eq. 12.4) describing the 3D flow of groundwater through a saturated porous material. It assumes that the flow process is a single fluid, mainly water, with constant parameters (such as density, viscosity, and temperature), in a single liquid phase (Loudyi et al. 2014). It assumes laminar and linear flow in accordance with the Darcy equation (Loudyi et al. 2014). The direction of the hydraulic conductivity is taken in three directions that is x, y, z. Using the standard MODFLOW notation, the equation solved is given as

$$\frac{\partial}{\partial x}\left(K_{\mathrm{xx}}\frac{\partial h}{\partial x}\right)+\frac{\partial}{\partial y}\left(K_{\mathrm{yy}}\frac{\partial h}{\partial y}\right)+\frac{\partial}{\partial z}\left(K_{\mathrm{zz}}\frac{\partial h}{\partial z}\right)-W=S\frac{\partial h}{\partial t} \tag{12.4}$$

where “K_{xx}”, “K_{yy}”, and “K_{zz}” is hydraulic conductivity in the x, y, and z direction. (Cartesian coordinate axes)

“*H*” is the potentiometric head.

“*W*” is a volumetric flux per unit volume and includes sources and/or sinks.

“Ss” is the specific storage of the porous material. And “*t*” is time [T].

The three different boundary conditions—the Dirichlet, Neumann, and Cauchy conditions can be simulated using MODFLOW software (Eq. 12.4), which is combined with the specification of flow and head conditions at an aquifer’s boundary condition (Loudyi et al. 2014).

12.6 Conclusion

Fate and transport of chromium contaminants depend on phenomena such as physical processes and chemical process which effect the behavior of chromium contaminant in environment. Mathematical modeling can be used to predict the fate of chromium contaminate which will be based on equation related to the physical process as well as chemical process. Physical processes such as advection, diffusion, and dispersal play a significant role in the transport of contaminating particles. Due to these processes, the particle travels through the fluid (water and air). Because of the physical process, it is possible to trace the movement of contaminant particles. Using these equations, it is possible to predict the motion of contaminating particles in groundwater.

Chemical processes like absorption, adsorption, oxidation, reduction etc., are very important processes in the fate and transport of chromium particles (Stanin and Pirnie 2004). This chemical process will control how chromium will be found in the environment, whether hexavalent or trivalent. The formation of complexes would likely improve the mobility of Cr(III) due to their reduced sorption or increased solubility compared to the non-complex form of Cr(III) (Davis and Olsen 1995). Iron hydroxides significantly adsorb to Cr(VI) (Seigneur and Constantinou 1995). The Freundlich isotherm best fit for sorption (Davis and Olsen 1995). However, it is seen that it exhibits Langmuirean behavior at neutral pH and that its Kd decreases with concentration (Griffin et al. 1977).

The motion of chromium particles in the soil is impacted by adsorption. Studies show that overall adsorption capacity was low in silt-sand soil. This fact suggests that Cr(VI) is less adsorbed and more mobile in the silt-sand soil (Khan et al. 2010).

Mathematical models are an inexact representation of reality, built upon a suite of assumptions and simplifications. The precision of a mathematical model will depend on the validity of the assumptions, the representativeness of the simplifications and the quality of the input data required to implement the model. Mathematical models use finite difference and finite element methods to solve Advection Dispersion Equations and other differential equations with boundary conditions. Lastly, for better prediction, field observation is crucial so that the prediction from different models can be validated and improvement in the mathematical models can be suggested.

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Chapter 13
Iron-Based Modified Nanomaterials for the Efficacious Treatment of Cr(VI) Containing Wastewater: A Review

Anjali Kumari, Alok Sinha, and D. B. Singh

Abstract Chromium, mainly in the hexavalent form [Cr(VI)], has become a worldwide menace due to its extensive industrial applications and mining activities. According to the USEPA, it is one of 129 priority pollutants and 25 hazardous compounds, due to its higher toxicity, persistency, carcinogenicity, and mutagenic effects. Cr(VI) is hundred times more toxic than its trivalent form which is principally of geological origin. Cr(III) is generally insoluble and stable in the environment, primarily required for lipid and fat metabolism in human. In an aqueous solution, Cr(VI) is mostly found as the oxyanions $HCrO_4^-$ (pH 2), $Cr_2O_7^{2-}$ (pH 2–6), and CrO_4^{2-} (pH > 6), which has very high mobility. Several figures show that Cr(VI) concentrations are significantly higher around the world, despite the fact that the acceptable limit for portable water is 0.05 mg/l and surface water discharge is 0.1 mg/L. Therefore, effective elimination of Cr(VI) from the water source requires long-term water management sustainable technology. Nano-remediation technology has gained a larger insight in the toxic contaminant removal due to its high surface area, non-toxic, vast reduction capacity, and cost-effective nature. It could be a state-of-the-art approach for the safe exclusion of heavy metals (Cr, As, Cd, Pb, and Hg) and organic compounds like pharmaceutical waste, organic solvents, phthalates, hydrocarbons, and persistent organic pollutants (POPs) from the wastewater. Carbon nanostructure, iron-based nanomaterials, metal organic framework, nano-photocatalyst, nanosensors, zeolites, and other methods are available for the reduction of Cr(VI) into Cr(III). Currently, iron-based nanomaterials are being investigated as a promising method for the effective reduction of Cr(VI) into Cr(III) from the aqueous solution, as its negative standard potential ($E^0(Fe^{2+}/Fe^0) = -0.44$ V, favors reaction process. Despite all the advantages of iron particles, the pH dependency, agglomeration, and particle passivation limit the procedure. This chapter will discuss the occurrences, environmental cycle, health effects of chromium, as well as

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current developments in nanomaterial synthesis/modification via physico-chemical methods, probable reaction mechanisms, and the impact of various environmental conditions on Cr(VI) reduction capabilities in aqueous solution.

Keywords Hexavalent chromium · Iron-based nanomaterials · Planetary ball mill · Adsorption-reduction · Regeneration

13.1 Introduction

The ever-increasing concentration of organic and inorganic pollutants in the environment has become a global concern. Rapid urbanization, industrialization, and mining activities have harmed the environment by releasing toxic heavy metals in the name of a prosperous economy (Bilal et al. 2019; Feng et al. 2022; Sutherland et al. 2012; Yu et al. 2021). Heavy metals, i.e., arsenic, mercury, chromium, lead, and cadmium, have primarily become a global issue due to their toxic, non-biodegradable, and bioaccumulative characteristics, which poses the substantial risk to human health even at low concentrations (Gong et al. 2017; Jobby et al. 2018; Zhang et al. 2020). Water characteristics are changing significantly as a result of changes in hydro-chemical composition and an upsurge in heavy metal concentration. Water contaminated with heavy metals can pose serious health impacts on human body and leads to the neurotoxicity, carcinogenicity, nephrotoxic, hepatotoxic, cardiovascular toxicity, immunological toxicity, skin problem, genotoxicity, and developmental toxicity (Mitra et al. 2022). Among all these heavy metals, hexavalent chromium [Cr(VI)] has emerged as a foremost environmental problem due to its higher persistence, mobility, and carcinogenicity to humans (Choppala et al. 2013; Markiewicz et al. 2015; Zhu et al. 2018a, 2016, 2018b).

Chromium, is 24th transition metal, commonly used in industries like electroplating, mining, wood preservation, chromate manufacturing, dyeing, and other industrial manufacturing sectors (Coetzee et al. 2020; Motzer and Engineers 2004; Oze et al. 2007; Zissimos et al. 2021). Chromium's oxidation state varies from − II to + VI, with Cr(III) and Cr(VI) being the most available forms in the environment. Cr(III) is mostly geological in origin, is generally insoluble and stable in the environment, and is considered necessary in the human body. Whereas Cr(VI) is primarily of industrial origin, some natural formation is known through the conversion of Cr(III) in the presence of Mn-oxides and organic acid in soil (Saha et al. 2011). By origin, Cr(VI) is more mobile, has greater solubility, and is 100 times more toxic than Cr (III) (Zhang et al. 2012). As a result of its high mobility and toxicity (carcinogenic and mutagenic) nature, Cr(VI) has become a serious global issue, particularly in water system, as it is one of the chief routes of pollutant entry in the human body (Ding et al. 2018; Fang et al. 2020; Wu et al. 2019). The permissible limit of Cr(VI) in portable water is 0.05 mg/L (EPA 2021). However, there are numerous statistics that show a higher concentration of Cr(VI) in aquatic medium. So, to address the issue of Cr(VI) contamination in water, sustainable water treatment technology that can effectively remove Cr(VI) from water or convert it to a less toxic and stable form, i.e., Cr(III) is required.

The use of nanoparticles (1–100 nm) for the treatment toxic non-biodegradable pollutant can be decent approach. Nanomaterials can be produced by the top-down (physical) and bottom-up (chemical and biological) methods (Sepeur 2008). The physical methods of nanomaterials synthesis through ball mill and planetary ball mill have recently come into light due to its simpler process. Lately, the use of metal-based nanomaterials especially iron (ZVI, nZVI, and iron oxides) for the exclusion of Cr(VI) from wastewater has gained a larger interest owed to its high surface area, reactivity, pore volume, non-toxic, and cost-effective nature (Montesinos et al. 2014; Qu et al. 2022b; Shen et al. 2020; Sinha et al. 2022). The negative potential value of Fe^{2+}/Fe^0 −0.44 V enable them working as effective electronic donor (Lv et al. 2019). However, the zerovalent iron form's high reactivity results in the formation of an oxide layer, which reduces the adsorbent efficiency. Accordingly, there is a need of surface modification technology, which will confiscate the problem of oxide layer and agglomeration of nanoparticles. Surface modification via physical means, i.e., ball mill, has gained a distinct attention due to its simpler process (Kumar et al. 2020; Montesinos et al. 2014; Qu et al. 2022b; Shen et al. 2020; Sinha et al. 2022). It has seen that surface modification of nanoparticles through activated carbon, biochar, clay, metal can enhance the removal rates. This book chapter will review the impacts of heavy metals, especially chromium. It will comprehensively discuss the source, toxicity, speciation of chromium compounds, environmental cycle, human health risk, and sustainable remediation using iron-based nanomaterials. The chapter also briefly outlines the different controlling factors that affect Cr(VI) removal processes and adsorbent regeneration capabilities.

13.2 Heavy Metals Contamination and Health Impacts

Currently, the occurrence and influence of organic and inorganic pollutants in aquatic system has become a foremost environmental concern, since they are toxic, persistent, carcinogenic, and bioaccumulative in nature (Luo et al. 2022; Saravanan et al. 2021; Wu et al. 2021). Various priority pollutants (PPs) prevail in nature which are considered to be the major threats to the environment. It can be found almost everywhere, in our food, soil, air, and water. Humans, flora, and fauna all over the world carries the trace amounts of above-mentioned pollutants in their bodies, which can cause serious harm.

Heavy metals are the metals which has a higher density (5 g/cm^3), toxic at low concentrations, persistent, non-biodegradable, and bioavailable in nature (Cengiz et al. 2017; Esen et al. 2021; Liu et al. 2021, 2018; Su 2015; Zou et al. 2021). These heavy metals comprise chromium (Cr), cadmium (Cd), arsenic (As), lead (Pb), copper (Cu), and mercury (Hg). Heavy metals are primarily derived from natural or anthropogenic sources. The most significant natural contributor of heavy metals is considered to be weathering of rock. In general, the geologic procedure is influenced by the nature of the rock and the surrounding environment, has a significant impact on the concentration and composition of heavy metals (Abdu et al. 2011). Volcanic eruption, forest fire, aerosols, and natural vegetation are the probable natural source of heavy metal in environment (Srivastava et al. 2017). Anthropogenic actions such as inorganic fertilizers, mineral source development, metal processing and smelting, chemical production, industrial, and effluent discharge have been associated with heavy metal pollution (see Fig. 13.1). Heavy metal toxicity has proven to be a serious menace, posing a range of health risks. The adverse health impacts of heavy metals include gastrointestinal and kidney dysfunction, nervous system disorders, skin diseases, endothelial dysfunction, immune system disorder, birth defects, and carcinogenicity in the body (Mitra et al. 2022). Despite the fact that these metals have no significant biological function except (iron and zinc), their toxicity effects are still present in some form that is detrimental to the human body and for its efficient functioning. They can sometimes act as an invisible element of the body and can even interfere with metabolic pathways. In all of these heavy metals, chromium, particularly in hexavalent form [Cr(VI)], has become a worldwide problem due to its diverse range of industrial applications and severe health impacts on humans.

Fig. 13.1 Anthropogenic sources of heavy metal in environment

13.3 Chromium

Chromium is an economically valuable metal that is used in a number of industries due to its hardness and corrosion resistance. It is the 24th transition metal, with the electronic configuration [Ar] $3d^5\ 4s^1$, and is an economical viable metal naturally found in the earth's crust. Cr exists in a variety of oxidation states ranging from − II to + IV, with trivalent (III) being the most stable and hexavalent (IV) being the most mobile. Due to wide number of applications, chromium in its (VI) form has become a widespread concern in the environment (Khezami and Capart 2005; Zayed and Terry 2003). Because of its widespread industrial and mining activities, Cr(VI) has become a major pollutant in water, air, and soil. Geochemical facies regulate the speciation, transport and, fate of chromium in the atmosphere. Adulteration in ground and surface water by Cr(VI) mainly occurs due to seepages from industrial metal processing, mining pit wastes, industrial lagoons, wood preserving facilities. These runoffs may contain up to 100 mg/L of Cr (VI) and Cr (III) in total. Cr(VI) human impacts includes gastric damage, kidney, liver, lung cancer, and skin irritation. According to USEPA, chromium is one of 129 predominance pollutants and also listed among the 25 hazardous materials which can pose the most substantial menace to human health at different polluted sites around the world (EPA 2021). The oxo-species of chromium, $HCrO_4^-$, CrO_3^-, and CrO_4^{2-} act as a powerful oxidizing agent, reacting with organic matter or other reducing agents to form Cr(III), which eventually precipitates as $Cr_2O_3.xH_2O$. The chromium oxidation state has a substantial impact on the fate and transport, as well as the type and cost of treatment needed to reduce concentrations below the allowable limit (0.05 mg/L) (IS-10500, B.I.S. 2012). Hence, conversion of Cr(VI) to Cr(III) is beneficial for the environment health and it is only probable technique for exclusion of Cr(VI) from the system (Zhao et al. 2019).

13.3.1 Occurrence of Chromium in Environment

Chromium originates in the environment via natural and anthropogenic pathways, and presents in air, soil surface, and groundwater and seawater. Naturally chromium is found as $FeCr_2O_4$ ore in serpentine and ultramafic rocks, other minerals contain chromium in complex with other elements, especially with lead, magnesium or aluminum, like Bentorite $Ca_6(Cr, Al)_2(SO_4)_3$, Vauquelinite ($CuPb_2CrO_4PO_4OH$), Tarapacaite (K_2CrO_4), Knorringite ($Mg_3Cr_2(SiO_4)_3$, Phoenicochroite (Pb_2OCrO_4), and Crocoite ($PbCrO_4$) (Babula et al. 2009). It is the 21st abundant element with an average concentration of 100 ppm and a relative abundance of 0.014% of the earth's crust (Avudainayagam et al. 2003; Gauglhofer et al. 1991; Merian et al. 2004). Table 13.1 represents the chromium concentration in different environmental media.

Anthropogenically, chromium release into the environment through the industrial activities like mining operation, leather industry, metallurgy, chrome plating,

Table 13.1 Concentration of chromium in different medium (Thakur et al. 2007; Zayed and Terry 2003)

Medium	Concentrations
Air	100 ngm^{-3}
Natural soil	10–15 $mgkg^{-1}$
Serpentine soil	634–125,000 $mgkg^{-1}$
Vegetation	0.006–18 $mgkg^{-1}$
Animals	0.003–1.5 $mgkg^{-1}$
Freshwater	0–117 $\mu g\ L^{-1}$
Seawater	0–0.5 $\mu g\ L^{-1}$
Sediment	0–31,000 $mgkg^{-1}$

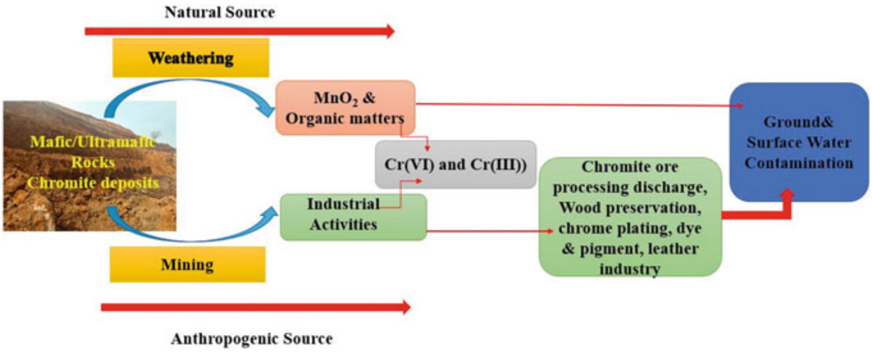

Fig. 13.2 Source representation of Cr(VI) and Cr(III) in water system

chromate manufacturing, wood preservatives, alloys, dyeing, and other industrial manufacturing sectors (see Fig. 13.2). These sources contribute up to 75,000 tonnes of chromium into the environment among which 33% are the toxic hexavalent form, whereas 54,000 tonnes of chromium come from the natural source (Kieber et al. 2002).

13.3.2 Chromium Speciation Compounds

The biogeochemistry of chromium in water and soil determines the chromium speciation process. Chromium oxidation states vary from − II to + VI, and under natural conditions, in which Cr(III) and Cr(VI) are the most stable. Cr(III) mainly occurs as cation, i.e., $Cr(III)^{+}$, $Cr(OH)^{2+}$, $Cr(OH)_3$, and $Cr(OH)^{4-}$, at pH > 3.5. Cr(III) retains on soil particles in neutral to alkaline conditions, resulting in low bioavailability and mobility in the environment (see Fig. 13.3). It also forms polynuclear complexes with adjacent molecules of the same species, which eventually precipitate as $Cr(OH)_3$

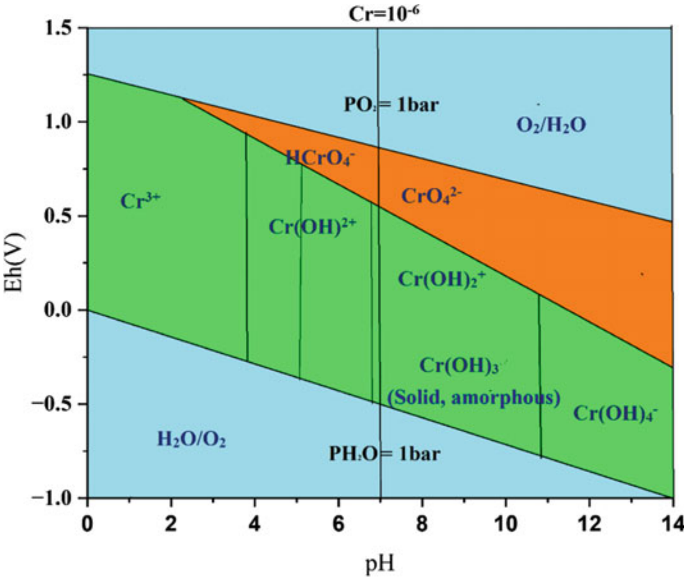

Fig. 13.3 EhpH diagram of chromium [adapted and modified from Kotaś and Stasicka (2000)]

(Choppala et al. 2013; Salem et al. 1989). Furthermore, anionic species such as Cl^-, $SO_4{}^{2-}$, and NO^{3-} do not react with Cr(III) to form complexes.

Alternatively, Cr(VI) is very mobile, extremely soluble, higher oxidation potential, and more poisonous than Cr(III). In absence of reductants, Cr(VI) is very stable under high reduction potentials (Adriano 2001). Cr(VI) oxyanions occurs as hydro chromate $HCrO_4{}^-$ (pH < 2), dichromate $Cr_2O_7{}^{2-}$ (pH 2–6), chromate $CrO_4{}^{2-}$ (pH > 6) in water, which makes them easily bioavailable (Kotaś and Stasicka 2000; Liu et al. 2019). However, $CrO_4{}^2$ is the foremost state of Cr(VI) in the water and soil (Richard and Bourg 1991). Cr(VI) anions are highly mobile in soil where clay minerals predominate due to the repugnance between clay and Cr(VI) anions (James et al. 1995).

13.3.3 Chromium Cycle in Environment

Circulation of chromium in the environment is primarily affected by the weathering phenomenon and controlled by three important reactions: oxidation–reduction (redox), sorption–desorption, and precipitation-dissolution (see Fig. 13.4). In the natural environment, both chemical species of Cr coexist. The reduction/oxidation mechanisms of Cr(VI) and Cr(III) in soil are thermodynamically spontaneous and can occur concurrently (Coetzee et al. 2020; Motzer and Engineers, 2004). The expected resistance time of chromium in the atmosphere is < 10 days (ATSDR 2012). Cr(III),

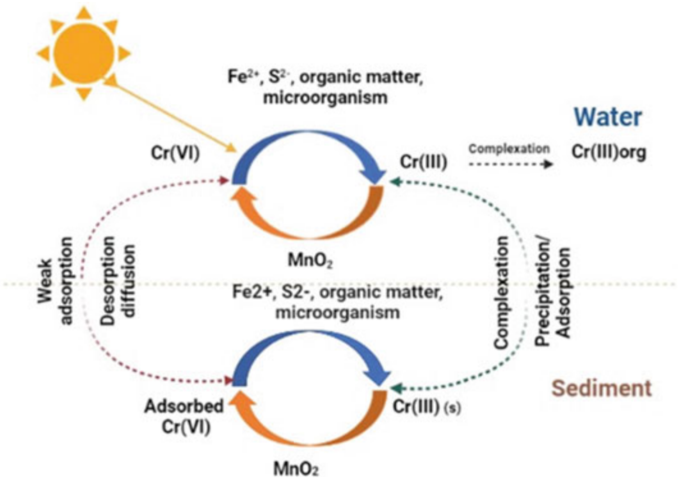

Fig. 13.4 Atmospheric chromium cycle [modified and reproduced with authorization from Markiewicz et al. (2015), Copyright 2022, Elsevier]

being less soluble in water and dominant in the soil at pH 6–9, and is less bioavailable to the environment (Saha et al. 2011), whereas Cr (VI) from soil can easily percolate into water due to its high mobility and solubility at all pH levels, since it can precipitate with divalent cations (Bartlett 1991; Coetzee et al. 2020; Kimbrough et al. 1999). Oxidation of Cr (III) to Cr (VI) in the soil environment is catalyzed by the manganese (Mn) bearing minerals at neutral pH, which has probable half-life period of 0.58–37.2 years (Eq. 13.1) (Coetzee et al. 2020; Loyaux-Lawniczak et al. 2001; Markiewicz et al. 2015).

$$Cr^{3+} + 1.5MnO_2 + H_2O \rightarrow HCrO_4^- + Mn^{2+} + H^+ \tag{13.1}$$

While the conversion of Cr(VI) to Cr(III) is facilitated by the iron (Fe) bearing mineral, sulfide, and organic matter (Eq. 13.2). This reduction rate is very high in the conversion of Cr (III).

$$C_6H_6O_2 + CrO_4^{2-} + 2H_2 \rightarrow 0.5Cr_2O_3 + C_6H_6O_2 + 2.5H_2O + 2OH^- \tag{13.2}$$

13.3.4 *Chromium Species:—Significance and Health Impacts*

Cr(III) is a vital trace element that is necessary for metabolic activities in the human body. It enters the blood through the digestive tract and is transported to the tissues, where it accumulates. Significant amounts of chromium (III) are found in nucleic acids. It has an impact on metabolism, replication, and transcription. The ion lowers the concentration of corticosteroids in plasma while increasing the functional activity of the organism's immune system. The primary response of the organism to chromium (III) deficiency is decreased glucose tolerance, which is caused by changes in insulin affinity to its receptors on cells (Mertz 1983; Swaroop et al. 2019; Zafra-Stone et al. 2007) (see Fig. 13.5a).

The routes of chromium entry into the human body are dermal absorption, inhalation, and ingestion (Miguel et al. 2007; United States 1989; USEPA 1989). The range for carcinogenic value varies from 1×10^{-6} (one cancer case in one million exposure) to 1×10^{-4} (one cancer case in ten thousand exposure). Cancer risk is low when value range between $\leq 10^{-6}$, moderate for $> 10^{-6}$ to $< 10^{-4}$, and high for $\geq 10^{-4}$ (USEPA 2004). In adults, the main injection route of exposure is through Cr(VI) contaminated drinking water and food consumed orally, whereas in children

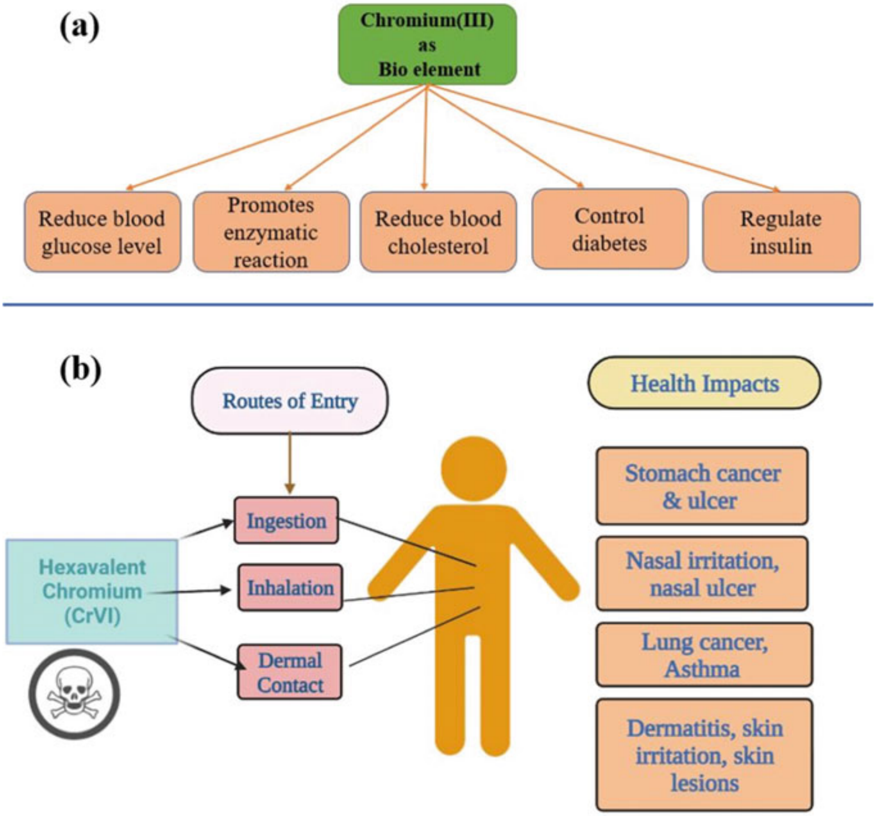

Fig. 13.5 **a** Trivalent chromium as bioelement in human body; b Cr(VI) routes of entry and its health impacts

it is through injection of contaminated soil. Cr(VI) has an acute oral toxicity varies from 1.5 to 3.3 mg/Kg (Katz and Salem 1993). According to ATSDR, (2015) the growing concentration of chromium (0.06-156 μg/L) in breast milk may be a source of chromium in children. Drinking water with chromium concentrations greater than 25 mg/L contributes to chromium toxicity (Agency for Toxic Substance and Disease Registry (ATSDR) 2015). After entering the body, gastric juice converts it to Cr(III), and only about 3% reaches the gastrointestinal tract. There is little evidence of carcinogenicity through ingestion, but a study published by Sharma et al. (2012) shows an increase in gastrointestinal complaints due to chromium contamination of around 20 mg/L (Sharma et al. 2012). Skin contact with Cr(VI) is not considered to be carcinogenic to humans, and even though inhaling and ingesting chromium or its contaminated soil can cause some Cr(VI) to easily penetrate due to its high mobility and solubility in an aqueous medium. Furthermore, some Cr(VI) compounds are corrosive, resulting in skin burns (Guertin 2004). Aerosols, fumes, and dust are the main causes of chromium in the air. The daily intake of chromium (0.2–0.6 μg) via inhalation is safe (Pellerin and Booker 2000; Russell et al. 2001). The majority of Cr(VI) that enters the lungs is assimilated into the mucous and blood, while the residual chromium causes lung cancer (Agency for Toxic Substance and Disease Registry (ATSDR) 2015; Coetzee et al. 2020). A study conducted by Das and Singh (2011) reveals that the most common route of exposure in the area is through inhalation and skin contact. Inhalation of chrome dust is the main cause of occupational health hazards in workers in the chrome plating and metallurgical industries. More than 2 lakhs people and mine workers residing in the Sukinda area are affected by the contamination of Cr(VI) (Das and Singh 2011). Elimination of Cr (VI) from the body is a prolonged process, through higher chromium concentrations observed in human tissues even years after exposure stopped. The various routes of exposure in humans and its health impacts are given in Fig. 13.5b.

13.4 Nanomaterials

Nanomaterials have grown attention in technological innovation in recent decades as a result of their remarkable physical, chemical, and mechanical properties, as well as their wide spectrum of applications in various fields (Goutam et al. 2020; Khan and Malik 2019; Singh et al. 2022). Over the last decade, scientists show large interest in nanomaterials with diameters ranging from 1 to 100 nm, which is referred to as nanoparticles (NPs). The properties (physical and chemical) of nanomaterials are reliant on their surface atom. Since, rise in the surface-volume ratio decreases the grain size, also change in melting point of surface atom affects the properties (Ali 2020). Nanomaterials mainly divided into two types, i.e., dimension and materials based. Dimensional based includes (a) zero dimension (0D) (e.g., nanoparticles (NPs), nano-spheres, quantum dots, and nanoclusters); (b) one dimension (1D) (e.g., nanorods, nanotubes, and nanowires); (c) two dimensions (2D) (e.g., nanofilms and nanolayers); (d) three dimensions (3D) (e.g., multi-nanolayers, nanotube bundles, nanowires bundles) (Zissimos et al. 2021). 3D nanomaterials are the larger than the nanoscale (1–100 nm), they formed by the assembling 0D, 1D, and 2D materials (Singh et al. 2020). Materials-based nanomaterials includes (a) carbon based (e.g., fullerenes, carbon nanotubes (CNTs), carbon nanofibers, graphene, carbon black); (b) metal based (e.g., Fe, Cu, Ni, and so on); (d) semiconductor NMs; (e) nanocomposites (Endres et al. 2021; Kolahalam et al. 2019; Saravanan et al. 2021). The various properties of nanomaterials like physical, chemical, mechanical, and optical must be taken care as they important for the morphology of particles, chemical potential, oxidation process, catalysis, adsorption, hardness, and porosity of the materials (Abid et al. 2021).

13.4.1 Synthesis of Nanomaterials

Nanoparticles are synthesized using two methods: top-to-down and bottom-up approaches. Using a top-to-down method, bulk materials are transformed into nanosized particles (Goutam et al. 2020; Leonel et al. 2021). Ball milling, thermal evaporation, sputtering, and laser ablation are all examples of top-to-down method (Mattox 2002; Neikov and Yefimov 2009; Zagho et al. 2019). This is simple, chemical-free, efficient, and cost-effective method. Particles produced through this method can be heterogeneous in nature, while bottom-up methods include the chemical vapor deposition, sol gel, hydrothermal process, coprecipitation, and bio-reduction methods. The development and self-organization of atoms and molecules as their building blocks results in the formation of NMs with well-defined shape, size, and chemical composition (Jamkhande et al. 2019; Vaseghi and Nematollahzadeh, 2020). The top-down approach means decrease the shape to the nanoscale. Bottom-up involves the development of large nanostructures from smaller atoms and molecules (see Fig. 13.6).

13.4.2 Nanoremediation Approaches for Cr(VI) Removal

Various categories of novel (bare/modified) nanomaterials have been used in the water treatment due to their abilities like magnetic, optical, electrical, mechanical, high surface area, chemical stability, functional groups, and strong biding energy (Bhaumik et al. 2016; Dehghani et al. 2015; Herrero-Latorre et al. 2018). Besides, their state-of-the-art properties, few nanomaterials have process limitation such as high regeneration and preparation cost, hydrolytic instability, and selectivity challenges (Labied et al. 2018). Nano-based approaches like carbon nanostructure, metal organic framework, commercial materials (zeolites, activated carbon, and clay), and iron-based nanomaterials are available for the reduction of Cr(VI) into Cr(III). This section will discuss the different nano-based approach in the treatment of Cr(VI).

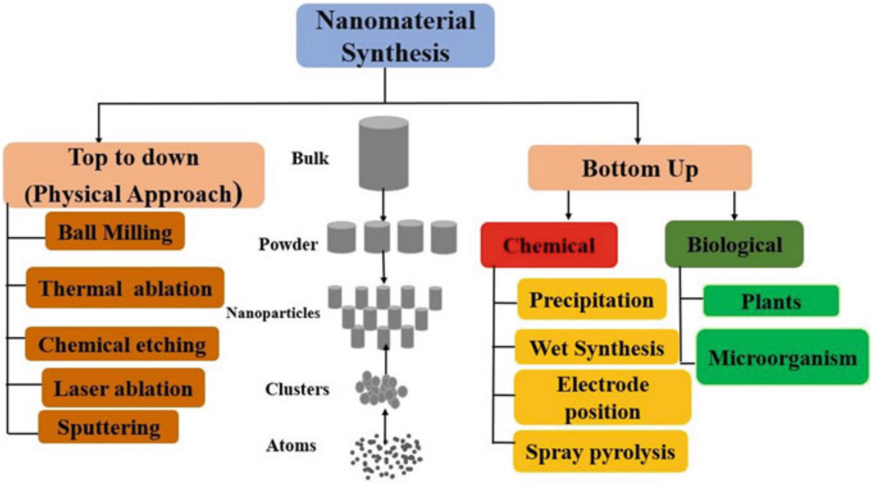

Fig. 13.6 Synthesis of nanomaterials

Carbon-based nanostructures (CNs) such as multi-walled carbon nanotubes (MWCNTs), carbon dots (CDs), graphene oxide (GOs), and carbon nanotubes (CNTs) are works as an efficient nanomaterials for absorbing Cr(VI) from aqueous solutions (Herrero-Latorre et al. 2018; Maitlo et al. 2019). Carbon nanostructure is preferred due to its mesoporous structure, strong binding energy, π-π electrostatic interaction, layered structure, high binding energy tiny size and, large surface area (Bhaumik et al. 2016). Besides having all favorable characteristics for adsorptions, CNTs have their substantial economic and technological hindrances (Luo et al. 2013). Modifications of carbon nanostructure with metals, clay, and polymer helps in their fast recovery. Studies reveal that the magnetic CNT nanomaterials doped with fluorine (F-MC) and nitrogen (NMC-100) shows the higher removal efficacies for Cr(VI) removal (Cao et al. 2016, 2017). Modification of MWCNTs with Fe_3O_4 and MnO_2 leads to the improvement of chromium removal at pH 2 with adsorption capacity of 186 mg/g due to electrostatic interaction and surface complexation mechanisms. Graphene is another carbon nanostructure which has 2D hexagonal framework that displays mechanical strength and thermal conductivity, ideal for the removal of heavy metals from aqueous solution (Peng et al. 2017b). Due to the presence of highly efficient functional groups (hydroxyl and carboxylic acid), monolayer graphite oxide is renowned for its high hydrophilicity, hydrophobic -interaction, and superior surface charge density (Ramesha et al. 2011). A study conducted by Mondal and Chakraborty (2020) reveals that GO prepared from graphite removes the 92.8% of Cr(VI) at pH 4 with dose of 0.01 g (Mondal and Chakraborty 2020). Yang et al. (2022) reveal that at initial concentration of 5 mg/L and pH 2, carbon quantum dots (CQD) have a removal efficiency of 94% in 120 min. Additionally, it has been observed that reactive oxygen species (ROS), which are created when peroxymonosulfate (PMS) is activated by

CQDs, can increase the efficiency by up to 99% even when the condition is neutral (Yang et al. 2022).

Metal organic frameworks (MOFs) are the crystalline materials which has high surface area and porosity that comprise of metal nodes linked by various organic connection (Huo and Yan 2012). MOFs have different structure and composition, together with organic and inorganic parts (Huo and Yan 2012; Mohammadi et al. 2017). Numerous MOFs have been used so far in the reduction of Cr(VI) are Uio-66 and Uio-66-NH_2 (Zhou et al. 2013), a silver-triazolato framework (Li et al. 2017), Cu-BTC (copper linked with benzene-1,3,5-tricarboxylate (BTC) framework (Maleki et al. 2015), and ZIF-67 (zeolitic imidazolate framework) (Li et al. 2015). Noraee et al. (2019) find that at initial concentration of 50 mg/L Cr(VI) and pH $\cong$ 3, the maximum adsorption capacity for ZIF-8 is 150 mg/g and Uio-66 is 85.6 mg/g. Higher adsorption capacity in case of ZIF-8 is due to the high surface area (1050 m^2/g) (Noraee et al. 2019).

Iron nanomaterials are known for their cost-effective nature, reusability, magnetic properties, and high surface area (Jain et al. 2018). Still, passivation and agglomeration are the major drawback of the iron nanomaterials (Zhu et al. 2018c). Various modifications have been applied to increase the effectiveness of iron in the aqueous solution. The chapter continues with a detailed discussion of iron nanomaterials in later part. Numerous commercially available nanomaterials like clay, zeolites, activated carbon are also available for the treatment of Cr(VI) in aqueous solution. When compared with novel NMs like CNMs, MOFs, and INMs, most of these commercial options perform worse in performance evaluations based on distribution coefficient (Kp) values (Qurie et al. 2013). In all these, activated carbon sorption capacity is good due to its microporous and mesoporous structure with high surface area and various functional group (Burakov et al. 2018).

13.4.3 Iron-Based Nanomaterials

Iron-based nanomaterials are appealing in eliminating the inorganic and inorganic contaminants from polluted water (Scaria et al. 2020; Upadhyay et al. 2019; Zhu et al. 2018a, 2016, 2018b). Iron-based nanomaterial comprises the iron oxides, nano zerovalent iron (nZVI), zerovalent iron (ZVI), bi and polymetallic zerovalent iron, and others modified iron-based materials (Brumovský et al. 2020; Diao and Chu 2021; Diao et al. 2018). Effectiveness of nano-iron forms are attributed to their high specific surface area (SSA), large reduction capacity, high efficiency, working under ranges of pH, non-toxicity, and low cost (Donadelli et al. 2020; Liu et al. 2018; Wang et al. 2020a). Furthermore, iron has a negative standard reduction potential ($E^0(Fe^{2+}/Fe^0) = -0.44$ V), making it as an effective electronic donor in the reduction and oxidation of pollutants (Mortazavian et al. 2018; Zou et al. 2021).

13.4.4 Process Mechanism of Iron-Based Nanomaterials

During the reaction process, Fe° in aqueous solution can produce Fe^{2+} and Fe^{3+}, as well as other iron derivatives. Iron-based materials can work as effective reducing agent and catalyst for the exclusion of contaminants from the aqueous medium and its conversion to their less toxic form (Montesinos et al. 2014; Zou et al. 2021; Wang et al. 2022a, 2022b; Qu et al. 2022a, 2022b). The schematic representation of reaction mechanism of iron with different contaminants in aqueous medium is given in Fig. 13.7. The most suitable mechanism for nZVI interactions in an aqueous solution is presented in Eqs. (13.3–13.5).

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + 2HO^- + H_2 \tag{13.3}$$

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + 2OH^- + H_2 \tag{13.4}$$

$$Fe^0 + 2Fe^{3+} \rightarrow 3Fe^{2+} \tag{13.5}$$

Still, owing to high of nZVI reactivity, an oxide film easily forms on its surface, averting further contact with contaminants, particularly in neutral and alkaline conditions (Gong et al. 2017; Tang et al. 2021; Wang et al. 2020a, 2020b, 2020c). So, there is the need of surface modifications of iron particles with catalytic metal, clay, biochar, surfactants, etc., to eliminate the agglomeration and increase the removal efficiency

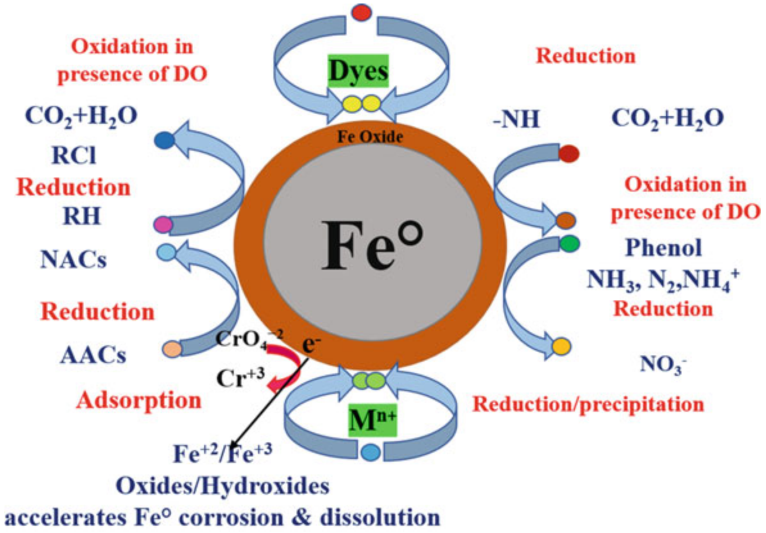

Fig. 13.7 Schematic representation of reaction mechanism of nZVI with different contaminants in aqueous medium [modified and reproduced with authorization from Lv et al. (2019), Copyright 2022, Elsevier]

(Dong et al. 2018; Fang et al. 2020, 2021; Lv et al. 2019; Rafiaee et al. 2020; Zhang et al. 2022a, 2022b).

13.5 Physical Modification

Physical modification of particles/adsorbents can substantially improve surface area, pore structure, pore volume, and other surface chemical properties. Physical modification is a straightforward and chemical-free process that can be accomplished via ball milling, sputtering, sonication, microwave pyrolysis, and gas activation (Kumar et al. 2020). The particles are transformed into fine particles under the influence of mechanical pressure or an energy field, resulting in higher SSA, and sufficient adsorption sites for the removal of pollutants such as chromium and arsenic (Li et al. 2020; Zheng et al. 2021). This chapter is mainly focused on the planetary ball mill/ball milling modification methods used in the iron-based materials in the treatment of Cr(VI).

13.5.1 Planetary Ball Milling Methods

Planetary ball mill has recently gained special attention as an innovative engineering technology in the development and modification of nanomaterials due to its simple process, higher efficiency, and lower production cost (Lyu et al. 2018; Zhang et al. 2020; Zou et al. 2021). Milling can increase the surface area of particles in a ball mill/planetary ball mill through the mechanism of high-speed grinding at the high-speed rotation of particles in jars with different types and sizes of balls. Milling can cause mechanical deformation on the structure of these nanomaterials, altering their chemical, physical, and mechanical properties, such as large surface area, surface activity, and specific affinity, which are frequently superior to those with coarser-sized grain (see Fig. 13.8). Conversion of micro into nano can be homogeneous or heterogeneous in nature (Zhang et al. 2022a, 2022b). Also, ball mill works as good loading agent, in which particles can be modified with the biochar, activated carbon, metals, clay, oxides (Deng et al. 2019; Wang et al. 2020a, b, c).

13.6 Cr(VI) Removal by nZVI/Modified nZVI and Its Mechanism in Aqueous Solution

Table 13.2 displays the list of Cr (VI) removal studies by the iron-based materials where materials prepared by the ball mill methods. Zou et al. (2021) show that modification of iron by biochar [Hickory (HC) and bamboo (BB)] by ball milling

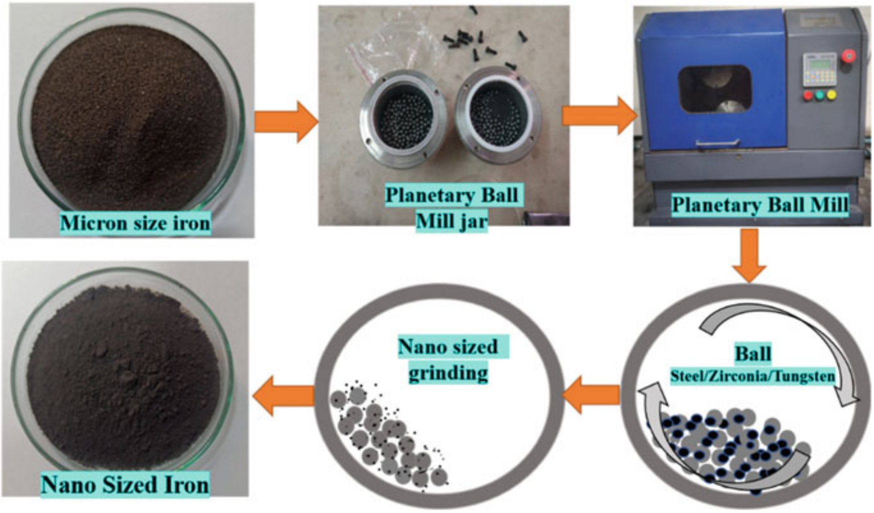

Fig. 13.8 Synthesis of nano-iron particles by the planetary ball mill from micro iron

has the removal capacity of (34.7 mg/g) for Cr(VI) at wide ranges of concentrations. Acidic pH favored the Cr(VI) removal, whereas competitive ions (Cl^-, SO_4^{2-} and PO_4^{3-}) inhibited Cr(VI) removal (Zou et al. 2021). Ye et al. (2021) suggested that for bimetallic Cu/Fe nanoparticles, with a copper loading rate of 3%, the removal capacity of Cr (VI) accelerated from 374.7 to 689.4 mg/g (Ye et al. 2021). Wang et al. (2020a, b, c) show that ball milled induced micro scale iron-carbon composite can remove the 94.01% of 20 mg/L Cr(VI) at dose of 1.0 g/L with shaking at 400 RPM within 2 h at pH 3. Furthermore, only 22.1% of Cr(VI) was reduced by simple mechanical mixing of ZVI and AC, which could be attributed to ZVI and AC's inability to form galvanic cells (Wang et al. 2020c). The maximum Cr(VI) removal percentage and capacity within 60 min for sodium citrate and biochar synergistic nZVI were 99.7% and 199.46 mg/g, respectively [Fe:C = 1:1, sodium citrate 1.12 mol%, temp. 25 °C, pH 7, and Cr(VI) initial concentration 20 mg/L] (Zhou et al. 2022). The pathway of Cr(VI) removal by an iron-based adsorbent, i.e., nZVI/modified nZVI, generally follows the adsorption, reduction, and coprecipitation process (Sinha et al. 2022; Wang et al. 2022a, 2020b). Since nanoparticles have a large surface area and pore volume, Cr(VI) is simply adsorbed on the surface of iron materials, additionally, the standard electrode potentials of $Cr_2O_7^{2-}/Cr^{3+}$ and Fe°/Fe^{2+} are + 1.36 V and – 0.44 V, respectively, which facilitates them in working as effective reductant (Zhu et al. 2018b).

The primary mechanism for Cr(VI) reduction by iron particles involves transfer of an electron from Fe° to Cr(VI) and its subsequent reduction to Cr(III) form, after which Fe° is instantly oxidized to Fe^{2+}. (Eq. 13.6) Following that, all of the Fe^{2+} present on the surface of the iron and some will be released into the solution. Further, Fe^{2+} will reduce the Cr(VI) on the surface of adsorbent (Eq. 13.7) (Zhao et al. 2019).

Table 13.2 List of studies for nZVI/modified nZVI to reduce Cr(VI) via ball milling

Base compound	Modifiers	Synthesis process	Surface area (m^2/g)	pH	Dose (g/L)	Initial Conc. (mg/)	Adsorption capacity (mg/g)	Removal (%)	Process mechanism/isotherm	References
ZVI (100 mesh)	EDTA	Planetary ball mill	0.25		1	2	–	95.7	Adsorption and reduction	Shen et al. (2020)
Ferric chloride	Rice husk and zinc chloride	Pyrolysis and ball milling	134.6	7	0.5	10	–	–	Electrostatic interaction and ion exchange	Sinha et al. (2022)
Commercial nano-iron	Fe_3O_4	–	20–25	3	–	–	–	–	Heterogeneous direct electron transfer	Montesinos et al. (2014)
Microscale ZVI	Enteromorpha Prolifera biochar	Planetary ball milling	5.99	5.4	4	20	–	99.7	Adsorption, reduction and coprecipitation	Wang et al. (2022a)
Magnetic mZVAl	Fe_3O_4	Ball mill grinding	6.51	7	3	10	8.14	95	Adsorption-reduction mechanism/Langmuir	Wang et al. (2022b)
Potassium ferrate	Corn straw	Pyrolysis ball mill grinding	–	3.2	0.5	10–100	117.49	–	Ion exchange, complexation, reduction and electrostatic attraction/Langmuir	Qu et al. (2022a)
Ferrous sulfate	Corn straws	Pyrolysis, liquid dispersion and ball milling	–	2	0.5	100	119.8	–	Electrostatic interaction complexation, reduction precipitation/Langmuir	Qu et al. (2022b)

(continued)

Table 13.2 (continued)

Base compound	Modifiers	Synthesis process	Surface area (m^2/g)	pH	Dose (g/L)	Initial Conc. (mg/)	Adsorption capacity (mg/g)	Removal (%)	Process mechanism/isotherm	References
Natural pyrite	Pine wood powder	Pyrolysis and planetary ball milling	292	5	0.25	–	118	22–100	Reduction, adsorption, surface complexation	Tang et al. (2021)
Micron iron	Activated carbon	High-energy ball milling	16.9	3	1	10	–	94.01	Adsorption, reduction and coprecipitation/Langmuir	Wang et al. (2020c)
Iron oxide	Hickory (HC) and bamboo (BB)	Ball mill grinding	241	5	0.5	50	48.1	–	Intra particle diffusion and surface electrostatic attraction/Langmuir	Zou et al. (2021)
Micron grade iron powder	Cornstalk	Planetary ball milling	29.71	–	2	30	14.59	97.8	Non-ideal sorption on heterogeneous materials/sips model	Wang et al. (2020b)

Reduction by Fe^{2+} is more active on the surface of adsorbent rather than solution, after that regeneration of Fe^{2+} occurs after the surface reaction between Fe° and Fe^{3+} (Eqs. 13.8–13.9). Following equations suggests the reduction of Cr (VI) into Cr(III) by nZVI/ modified nZVI adsorbent.

$$2HCrO_4^- + 3Fe^0 14H^+ \rightarrow 2Cr^{3+} + 3Fe^{2+} + 8H_2O \tag{13.6}$$

$$3Fe^{2+} + HCrO_4^- + 7H^+ \rightarrow 3Fe^{3+} + Cr^{3+} + 4H_2O \tag{13.7}$$

$$(1 - x)Fe^{3+} + xCr^{3+} + 3H_2O \rightarrow Cr_xFe(1 - x)(OH) \downarrow +3H^+ \tag{13.8}$$

$$(1 - x)Fe^{3+} + xCr^{3+} + 2H_2O \rightarrow Cr_x(1 - x)OOH \downarrow +2H_2O \tag{13.9}$$

Aside from that, the decline in Cr(III) concentration could have aided in the emergence of Cr(III)-Fe(III) co-precipitates (Eq. 13.8 and 13.9) (Diao et al. 2018; Montesinos et al. 2014; Zhu et al. 2018a, 2018b). XPS analysis provides the clear picture of the possible pathway of Cr(VI) removal by Fe° in aqueous solution. Zhao et al. (2019) used the novel amino-functionalized vermiculite supported iron (AVT-nZVI) for the elimination of Cr(VI) from the electroplating waste water (Zhao et al. 2019). 100% removal efficiency achieved at pH 5 with Cr(VI) 20 mg/L, whereas only 87.5% with bare nZVI in 60 min. It can be seen in the XPS spectra at Fig. 13.9a, new peak of binding energy 580 eV detected for AVT-nZVI after Cr(VI) reaction with iron. The XPS spectra for Cr 2p and Fe 2p for AVT-nZVI for before and after are given in Fig. 13.9b and c. Prior to the reaction, the peaks at binding energies 706.6 eV with Fe°, 710.4 and 723.9 eV with Fe^{2+}, and 712.6 and 726.0 eV were related with Fe^{3+} (Li et al. 2016). After the reduction of Cr(VI) into Cr(III), the Fe° peaks are indiscernible, whereas the new distribution of Fe^{2+} and Fe^{3+} peaks indicating the change in peak area. The new peaks at 579.0 eV and 588.8 eV were ascribed to Cr(VI), whereas peaks at 576.9 and 586.7 eV were allotted to Cr(III) (Fig. 13.9b, c) (Peng et al. 2017a; Wang et al. 2020b). According to these findings, a small quantity of Cr(VI) was adsorbed on the surface of the AVT-nZVI, and a significant proportion of Cr(VI) was reduced to Cr(III) by Fe° and Fe^{2+}, then oxidized to Fe^{3+} process as, (1) in aqueous solution, Cr(VI) is mainly present as the oxyanions, i.e., $HCrO_4{}^-$(pH 1–6), $Cr_2O_7{}^{2-}$ (pH 2–6), and $CrO_4{}^{2-}$ (pH > 6) (Bahador et al. 2021; Mohan and Pittman 2006; Zou et al. 2016); (2) $HCrO_4{}^-$ mainly exists between the pH 1–6 and, facilities the reaction due to its lower adsorption free energy (Wang et al. 2020a, 2020b; Zhuang et al. 2014); (3) under acidic condition, pH < PZC, the surface of the adsorbent is highly protonated and facilitates the electrostatic attraction between anion and adsorbents (Mohan et al. 2011); (4) corrosion of iron shell, expose more zerovalent particles leading to higher reduction reactivity of Cr(VI) and further precipitation of Fe-Cr^{3+} in solution adds more Fe^0/Fe^{2+} for the reaction (Huang et al. 2014; Mullet et al. 2004). While in alkaline condition, pH > PZC, so the surface of the adsorbent mainly dominated by the negative ion, which shows the electrostatic repulsion with $Cr_2O_7^{2-}$ and CrO_4^2 anions, hence decreases the reduction process, also the development of oxide and hydroxide films on the adsorbent surface blocks the reaction process (Calderon and Fullana 2015; Qu et al. 2022a, 2022b). Zhou et al. (2015) studied the impact of initial pH on Cr(VI) removal using ultrasonic assisted nZVI particles. The results show that at pH 3, removal efficiency is 100% within 5 min; however, once the initial pH is increased from 4 to 11, removal efficiency decreases from 91.1% to 37.3% at temperature 44.85 °C. As previously mentioned, at acidic pH, corrosion rate of nZVI improved due to the existence of H^+ ions and does the reactivity of Fe^{+2} ions. So, presence of both Fe^{2+} and H^+ improve the removal of Cr(VI) (Zhou et al. 2015). (Zhu et al. 2018a) discovered that when the pH increased from 5 to 7, Cr(VI) reduction capacity decreased from 100% to 40.5% when the bimetallic green synthesized nZVI (Gt-nZVI/Ni) were used. Another study discovered that at pH 3, 98.9% of Cr(VI) was removed in 10 min using a dose of 4 g/L of bare nZVI with an initial concentration of 10 mg/L, whereas at pH 7, it can take up to 100 min (Zhu et al. 2018a).

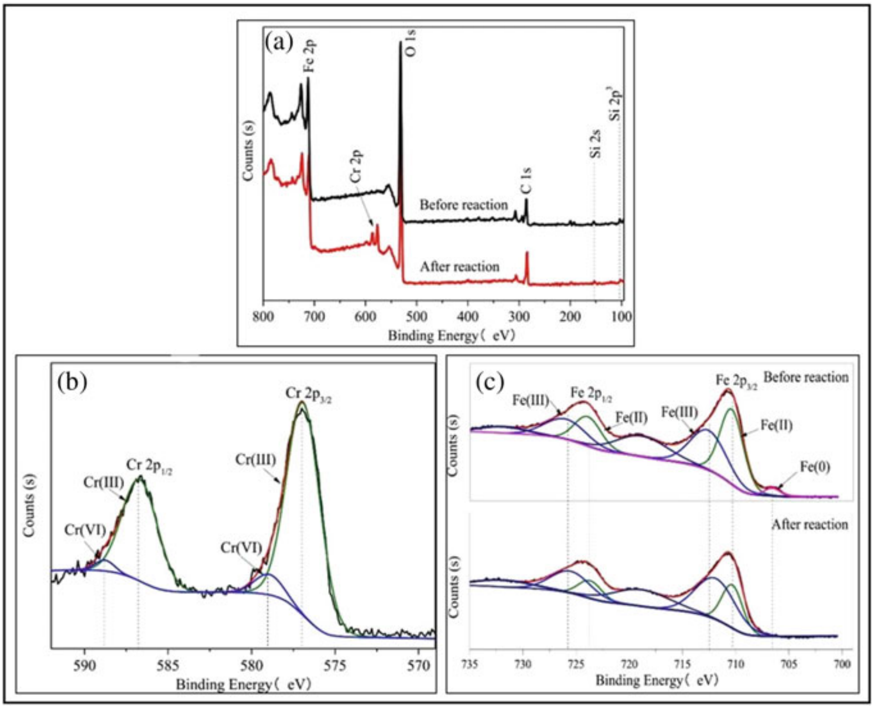

Fig. 13.9 **a** Wide scan XPS spectra of AVT-nZVI before and after Cr(VI) reactions, high-resolution XPS survey of **b** Cr 2p and **c** Fe 2p. Reproduced with authorization from Lyu et al. (2018), Copyright 2022, Elsevier

13.7 Influencing Factors in Cr(VI) Reduction

The pH, initial concentration, temperature, and co-existing anions are all important parameters in the Cr(VI) removal process. The following factors are discussed below.

13.7.1 pH

The pH of the aqueous phase is critical in the removal process because it can change the chemical form, ionization properties, and surface conditions of adsorbents (Dinda et al. 2013; Fan et al. 2019; Mortazavian et al. 2018; Wang et al. 2022a, 2014; Zhou et al. 2022). For the case of Cr(VI), acidic conditions mostly favors the reaction process as, (1) in aqueous solution, Cr(VI) is mainly present as the oxyanions, i.e., $HCrO_4^-$(pH 1–6), $Cr_2O_7^{2-}$ (pH 2–6), and CrO_4^{2-} ($pH > 6$) (Mohan and Pittman 2006; Zhuang et al. 2014; Zou et al. 2016); (2) $HCrO_4^-$ mainly exists between the pH 1–6 and, facilities the reaction due to its lower adsorption free energy (Fan et al. 2019; Liu et al. 2018; Qu et al. 2022b); (3) under acidic condition, $pH < PZC$, the surface of the adsorbent is highly protonated and facilitates the electrostatic attraction between anion and adsorbents (Bahador et al. 2021); (4) corrosion of iron shell, expose more zerovalent particles leading to higher reduction reactivity of Cr(VI) and further precipitation of $Fe–Cr^{3+}$ in solution adds more Fe^0/Fe^{2+} for the reaction (Huang et al. 2014; Mohan et al. 2011). While in alkaline condition, $pH >$ PZC, so the surface of the adsorbent mainly dominated by the negative ion, which shows the electrostatic repulsion with $Cr_2O_7^{2-}$ and CrO_4^2 anions, hence decreases the reduction process, also the development of oxide and hydroxide films on the adsorbent surface blocks the reaction process (Mullet et al. 2004; Qu et al. 2022a; Wang et al. 2022b). Zhou et al. (2015) studied the impact of initial pH on Cr(VI) removal using ultrasonic assisted nZVI particles. The results show that at pH 3, removal efficiency is 100% within 5 min; however, once the initial pH is increased from 4 to 11, removal efficiency decreases from 91.1% to 37.3% at temperature 44.85 °C (Fig. 13.10a). As previously mentioned, at acidic pH, corrosion rate of nZVI improved due to the existence of H^+ ions and does the reactivity of Fe^{+2} ions. So, presence of both Fe^{2+} and H^+ improve the removal of Cr(VI) (Calderon and Fullana 2015). Zhou et al. (2018) discovered that when the pH increased from 5 to 7, Cr(VI) reduction capacity decreased from 100% to 40.5% when the bimetallic green synthesized nZVI (Gt-nZVI/Ni) were used. Another study discovered that at pH 3, 98.9% of Cr(VI) was removed in 10 min using a dose of 4 g/L of bare nZVI with an initial concentration of 10 mg/L, whereas at pH 7, it can take up to 100 min (Zhu et al. 2018a).

13.7.2 Initial Concentration

A low initial pollutant concentration necessarily requires fewer active sites in the adsorbent, whereas a high concentration usually requires more active sites. It has been reported that as initial concentration increased, removal efficiency decreased, and overall adsorption rate increased in the process (Yavuz et al. 2006). The Cr (VI) concentration and $pH_{initial}$ affects the removal of Cr(VI) by Cu/Fe bimetallic nanoparticles, as removal efficiency decreases with increasing pH and Cr(VI) concentration. When the initial concentration was 50 mg/L, the removal efficiency of Cr(VI) was 89.25, and once the initial concentration rises to 100, 150, and 200 mg/L, the corresponding removal efficiencies were 68.9 5, 40.7 5, and 32.8 5, respectively (Zhou et al. 2022). Shyaa et al. (2015) reported that adsorption by polyaniline/zeolite nanocomposites, where Cr(VI) adsorption enhanced with increasing initial Cr(VI) concentration. This can be explained as initial Cr (VI) concentration increased, higher mass transfer resistance between Cr(VI) and the adsorbent increased the adsorption. This increases the likelihood of collisions between Cr(VI) ions and sorbent, resulting in increased metal uptake (Shyaa et al. 2015).

13.7.3 Effects of Temperature

The reaction temperature, which affects ion mobility and adsorbent reactivity, is among the critical factors influencing the Cr(VI) removal mechanism in aqueous solution (Dinda et al. 2013). Various results show that increasing the reaction temperature enhances the removal rates of Cr(VI) because it promotes ion dispersion in solution and raises the accessibility of active surface sites (Liang et al. 2017; Zhu et al. 2018a, 2018b). Removal of Cr(VI) with increasing temperature suggests it as an endothermic adsorption process (Fan et al. 2019). Yin and Wang (2017) used the bare nZVI particles, suggest that the increasing the temperature (10–30°) favors the reaction process. The value of ΔH was $+ 8.78$ kJ/mol which verifies the endothermic process, while positive value of $\Delta S = + 31.73$ kJ/K mol shows the high randomness between solid and liquid medium during the reduction process. Negative ΔG value in the reaction approves the spontaneous reaction on nZVI surface (Yin and Wang 2017). Lv et al. (2019) outlined that the sulfide modified nZVI removal efficiency increased from 42.6 mg/g to 59.9 mg/g, when reaction temperature raised from 283 to 313 K (Lv et al. 2019). Similar report by Lv et al. (2013) shows that by varying the temperature from 10 to 40 °C, removal percentage increased up to 32% and rate constant increase from 0.023 to 0.077 g/mg/min in 2 h with $Cr(VI)_{initial}$ 40 mg/L, pH $= 8$ and dose $=$ nZVI $= 0.05$ g/L $+$ $Fe_3O_4 = 0.60$ g/L (Lv et al. 2013).

13.7.4 Effects of Co-existing Ions

The existence of co-existing anions in aqueous solution is a crucial parameter in defining the pertinency of iron-based adsorbent at the field scale in real-time scenario. Co-existing anions can participate for active sites in the adsorbent, significantly reducing its adsorption capacity. Nitrate, sulfate, phosphate, chloride, carbonate, and bicarbonate are predominant anions found in real wastewater (Rajapaksha et al. 2022; Zhu et al. 2018a) The effects of anion on removal efficiency can be determined by the redox potential of the ions and the functional groups (O or N) present. As per Zhou et al. (2018), the Cr(VI) removal efficiency of nZVI/biochar was tested in the vicinity of NO_3^-, SO_4^{2-}, and PO_4^{3-}. In presence of NO_3^- at 20 mg/L, efficiency decreased from 100% to 92.8%, while SO_4^{-2} and PO_4^{3-} does not show any higher repressive effect. Higher impact of NO_3^- ion may be due to the higher redox potential (NO_3^-/NO) (Zhu et al. 2018b). Another study by Diao et al. (2018) reveals that the presence of > 5 mg/L of Malachite green (MG) in solution could effects the Cr(VI) removal, but when concentration raised up to 10 mg/L, removal efficiency decreased (Diao et al. 2018). Zhao et al. (2021) found that the existence of anions like SO_4^{2-}, Cl^-, HPO_4^{2-}, and NO_3^- has enhanced the Cr removal efficiency of O-rich biochar. The formation of coordination bonds between Cr(VI) and O-rich biochar is the main mechanism underlying this improved pollutant removal, while in presence of N-rich biochar, competing anions reduced the extent of Cr(VI) adsorption in the order of effect was $Cl^- > NO_3^- > SO_4^{2-}$ (Zhao et al. 2021). Analogous findings were reported by Shang et al. (2017) for biochar/nZVI composite, where the presence of sulfate and humic acid improved the removal of Cr(VI) from water solution. Since sulfate is corrosive, and HA collates on the adsorbent, this could be associated with increased accessibility of reactive sites. Because of their distinct molecular dimensions, charge density, and hydration degree, anions such as Cl, NO_3^-, SO_4^{2-}, and PO_4^{3-} compete for Cr(VI) adsorption (Shang et al. 2017). The least inhibiting effects were produced by Cl, while the most by PO_4^{3-} (Duranoğlu et al. 2012). Additionally, sorbent characteristics such as particle size, surface area, surface charge, and surface chemical composition have a significant impact on Cr(VI) sorption efficiencies (Rajapaksha et al. 2022).

13.8 Regeneration and Recycling Capabilities

The reusability of any nano-adsorbent is a critical consideration in determining whether it is a viable candidate for practical pollution removal. This is also an important consideration when determining whether or not the material is cost effective (Gao et al. 2018). It is critical to consider the adsorbent's reusability and regeneration capacity when designing materials for adsorption-based removal. Regeneration is the use of cost-effective procedures for the operational regeneration or reprocessing of used up adsorbent materials (Vakili et al. 2019). Another advantage of regeneration is the recovery of absorbed contaminants and their use as manufacturing feedstock. Various regeneration techniques, such as acid or alkali wash, are used to reuse spent materials. This is usually accomplished through a desorption process, in which the adsorption process is reversed and the adsorption sites become available for further cycles. In terms of recovery, the desorption ratio can be used to calculate the degree of regeneration in an adsorbent's adsorption sites (Eq. 13.1) (Zhou et al. 2018).

$$\text{Ratio of Desorption} = \frac{\text{Amount of Cr(VI)desorbed ions}}{\text{Amount f Cr(VI)adsobed ions}} \times 100 \tag{13.10}$$

n

The category of regenerating agent and the transformation mechanism should be considered when determining the best recovery method for a specific adsorption material.

13.9 Conclusion

Over the decade, it has been seen that Cr(VI) contamination in the aqueous solution is become a major concern due of its higher mobility, carcinogenicity, and toxic properties. Cr(VI) and Cr(III) are the most accessible categories of chromium in atmosphere, with the trivalent form works as a bioelement in human and the hexavalent form acting as a major pollutant. This chapter focused on the adverse impacts of hexavalent chromium [Cr(VI)] on water and methods used to treat it. The source, toxicity, speciation of chromium compounds, cycle, and human health risk have all been discussed extensively. Furthermore, the chapter discusses the long-term remediation using iron-based nanomaterials, various controlling factors that affect Cr(VI) removal processes and adsorbent regeneration capabilities. Various treatment technology is available for the conversion of Cr(VI) into non-toxic Cr(III) forms, but iron-based nanomaterials work as efficient adsorbent due to its negative reduction potential, i.e., $E^0(Fe^{2+}/Fe^0) = -0.44$ V) making it an effective electronic donor in the reduction process. Iron-based nanomaterials like nZVI and iron oxides remove Cr(VI) effectively, but their reactivity causes iron surfaces to become agglomerated and passivated. These problems can be fixed by using surface modification physical strategies like ball milling with biochar, activated carbon, metals, clay, etc. Numerous papers have been published on the reduction of Cr(IV) to Cr(III) via iron-based metal modification via ball milling. Adsorption, reduction, and coprecipitation are the primary reaction mechanisms for Cr(VI) reduction, with the Langmuir isotherm being the most commonly followed. Acidic pH facilitates the process due to electrostatic attraction between chromium species ($HCrO_4^-$) and H^+ ions, whereas alkaline pH decreases the process due to repulsion with OH^- ions. Initial concentration, temperature, dose, and presence of co-existing anion effects the process and too significant for testing the field scale studies. Adsorbent reusability is an important step in determining the adsorbent's cost effectives and use in the industrial scale. As a result, we can assume that using iron-based technology for Cr(VI) treatment could become an effective and long-term chromium removal technology.

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Part V
Membrane Technologies for Remediation of Persistent Pollutants

Chapter 14
Removal of Urea and Ammonia from Wastewater

Rashmi Ranjan and Swatantra P. Singh

Abstract Compounds like urea and ammonia form one of the major constituents of wastewater. Urea is a principal outcome of protein degradation in mammals and is abundant in sewage wastewater. Urea is also widely used as fertilizer in agriculture. The production of 1300 tons of urea per day results in a wastewater output of 650 tons per day. The discharged wastewater comprises 0.5–2 wt% urea, which contributes to water pollution and algal growth, leading to eutrophication. Ammonia is produced by the hydrolysis of urea, which is very hazardous and toxic to aquatic organisms. Ammonia and urea leach from breeding farms, agricultural runoffs, and many other industrial processes. These can be treated and recovered from wastewater for fertilizer and energy production, reducing the risk of water pollution. There are various technologies for the removal of urea and ammonia, some of which are widely used while others are relatively new. Physicochemical, electrochemical, as well as non-electrochemical methods can be utilized to remove urea and ammonia. Electrochemical and non-electrochemical methods can remove urea. Non-electrochemical treatment methods for urea removal are hydrolysis, enzymatic decomposition, biological degradation, decomposition by strong oxidizing agents, and degradation by catalysts. Electro-oxidation and bio-electro-oxidation are electrochemical methods to remove urea. Urea in urine can be utilized to produce energy through direct urine fuel cells and microbial fuel cells. There are various physicochemical methods for the removal of ammonia. Some of the methods, like air stripping, struvite precipitation,

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and ion exchange, are very common. Microwave radiation and ozone microbubbles are relatively new and costly. Membrane-based processes like reverse osmosis are gaining interest. The chapter focuses on various wastewater treatment methods for urea and ammonia removal. The chapter also aims to describe methods of using urea-containing urine waste streams for their potential application in space to produce energy.

Keywords Urea · Ammonia · Urea removal · Ammonia removal · Wastewater treatment · Fuel cells · Biological method · Electrochemical method

14.1 Introduction

Water pollution is the most concerning environmental problem. The global freshwater reserve is decreasing exponentially, and soon the water will be scarce even for drinking. Although we are facing a water shortage, there is little reduction in water pollution. Water is being polluted by the industrial, agricultural, health, and domestic sectors (Wald 2022). There are various wastewater streams generated due to different human activities. Treating wastewater is important to reduce water stress and prevent environmental pollution. Urea and ammonia are generated by fertilizer industries, agricultural runoff, animal breeding farms, and human urine discharge. Nitrogenous compounds in water (nitrate, nitrite, and ammonia) promote algal growth leading to eutrophication. Eutrophication causes the natural dying of lakes and other freshwater bodies. Ammonia and ammonium compounds harm aquatic and human life. Urea is used largely as fertilizer, but when it enters water streams, it has a detrimental effect. Urea slowly hydrolyses into ammonia. The ammonium ions at low pH and ammonia at high pH constitute the total ammonia content of water. $NH_{3,}$ an uncharged molecule, can easily diffuse into the cells of aquatic organisms compared to the NH_4^+ (Khuntia et al. 2013a) and hence is more dangerous. A study shows that in fish, ammonia could interfere with oxygen transfer (Ramadevi 2020; Yuan et al. 2016a). Ammonia is a volatile substance and is considered lethal and dangerous. High ammonia levels cause toxicity in fish, animals, and birds and also affect plant growth. Ammonia causes irritation and corrosion of the lungs, throat, and skin (Rahimpour et al. 2010).

Wastewater generated by industries can have ammonia ranging from 5 to 1000 mg/L. These comprise waste generated by fertilizer, coking, pharmaceutical, petroleum refinery, breeding farms, and catalyst industries (Adam et al. 2019). Urine constitutes approximately 75–80% of the nitrogenous compounds in domestic wastewater; however, the volume sums to 1% of the generated wastewater. Thus, it is important to treat this wastewater. Various techniques are currently in use, and some are being investigated for their potential application. Traditional techniques that have been used to treat urea-containing wastewater involve biological methods used for hydrolysis into ammonia. Biological methods are commonly used for the treatment of municipal as well as industrial wastewater (Capodaglio and Raboni 2015). The process involves the oxidation of ammonia to nitrate and nitrite (oxic conditions) by nitrifying bacteria, which are then converted to nitrogen gas by denitrifying bacteria (anoxic conditions). However, the process is sensitive to pH change, dissolved oxygen, and temperature (Pawlak-kruczek and Urbanowska 2019). Urea can be hydrolyzed into ammonia by the use of the urease enzyme, but the process efficiency is usually low. The most commonly used methods for the removal of urea are enzymatic and catalytic decomposition, the use of strong oxidants and adsorbents. Electrochemical methods have also been used, such as bio-electro-oxidation (Pawlak-kruczek and Urbanowska 2019). Due to the high urea and ammonia content in human urine, it can be used as an alternate source of fuel in space (Lu et al. 2019). Urea and ammonia are both hydrogen carrier compounds, but due to the toxicity of ammonia, it is rather difficult to store. Urea, on the other hand, is inflammable, can be easily stored, and is non-toxic. Urea has a gravimetric hydrogen content of 6.7 wt %, which amounts to a high energy density for use as fuel (Nagao et al. 2015). Therefore, urine wastewater can be directly used to produce energy or treated to recover water. Direct urea fuel cells and microbial fuel cells have been tested for energy production from urine. They have shown promising results and can also be used for urine water recovery or to produce energy (biohydrogen) in space (Lan et al. 2010; Lu et al. 2019).

The ammonia/ammonium produced by urea hydrolysis or free ammonia from industrial discharge can be sequentially removed by ammonia stripping under alkaline conditions (Yuan et al. 2016b) or precipitation by magnesium salts into struvite (Shin and Lee 1998). The reduction of the nitrogen load through struvite precipitation ($MgNH_4PO_4 \times 6H_2O$) is affected by various parameters like pH, temperature, and amount of magnesium, phosphorus, and calcium. Maintaining a weakly alkaline condition may be required in case the wastewater has an excessive amount of NH_4^+ ions. The ion-exchange (IE) process is another popular method owing to its low cost, availability of natural minerals like zeolites or bentonites, and relative ease of application. Furthermore, ammonium can be recovered and reused in various ways, e.g., as an N-fertilizer by ion exchange (Karri et al. 2018; Pawlak-kruczek and Urbanowska 2019). There are other methods, like microwave radiation and ozone microbubbles, that can remove ammonia from the water. Their high cost and efficiency are still a hurdle in their practical application. Membrane-based technologies like reverse osmosis can remove even low concentrations of ammonia from wastewater. Reverse osmosis needs pre-treated water and suffers from membrane fouling.

Every technology has its own merits and demerits, so there is a constant need to develop a technology that has relatively low disadvantages. Urine-containing wastewater is a rich source of nitrogen (N), phosphorus (P), and sulfur (S) nutrients. Resource recovery from urine wastewater would be helpful for pollution control and also benefit agriculture (Lu et al. 2019). The chapter focuses on the various technologies available to treat wastewater containing urea and ammonia in detail. Furthermore, different electrochemical and non-electrochemical methods for urea removal have been discussed. The application of urea and ammonia as alternate energy sources in space has also been described. Furthermore, the techniques to remove ammonia by various physical and chemical methods have been elaborated. For the efficient recovery of nitrogen from urea and ammonia wastewater, it is important to use various technologies together to target each compound. Various state-of-the-art technologies utilizing the technologies mentioned in the chapter have been proposed for the removal of urea and ammonia (Larsen et al. 2021). The understanding of these techniques can help treat the urea and ammonia-rich wastewater generated by various sources.

14.2 Treatment Methods for Removal of Urea

Urea is the most widely used compound in agricultural fertilizers, and also, it is one of the important components of human urine. Urea and it's breakdown product, ammonia is toxic to aquatic life. When it enters natural water bodies, urea, a nitrogenous compound, promotes algal growth and thus causes eutrophication. It is very important to treat the wastewater containing urea and reduce the nitrogen load of wastewater before discharge.

14.2.1 Non-electrochemical Methods

Hydrolysis of Urea. The urea-containing wastewater is allowed to come in contact with high-pressure steam. The process operates under conditions of high temperature and pressure. The process's decomposition outcomes are ammonia gas and carbon dioxide gas, which are then separated. Around 94% reduction in the nitrogen content of wastewater occurs. One method for urea hydrolysis involves heating wastewater at 200–220 °C for around 0.5 h under 2–3 MPa pressure. The cooling of the hot wastewater is done by feeder wastewater. The flash separator then separates the gaseous phase and condenses the liquid (Urbańczyk et al. 2016a).

Enzymatic Decomposition of Urea. The enzyme used in the process is urea amidohydrolase (urease), which may be used either as free or immobilized to some support. Urease is a nickel-dependent enzyme (made up of binuclear Nickel as an active center), found in numerous plants and microorganisms. Urease acts as a catalyst in the breakdown of urea to ammonia and carbamic acid (reaction 14.1), which is eventually broken down to ammonia and carbon dioxide (reaction 14.2) (Estiu and Merz 2004). This urease-catalyzed urea breakdown reaction is pH-dependent. Immobilized urease shows less sensitivity to changes in pH, and the enzyme activity is not easily lost. The initial activity of the enzyme, which is 86% retained even after using it through 15 cycles (Estiu and Merz 2007; Urbańczyk et al. 2016a).

$$\mathrm{CO(NH_2)_2} \xrightarrow{\mathrm{H_2O,\ urease}} \mathrm{NH_3} + \mathrm{NH_2COOH} \tag{14.1}$$

$$\mathrm{NH_2COOH} \xrightarrow{\mathrm{yields}} \mathrm{NH_3} + \mathrm{CO_2} \tag{14.2}$$

A conjunction of the electrodialysis process and enzyme urea hydrolysis can also be used. The method requires placing the immobilized urease in the electrodialysis between the cation exchange membranes (CEM) and anion exchange membranes (AEM). This is a very efficient method for removing the products of the decomposition of urea in the presence of an electric field (Urbańczyk et al. 2016a).

Urea removal by biological method. The urea wastewater is allowed to flow through biofilters or bioreactors in a series made up of different bacterial strains that decompose urea's organic nitrogen into nitrogen. The first stage in the process is Ammonification, in which urea is converted into ammonium ions. The next stage is nitrification where ammonium ions are converted into nitrite by *Nitrosomonas* (reaction 14.3). The nitrite is then converted into nitrate by *Nitrobacter* (reaction 14.4) (Ghaly and Ramakrishnan 2013). The nitrification process occurs under oxic conditions. The final stage is denitrification, where nitrite or nitrate is converted into molecular nitrogen gas (reaction 14.5) in the absence of oxygen (Urbańczyk et al. 2016a).

$$NH_4^+ + \frac{3}{2}O_2 \xrightarrow{Nitrosomonas} HNO_2^- + H_2O + 2H^+ \quad (14.3)$$

$$NO_2 + \frac{1}{2}O_2 \xrightarrow{Nitrobacter} NO_3 \quad (14.4)$$

$$2NO_3^- + 10e^- + 12H^+ \rightarrow N_2 + 6H_2O \quad (14.5)$$

The challenge associated is the sensitivity of the microbes to different factors, complex reactions, and difficulty in control. Thus, it is very important to control the different parameters like pH and temperature. The other limiting factors are the presence of inhibitors and the flow rate of urea. Extensive research is required to investigate microbial resistance to harsh pH, temperature, and initial urea concentration.

Decomposition by use of strong oxidants. Strong oxidants like ozone and sodium chlorate are employed in this method. The process is very effective, but the cost for the production of ozone required is very high. Decomposition products include nitrate ions when treated with ozone. Nitrogen, carbon dioxide (reaction 14.6), which are non-toxic gases, and sodium chloride were formed as decomposition products when sodium chlorate is used (Muhammad Yusuf et al. 2019; Urbańczyk et al. 2016a).

$$CO(NH_2)_2 + O_3 \rightarrow N_2 + CO_2 + 2H \quad (14.6)$$

Removal of urea using adsorbents. The method is based on urea wastewater flow through a bed of adsorbents which may consist of activated carbons, zeolites, ion-exchange resins, and silica particles. Porous polymers and silica gels are common adsorbents. Chitosan and its derivatives are some materials that are good adsorbents. Urea removal using chitosan and its derivatives was studied, and the kinetics were also determined. Cross-linked chitosan derivatives showed a high rate of uptake (Xue and Wilson 2016). The highest degree and capacity of urea uptake were observed for Cu (II) complex cross-linked with chitosan. Adsorption of urea was also studied in Cu (II)/chitosan membrane. The study showed highest adsorption capacity was 78.8 mg urea/g membrane. These membranes could be used for hemodialysis (Urbańczyk et al. 2016a).

Catalytic decomposition of urea. The urea can be catalytically decomposed using Pt/SiO_2 catalyst. This can be carried out in nitric acid and formic acid solution in water in a temperature range of 58.5–76 °C. This initially forms fulminic acid, which reacts with nitric acid forming nitrogen. Some other by-products, like ammonium ions and carbon dioxide, are also formed. The reaction is initiated by the nitrite ions formed at the active site of the Pt catalyst. Alumina (Al_2O_3) can also be used as a catalyst for urea decomposition. The highest catalytic activity was exhibited by η form of alumina compared to other forms (Urbańczyk et al. 2016a).

The different methods have different principles, mechanisms, and products obtained. The points of comparison have been listed in Table 14.1.

14.2.2 Electrochemical Methods for Urea Removal

Electrochemical oxidation of urea. Electro-oxidation is a type of advanced oxidation process (AOP) that comprises electrodes that convert wastewater components (water, oxygen, and chloride) to oxidants such as reactive oxygen species (ROS) (Enache et al. 2009; Hu et al. 2020; Thostenson et al. 2017) and chlorine-containing species (CCS). Electro-oxidation process using different electrode pairs has been studied and investigated. Commonly used anodes in the process are TiO_2 (Simka et al. 2009), IrO_2 (Lei et al. 2009), Pt, graphite, and Boron-doped diamond (BDD) (Arai and Fricker 2021). Nickel (Yan et al. 2012), zirconium, and tungsten are frequently used cathodes (Arai and Fricker 2021; Kim et al. 2005). Electrochemical removal of urea can be achieved through direct or indirect methods. The anodic treatment is the most straightforward method for the removal of electrochemical urea waste. In the direct method, urea oxidation takes place at the electrode surface. Urea in an aqueous solution is oxidized on the anode and converted into nitrogen (anode reaction 14.7) (Urbańczyk et al. 2016a). A study used nickel-based electrodes for the electrochemical oxidation of urea and potassium hydroxide as the alkaline media (Yan et al. 2012). The nickel-based electrode produces hydrogen at a very low voltage of 0.37 V compared to the 1.23 V required in the splitting of water for hydrogen. The electrolysis of urea is catalyzed by trivalent nickel (NiOOH) ions (Boggs et al. 2009). This approach can be utilized for energy production in space to decrease the amount of stored hydrogen needed. Indirect electrochemical oxidation of urea occurs through reactive species. The hydroxyl radicals act as the oxidizing agent (Zaher and Shehata 2021). Urea is removed by a chemical reaction of urea with the reactive species formed at the electrodes. An important benefit of this technique is that the

Table 14.1 Comparative analysis of various non-electrochemical methods of urea removal (Urbańczyk et al. 2016a)

Method of decomposition of urea	Principle	Process parameters	Degradation products	References
Hydrolysis	Application of high temperature and pressure	Temperature (120–236 °C), pressure (1.7–3.7 MPa), and residence time	NH_3 and CO_2	Simka et al. (2009)
Enzymatic hydrolysis	Urease enzyme application	Immobilization or modification of the enzyme and pH (6.5–7.5)	NH_3 and CO_2	Krajewska (2009)
Biological degradation	Flow through biofilters	Bacterial strain, pH (7.0–9.0), flowrate (e.g., 100 L h^{-1})	N_2 or NO_2^- ions and CO_2 (depends on the strain)	Simka et al. (2009); Wong-Chong and Loehr (1975)
Decomposition by strong oxidants	Addition of a strong oxidizing agent	Oxidant (ozone, sodium chlorate, metal ions), pH	N_2 or NO_2^- ions and CO_2 (depends on the oxidant)	Simka et al. (2009)
Adsorption	Flow through a bed or addition of a sorbent	Adsorbents (activated carbon, zeolites, ion-exchange resins, or silica), flow rate	N/A	El-Lateef et al. (2019)
Catalytic decomposition	Addition of a catalyst	Catalyst (Pt, Al_2O_3, TiO_2), temperature (R90 C)	N_2, NH_3, NO_2^- ions, and CO_2	Yang et al. (2019)

decomposition products obtained are gaseous and are not harmful to the environment (Urbańczyk et al. 2016a). Urea electro-oxidation occurs according to the following half-reactions (reactions 14.6–14.8) in direct electrochemical oxidation.

$$\text{Anode}: \quad CO(NH_2)_{2(aq)} + 6OH^-_{(aq)} \rightarrow N_{2((g))} + 5H_2O_{(l)} + CO_{2(g)} + 6e^- \quad (14.7)$$

$$\text{Cathode}: \quad 6H_2O_{(l)} + 6e^- \rightarrow 3H_{2(g)} + 6OH^-_{(aq)} \quad (14.8)$$

$$\text{Overall}: \quad CO(NH_2)_{2(aq)} + H_2O_{(l)} \rightarrow N_{2((g))} + 3H_{2(g)} + CO_{2(g)} \quad (14.9)$$

Direct urine Fuel cells. Direct urine fuel cells (DUFCs) use urea as an energy source. The urea oxidation reaction (UOR) in DUFCs occurs on the anode catalyst, which is

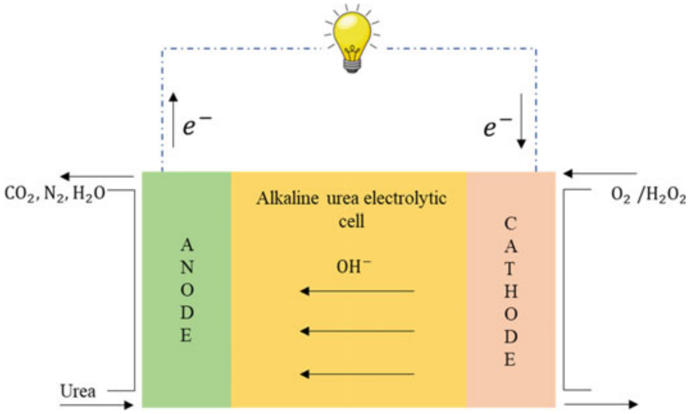

Fig. 14.1 Scheme of DUFC

an important component. Metals like Pt, Pd, etc., were very widely used as electrodes (Boggs et al. 2009). However, nickel is a very reliable and cost-effective alternative to such expensive electrodes. Nickel–cobalt bimetal can be used as an anode in DUFCs to produce electricity directly. The theoretical open-circuit voltage (OCV) of DUFCs is calculated to be 1.146 V (Guo et al. 2016). The voltage obtained in DUFCs is very faintly lower compared to H_2/O_2 fuel cells. Thus, DUFC is an attractive alternative that combines both waste utilization and power generation thus useful for the ISS power generation system (Urbańczyk et al. 2016a). Figure 14.1 depicts the diagram of DUFC for H_2 production from urea.

Bio-electro-oxidation of urea. It is a system that combines electrochemical oxidation and urease enzyme. The process of bio-electro-oxidation of urea was studied using urease immobilized on a carbon electrode. Urea degraded into ammonia and carbamic acid in the presence of urease. The carbamic acid was broken down into ammonia and carbon dioxide, and finally, the ammonia was converted into molecular nitrogen. This process has potential uses for the treatment of urine at ISS (Nicolau et al. 2014; Urbańczyk et al. 2016a). Firstly, urea undergoes conversion into ammonia in a biological reactor containing urease. Urea Bioreactor Electrochemical System (UBE) is comprised of a bioreactor that has urease immobilized on granular activated carbon (GAC-urease) for urea conversion into ammonia and an electrochemical cell for the oxidation of ammonia (Fig. 14.2) (Nicolau et al. 2014). The ammonia is then utilized by the electrochemical cell, which converts ammonia to hydrogen and can be used as fuel (Fig. 14.2). The proposed system brings about 80% TOC removal and 86% conversion of urea to ammonia (Nicolau et al. 2014).

Microbial fuel cells (MFCs). MFCs are modified bio-electrochemical degradation of urea that involves the use of microorganisms. MFCs make use of microbial biochemical degradation pathways to decompose urine, producing electrons, which generate power (Urbańczyk et al. 2016a). Electroactive bacteria grow on the anode degrading

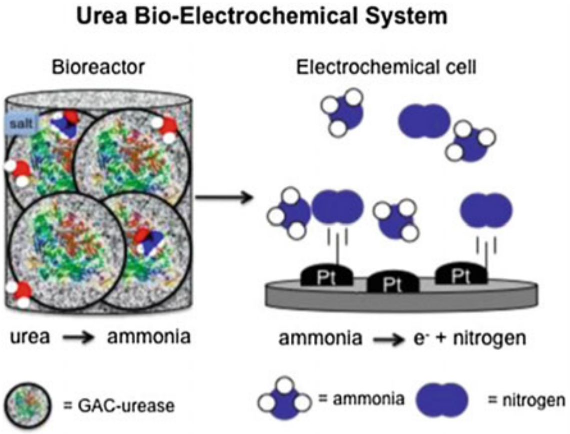

Fig. 14.2 UBE system showing the bioreactor containing immobilized urease. Reprinted with permission from Nicolau et al. (2014), 2014, American chemical society

urea, releasing electrons that generate current in the external circuit or hydrogen gas. Fresh urine can be directly fed in batch or continuous mode (Ieropoulos et al. 2012). Struvite precipitation can also be done along with MFC for resource recovery. A three-stage integrated MFC system can provide energy and hydrogen gas and help recover resources from urine (Gajda et al. 2019; Jadhav et al. 2020). Bacterial biofilm is formed on the anode of the fuel cell. A proton exchange membrane (PEM) is employed for the separation of the two electrode chambers (Gude 2016). Ieropoulos et al. (2012) conducted field trials for human urine energy production and obtained a maximum power of 800 mW connecting 432 MFC units, and a 95% COD reduction was observed. Bacterial activities limit the performance of MFCs in the anode chamber. The biochemical pathway of such electrogenic bacteria is still under investigation (Jadhav et al. 2020).

14.3 Treatment Methods for Removal of Ammonia

Ion-Exchange (IE) Process

Using Zeolites. In recent years, the application of the ion-exchange process has been very wide in many fields. It has been used for ammonium ions removal from water. The most used ion exchanger for the removal of ammonium was Zeolites. Zeolites are very porous alumino-silicates having cavity structures of negative charges in a 3-D framework (Lei et al. 2009). The negative charge on the zeolites is stabilized by the oppositely charged ions. The zeolites are attractive adsorbents for ammonia removal. Due to their high capacity, enormous adsorption surface area, high efficiency, and very low price, zeolites are preferred.

Using Polymeric Ion-exchangers. Polystyrene cross-linked with divinylbenzene used as IE resins is one of the most common polymers. They have extraordinary adsorption capThe system comprises controlsacity and high kinetics compared to zeolites at high temperatures, although applications at such high temperatures are not common but may be very important in some processes. Dowex 50 w- × 8 (the Dow Chemical Company) is an example of a polymeric ion exchanger. It is a polystyrene polymer that is cross-linked with divinylbenzene (Capodaglio and Raboni 2015).

Adsorption. The most common type of adsorbents is activated carbon, metallic oxides, and zeolites. Natural zeolites like clinoptilolite and clays can also be used to remove ammonia (Huang et al. 2018). Ammonia on reaction with chlorine in water forms chloramines like monochloramines, and dichloramines which can be easily absorbed by activated carbon (Xiang et al. 2020). A carbon intermediate (CO*) is formed due to the catalytic reaction involved in the process. Activated charcoal of very fine mesh size removes chloramines more effectively than the coarse one due to more surface area for adsorption and faster access to the active site for the reaction. Selecting AC having increased sites for CO* formation leads to improved removal of chloramines (Capodaglio and Raboni 2015).

Ammonia Precipitation (Struvite Precipitation). Ammonia (NH_4^+-N) can be precipitated as Magnesium Ammonium Phosphate (MAP), commonly known as Struvite, by adding Mg salts (Karak and Bhattacharyya 2011). This process has been used in many different types of wastewater treatment processes. MAP is almost insoluble in water and hence can be easily separated from water. MAP is composed of magnesium, phosphorous, and nitrogen, similar to the fertilizers available on the market and hence can be used as fertilizers (Karak and Bhattacharyya 2011; Wei et al. 2018).

The Struvite precipitation process depends on pH as well as temperature. The presence of impurities like calcium can also affect the process (Nagy et al. 2019). The most common reagent used in precipitation is $MgCl_2$. The salt is added to urine wastewater in a reactor which reacts with the ammonia and phosphate present in urine to produce MAP (Fig. 14.3). MAP precipitates in the solution and can be easily removed (Tilley et al. 2008). The main constraint in the application of struvite precipitation in nutrient recovery is the high cost involved in the addition of magnesium salt, which is not economical. The reactors commonly used in the process are fluidized bulk reactors and stirred tank reactors (Capodaglio and Raboni 2015).

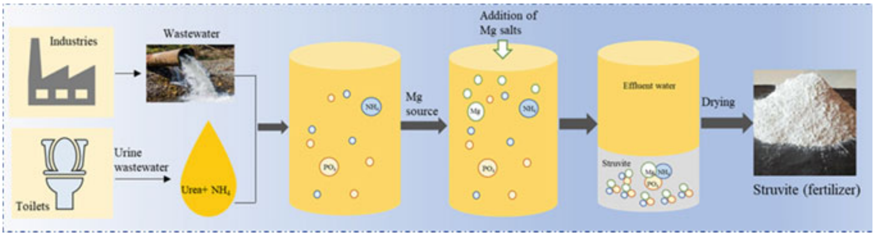

Fig. 14.3 Struvite precipitation using magnesium salts

Ammonia stripping. The ammonia stripping technique is frequently operated in urea fertilizer industries to decrease ammonium concentration in discharged wastewater (Machdar et al. 2018). Ammonia stripping can be of two types—air or steam stripping. Two packed towers are involved in the process, which allows the transfer of ammonia in the wastewater to the gas phase and the conversion of the gaseous ammonia into a stable ammonium salt using an acid solution. The salt obtained can serve as an alternative to fertilizer. The addition of lime and other caustic substances is done in the process of increasing the pH to 10.8–11.5 std. units. The increased pH allows the coercion of ammonium hydroxide to ammonia gas. The process of air stripping is more common as compared to steam stripping (Capodaglio and Raboni 2015; Wei et al. 2018).

Steam stripping is similar to air stripping except that it requires a higher temperature to operate, which is more than 95 °C. When recovery of ammonia is economical, steam stripping is used. Ammonium sulfate is formed by the reaction of ammonia with sulfuric acid. To determine the operating conditions for effective removal of ammonia and the effects on other parameters, an experiment was conducted (Yuan et al. 2016a). The experimental setup (Fig. 14.4) for the ammonia stripping process is described below.

The system comprises controls for gas and liquid feed, RPB, effluent analyzer, and exit gas neutralizer. The RPB packing material comprises grade 304 stainless steel wires which are interconnected. The feed rate of the aqueous ammonia solution

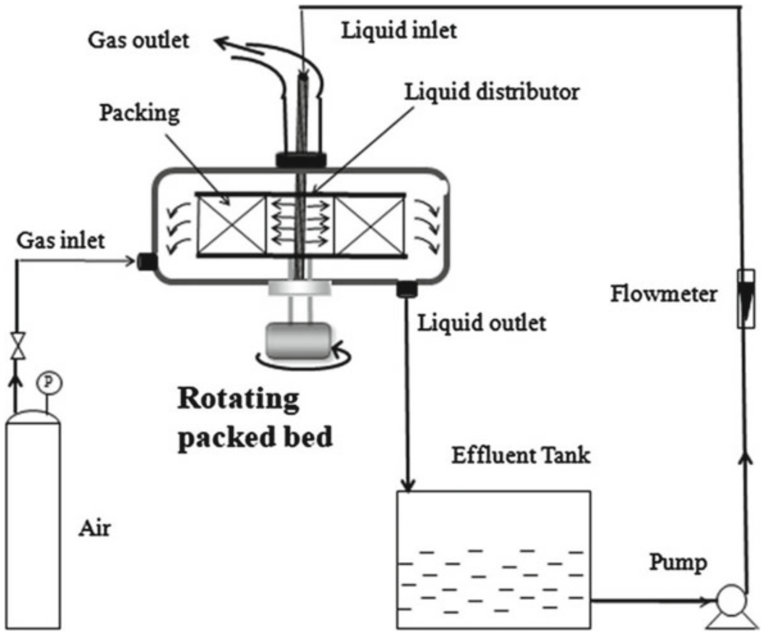

Fig. 14.4 Experimental diagram of the rotating packed bed (RPB) system for ammonia stripping. Reprinted from Li et al. (2020), 2020, with permission from Elsevier

into the RPB was controlled after adjusting the initial ammonia concentration and a pH of 11. In the RPB, the evaporation of ammonia was brought by centrifugal force and airflow. The feed and effluent ammonia concentrations were determined by the use of ion electrodes (Yuan et al. 2016a).

The continuous flow RPB is an efficient method of ammonia stripping from concentrated wastewater. The stripping efficiency and overall gas–liquid mass transfer coefficients (K_La) were determined. The overall K_La value was obtained to be 12.3–18.41/h. The results showed that the ammonia stripping process in RPB is more sensitive to Q_G (air flow rate) and Q_L (liquid flow rate) for the liquid–gas mass transfer and less sensitive to ω (rotational speed) and temperature (Yuan et al. 2016a).

The process is very simple. The only requirement is the maintenance of stable pH and temperature. The problem associated with the system is it cannot be performed in freezing temperature conditions, and $CaCO_3$ scaling occurs. The process involves coagulation-flocculation at pH greater than 11; heating of water at 38 °C; air stripping; and retrieval of ammonia by absorbing in a solution of sulfuric acid (Yuan et al. 2016c).

Removal using Ozone microbubbles. The ozone lifetime in water is short, and the rate of reaction with ammonia is quite slow. Recently, there has been extensive use of ozone microbubbles, i.e., bubbles of dia., less than 50 μm in wastewater treatment processes (Capodaglio and Raboni 2015). The microbubbles provide a large interfacial area increasing the efficiency of the process due to the increased area for the interaction (Khuntia et al. 2013a). A small amount of ozone is required as hydroxyl ions are generated in the process, which causes ammonia oxidation. This process is faster and can be used in a broad range of pH. Ammonia reacts with ozone according to reaction (14.10):

$$NH_3 + 4O_3 \rightarrow H^+ + NO_3^- + H_2O + 4O_2 \tag{14.10}$$

The mechanism by which ammonia oxidation occurs through ozone microbubbles has been investigated in the experiment using a pilot plant ozone microbubble generator (Khuntia et al. 2013b). The effects of parameters like pH and feed rate of ozone have been studied. The experimental setup is demonstrated in Fig. 14.5:

Oxygen having 98% purity was converted into ozone using the ozone generator based on the corona discharge method. The rate of ozone generation ranges from 0 to 3×10^{-6} kg/s. The microbubbles have a mean diameter of 25 μm (Khuntia et al. 2013a). The MBG operates in recirculation mode, continuously generating microbubbles. The polycarbonate reactor contained the aqueous phase reaction mixture (Fig. 14.5). The undissolved excess gas was allowed to pass through the ozone destructor, which was then released into the atmosphere. To maintain the reaction temperature, the reactor was kept in the water reservoir. The concentration of the formed NO_3^- was measured using UV–Vis spectrophotometry (Khuntia et al. 2013b).

The results showed effective oxidation of the dissolved ammonium ions by the ozone microbubbles. Effective oxidation occurs at pH > 7 and increases with an

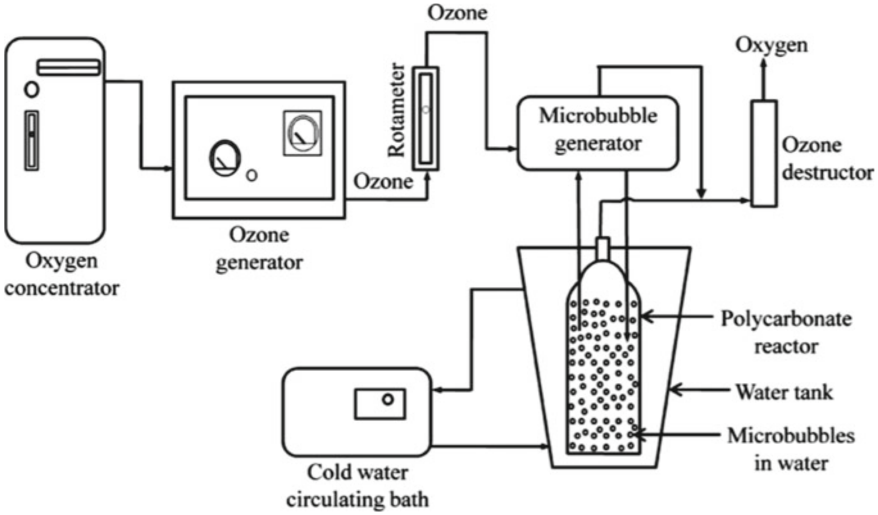

Fig. 14.5 Experimental setup for urea removal by ozone microbubbles. Reprinted with permission from Khuntia et al. (2013b), 2014. American chemical society

increase in pH. Ozonation of ammonia at pH ≥ 8 occurred directly by molecular ozone, whereas there was also a small contribution of hydroxyl ions at pH 6 and 7 (Urbańczyk et al. 2016b). During the Ozonation of ammonia, there is a continuous decrease in the pH of the solution due to the H^+ ion generation. The rate of oxidation increased in the presence of bromide ions, which also gives an advantage of converting the nitrate formed in the reaction to nitrogen (Yuan et al. 2016a).

Ammonia removal by microwave radiation. Microwave radiation is an efficient technique for removing ammonia from urine wastewater in a very short duration. The process depends on pH and the radiation duration. There were few effects of the aeration process and initial concentration of ammonia on the process. Both thermal and non-thermal effects of microwave radiation are important in ammonia removal but a key role is played by thermal effects (Lin et al. 2009a). Compared to the steam stripping method, MW radiation provides higher removal efficiency of ammonia. Heating occurs at the molecular level, and therefore, homogeneous and fast thermal reactions occur in MW. Approximately 74–84% was observed, which would be higher if aeration is provided (Lin et al. 2009b).

The optimal pH of 11 was found for 98% removal efficiency. An equilibrium was found between soluble NH_4^+ ions and molecular ammonia, which was pH-dependent (Lin et al. 2009a). It was observed that almost all volatile ammonia got removed from the solution. On increasing the temperature to the boiling point, ammonia started escaping in the form of gas bubbles. It was found that MW radiation caused a reduction in the activation energy of the process and also weakened the bonds in molecules, which proved to be advantageous in the ammonia removal process. Almost 98% of ammonia removal was attained within 3 min of radiation time (Lin et al. 2009a). A longer time would provide more heat for molecular motion and help the escape of ammonia, but that would be costly. Aeration enhanced the ammonia removal from the wastewater. The initial concentration of NH_3 had a negligible consequence on the removal efficiency.

The removal mechanism is the thermal as well as non-thermal effects of MW radiation. The heat generated due to the energy absorption from MW radiation by the water and other polar molecules, which causes polarization, which may be permanent or induced, produces the thermal effect. The non-thermal effect leads to changes in the chemical, physical, or biochemical nature of the system where temperature and other parameters do not change. The removed ammonia was collected in the sulfuric acid bottles completely, and the concentrations were determined. Thus, the removal happened because of the volatilization of ammonia from the water to the gaseous form by the thermal as well as non-thermal effects of MW radiation (Lin et al. 2009a).

Reverse Osmosis (RO) Process to remove ammonia. RO is a popular method to remove proteins, organics, etc., which conventional methods cannot easily remove. Treatment efficiency and performance are stable. It is a regenerative technology as it requires around 1–2 replacements per year (Lee and Lueptow 2001). Rejection of solutes by RO is dependent on the physical characteristics of the solute, feed stream, and membrane and also the difference in the pore size of the membrane. The degree of separation in ionic solutes depends on the size as well as the ionic charge. For organic solutes, the separation efficiency depends on the chemical affinity as well as the molecular weight of the solute.

The characteristics of the RO membrane for organic and inorganic substance rejection were analyzed in wastewater for its application in space. Wastewater of different chemical compositions was used to compare seven different types of RO membranes. Wastewater includes urea as well as ammonia as their constituents to represent human urine. The membranes used were thin-film composite type (TFC) made from polyamide (Lee and Lueptow 2001).

The test for urea wastewater showed that rejection of urea by the RO membrane is a bit difficult. The low rejection is due to the interaction of urea with the membrane (Lee and Lueptow 2001). Rejection of ammonia by RO membrane was found to increase with the decrease in pH because, at low pH, the dominant form is NH_4^+ ion. The overall flux in the case of ammonia wastewater was found to be lower as compared to urea wastewater due to the high osmotic pressure observed for ammonium ions. LPRO membrane was most effective for high solute rejection as well as raised flux for either of their category. Thus, hydrolysis of urea to ammonia is much more advantageous for rejection by RO membrane for producing potable water (Lee and Lueptow 2001).

Electrochemical removal of ammonia. The electrochemical method for ammonia removal has been widely used. Different electrode pairs are utilized to treat ammonia-rich wastewater. Electrochemical treatment of ammonia depends on factors like Cl^- concentration, pH of the solution, current density (Bukhari 2008; Bouhezila et al. 2011), applied voltage (Chou et al. 2009), and material used, especially the type of anode (Alfaro et al. 2006; Chiang et al. 1995; Liu et al. 2009). The type of material used for the anode and applied voltage are the most critical factors among all the factors listed above as they determine the operational cost and efficiency of removal (Marinčić and Leitz 1978). Direct or indirect oxidation is utilized in electrochemical ammonia removal. Hydroxyl radicals oxidize the organic nutrients in the direct method (Marinčić and Leitz 1978; Nicolau et al. 2014). Marinerc et al. (Marinčić and Leitz 1978) compared the oxidation of ammonium between platinum and titanium as the positive electrode and observed that the platinum anode showed better performance. Titanium electrodes coated with very thin layers of noble metals (Vigo et al. 1988), ruthenium (Murphy et al. 1992), and boron-doped diamond (BBD) (Alfaro et al. 2006) are also utilized in direct ammonium oxidation. In indirect electro-oxidation, oxidizing agents generated on the anode (such as peroxide or hypochlorite) are involved (Vigo et al. 1988). Titanium coated with IrO_2 is most commonly used in the indirect method (Kim et al. 2005).

14.4 Conclusion

There are many different electrochemical and physicochemical methods for the treatment of urea and ammonia wastewater. There are many benefits and challenges associated with each technique. Electrochemical urea treatment methods mostly make use of the hydrolysis of urea into ammonia, and further electro-oxidation occurs. So, the electrochemical oxidation of urea and ammonia is very useful. DUFCs and MFCs are being investigated for their application in space to recover water from urine. They have shown great potential in water recovery as well as energy generation. Their terrestrial application can also provide an alternative energy source. Biological urea removal has been widely utilized in the treatment of wastewater and is an established process to remove nitrogenous components from water. The ion exchange and ozonation methods are very costly when treating a large amount of wastewater. The application of microwave radiation for treating effluent wastewater is quite challenging. Many of the urea or ammonia treatment method uses struvite precipitation as the final step to recover the residual nutrients in the form of fertilizer. This is frequently used in ammonia stripping towers. Membrane-based technologies like reverse osmosis are very effective in the removal of all contaminants, but the treatment is costly as they have high power requirements, and also, they suffer from membrane fouling. So, an energy-efficient and cost-effective system is needed for the treatment of wastewater. Researchers are investigating the application of forward osmosis integrated with membrane distillation in the treatment of urine wastewater. The preliminary research has shown promising results. The practical application of membrane-based systems still has a long way to go, and more extensive research is needed.

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Chapter 15
Biofouling Mitigation Strategies in Membrane Systems for Wastewater Treatment

Akhila M. Nair and Swatantra P. Singh

Abstract Membrane technology has grown significantly due to its application in the industrial separation processes, as well as for desalination and wastewater treatment. However, these membrane systems encounter a major challenge of fouling which comprises of biofouling, colloidal fouling, organic fouling, and inorganic fouling. Of these, biofouling can impose a number of negative impacts on the membrane systems because of the undesirable deposition and microbial growth on the surfaces, which can hamper the efficiency of water and wastewater treatment plants. Biofouling can be defined as a complex process of unwanted growth and attachment of microorganisms induced by the release of EPS on surfaces. They have the ability to limit membrane permeability and flux, necessitating the use of high pressure to overcome them, potentially increasing the energy consumption. Biofilms in the water system can also be a reservoir of pathogenic microorganisms, compromising public health and hygiene. As per reports, biofouling in wastewater treatment facilities is to blame for over 80% of bacterial illnesses in humans. Thus, biofouling monitoring and control measures need to be implemented for successful and affordable water and wastewater treatment processes. Therefore, this chapter tries to provide an overview of the several approaches employed to control membrane biofouling, focusing on the physical, chemical, and biological methods. Further, recent advances in the development of biofouling mitigation techniques, to improve treatment performance, are also highlighted.

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Keywords Membranes · Biofouling · Modified membranes · Biological methods

15.1 Introduction

Dating back to 1684, Antonie van Leeuwenhoek, a Dutch scientist, studied dental plaque using his self-constructed microscope (Henrici 1933). This was one of the first instances of acknowledging the presence of bacteria in the surrounding. During the initial phase of the twentieth century, scientists began to realize that microorganisms can be found attached to the surfaces along with their free-floating nature. In 1978, the formation of the glycocalyx on teeth induced by *Streptococcus mutans* biofilm was reported by Clark (Rabin et al. 2015a). With the emergence of various reports on the existence of a sessile mode of living, Costerton in 1978 coined the term 'Biofilm' (Mclean et al. 2012). Biofilm is defined as aggregates of microorganisms firmly adhered to a surface and incorporated into the extracellular matrix. The microbial assemblage of bacteria, fungi, viruses, archaea, protozoans, and algae form the components of the biofilm. The formation of biofilm is a combination of complex events whereby extracellular polymeric substrates (EPS) provide structural support and mechanical stability and promote microbial adhesion on surfaces (Karygianni et al. 2020). Both biotic and abiotic (plastic, wood, metals) surfaces can serve as the surface for biofilm formation (Jamal et al. 2018).

Microbial biofilms have played a vital role in causing prolonged infectious diseases. According to National Institute of Health reports, approximately 80% of chronic infections are caused due to bacterial biofilms (Jamal et al. 2018). Undesirable deposition on surfaces of industrial processing units and water distribution systems has also affected the product quality and hampered the treatment performances. Biofilms in the drinking system can be a reservoir of pathogenic microorganisms, compromising public health and hygiene. Along with these, in the membrane filtration processes, membrane fouling is a critical issue raising the economics of treatment processes due to the frequent replacement of membranes (Pichardo-Romero et al. 2020). On membrane surfaces, fouling can take four main forms: organic fouling, inorganic fouling/scaling, particulate fouling, and biofouling (Nguyen et al. 2012a). Among these fouling types, biofouling is viewed to be the Achilles heel in membrane processes (Flemming et al. 1997).

Biofouling can be defined as an undesirable growth of microorganisms that results in the formation of biofilms on the surfaces. Biofouling is an important problem in wastewater treatment units which causes unwanted growth of microorganisms on surfaces. Membrane systems are susceptible to various negative impacts from biofouling, such as membrane flux reduction, increased feed pressure, concentration polarization, membrane biodegradation, and high energy consumption (Nguyen et al. 2012a). Around 45% of the membrane fouling is caused by biofouling, which reduces the effectiveness of reverse osmosis (RO), nanofiltration (NF), and ultrafiltration (UF) membrane systems (Vrouwenvelder and Kooij 2003; Wu et al. 2020). Thus,

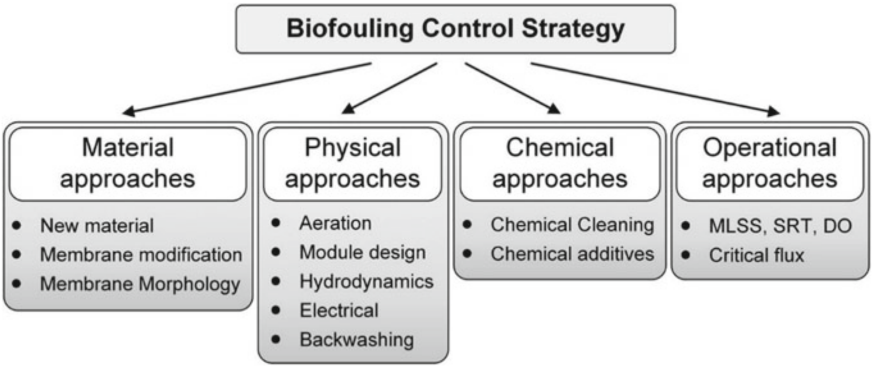

Fig. 15.1 Control methods for biofouling over the past 30 years. Adapted from Oh and Lee (2018)

biofouling monitoring and control strategies to mitigate them becomes important to improve the efficiency of treatment processes.

The last few decades have witnessed the development of numerous cutting-edge methods and approaches for the mitigation of biofouling. The conventional and emerging strategies can be majorly categorized into physical, chemical, and biological approaches and surface modifications of the membrane material (Fig. 15.1). This chapter majorly aims to discuss these methods that can be employed as an anti-fouling agent. To understand the underlying cause of biofilm formation leading to the fouling phenomenon, the four stages of this multi-step process formation are discussed in the initial section of the chapter. This chapter also focuses on shedding some light on the techniques which are in the developmental phase for their implementation as an antifoulant.

15.2 Formation of Biofilm

A complex process where microbial communities form aggregates on surfaces through a series of events is called as biofilm formation. The upregulation and expression of genes that aid the formation of biofilm are observed when there is a change or switch from the planktonic to the sessile mode of growth. Various environmental factors like nutrient availability, temperature, flow velocity, water conditions, and quorum sensing affect this multi-step biofilm growth process. There are primarily four stages of biofilm formation:

I. Attachment
II. Micro-colony formation/Colonization
III. Maturation
IV. Detachment

I. Attachment

For the attachment process to initiate, microorganisms should be in close proximity to the surfaces, where repulsive and attractive forces come into play (Fig. 15.2). The negative charges on surfaces cued by the environmental conditions repel the negative charges present on the bacterial surfaces. At a distance lesser than 10–20 nm, these negative charges are replaced by attractive Van der Waal forces, exhibiting the attachment mechanism. A perfect solid–water interface with rough, hydrophilic-coated surfaces is an ideal environment for biofilm attachment to occur (Jamal et al. 2015). Locomotor components like cilia and flagella are also crucial for initial attachment or interactions between cells and surfaces. The attachment process can be further classified into a reversible attachment or an irreversible attachment. Planktonic cells (surface naive) very briefly interact with the surfaces expressing low levels of cyclic adenosine monophosphate (cAMP), called reversible attachment. Activation of various surface sensing systems due to altered attachment and detachment processes increases the cAMP levels in cells leading to the long association of cells with the surfaces, contributing to irreversible attachment, and ultimately developing into biofilms (Armbruster and Parsek 2018).

II. Micro-colony formation

Once microorganisms get attached to the surfaces, many new cells get recruited near the surfaces to form 3–5 layers of stable interactions leading to the formation of a micro-colony (Fig. 15.2). These micro-colonies are held together by stable cell-to-cell interactions and clonal growth. Along with colonization, chemical signals activate certain signal transduction pathways for the progression of cellular multiplication. These pathways also express the production of exopolysaccharides embedded

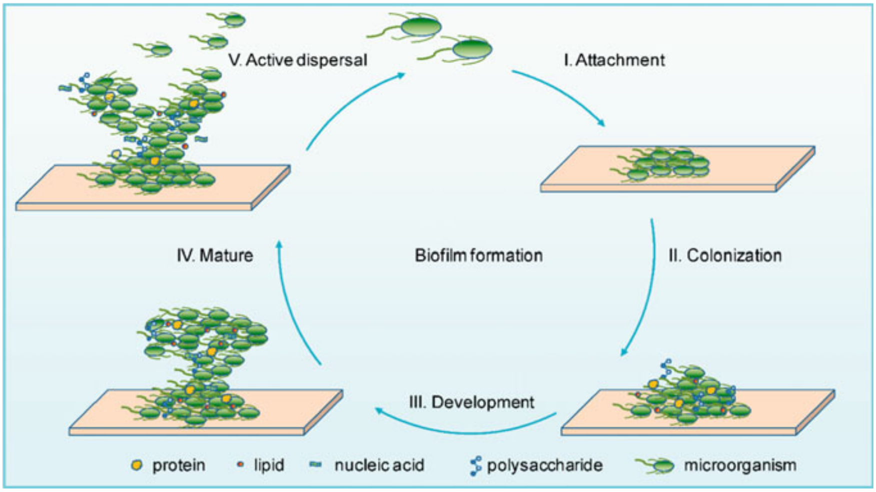

Fig. 15.2 Schematic representation of biofilm formation. Adapted from Yin et al. (2019)

in the matrix for cell-to-cell interactions to mediate. A locomotor structure like pili plays a major role in micro-colony formation. For e.g., in *Pseudomonas aeruginosa*, type IV pilus has been responsible for the production of exopolysaccharides and enabling micro-colony formation (Stanley and Lazazzera 2004).

III. **Maturation**

After micro-colony formation, maturation is a three-dimensional structure formation process with > 100 layers of thick biofilm arranged to form tower or mushroom-like structures (Fig. 15.2). Genes responsible for complex matrix formation are expressed, rendering a thicker and more stable biofilm. Nutrients are transported across the biofilm matrix via various water-filled channels, which act as nutrient influx and waste efflux. In this process, microorganisms also rearrange themselves according to their metabolism and aerotolerance. Anaerobic microorganisms grow deep inside the biofilm matrix to avoid exposure to oxygen. As the maturation process progresses, the entrapped microorganisms release structural proteins, extracellular proteins, DNA, and polysaccharides into the biofilm matrix, forming matured biofilm matrix (Jamal et al. 2015; Rabin et al. 2015b).

IV. **Detachment**

After the maturation step, microorganisms leave the biofilm structure on a regular basis. This process of detachment or dispersion of cells from the biofilm life cycle follows a natural pattern. The factors responsible for the detachment mechanism can be nutrient availability, mechanical stress, microbial competition, an outgrowth of another population, and many more. For e.g., investigations related to the dispersal mechanism of *Candida albicans* indicated the importance of the carbon source and the medium's pH during the growing condition of the microorganism. The dispersed *C. albicans* showed varied phenotypic expression as compared to its planktonic counterpart. Increased pathogenicity with higher expression of 'virulence genes,' filamentation, and enhanced adherence were some distinct properties exhibited by the dispersed *C. albicans* (Uppuluri et al. 2010). In most cases, cessation in the production of EPS detaches either a part of the biofilm or the whole biofilm. At times, detachment of newly attached cells from surfaces promotes detachment of stable microbial surfaces due to flow velocity or quorum sensing. Certain characteristics adapted by the microorganisms present within the biofilm matrix are retained by them, post-dispersal from the biofilm layer, such as antibiotic resistance (Jamal et al. 2015).

15.3 Impact of Fouling on Membrane Function and System

Fouling on membranes can impact both the process and physical characteristics of membranes. The various adverse effects of biofouling (Abd El Aleem et al. 1998; Baker and Dudley 1998; Coetser and Cloete 2008; Flemming 1997; Nguyen et al. 2012a) are as follows:

(a) Decline in membrane flux: Biofouling leads to the formation of a fouling layer with lower permeability on the membrane surface, thereby declining the membrane flux. This happens because the EPS generated by the bacteria hinders salt back diffusion and increases the membrane's hydrolytic resistance.

(b) Increased salt passage: Fouled membranes accumulate dissolved ions at the surface, thus increasing concentration polarization, inhibiting convectional transport, and reducing the quality of permeate.

(c) Concentration polarization: This happens because of salts building up on the membrane surface, which results in a higher salt concentration there as compared to the bulk solution. Concentration polarization can lower the driving pressure across the membrane and result in membrane scaling as a result of more precipitation.

(d) Membrane biodegradation: The acidic by-products produced by the microorganisms concentrate at the membrane surface and degrade them. An example is the biodegradation of cellulose acetate membranes (Murphy et al. 2001).

(e) Biofilm resistance can cause an increase in the differential pressure and feed pressure.

(f) Increased energy consumption: The flux decline, biofilm resistance, and high feed pressure add to the energy requirement.

(g) Chemical cleaning: The frequency of chemical cleaning is increased as a result of biofilm formation on the membrane surface, which raises treatment costs and shortens the life span of the membrane. An example is the operation of a RO plant, where membranes at desalination treatment plants account for about 50% of the overall cost.

(h) High cost: A significant financial burden is caused by high energy demand, regular cleaning, and membrane replacement.

15.4 Control and Prevention of Biofouling

15.4.1 Biocide Treatment

It is the conventional anti-fouling method wherein the water in the treatment plant is treated with powerful bactericidal agents. Among the biocides used, chlorination is the most facile, inexpensive, and widely used method to treat water and reduce biofouling. Free chlorine that constitutes hypochlorous acid (HOCl) and hypochlorite ion (OCl^-) can effectively reduce microbial contamination (LeChevallier 2013). However, the formation of DBPs like trihalomethane and haloacetic acids, which are suspected carcinogens generates undesirable effects. Also, chlorine species can react to the polymeric network present in the membranes, reducing their shelf life and raising the expense of running membrane plants (Al-Abri et al. 2019). Chlorine dioxide is another chlorine-based disinfectant that is more effective than chlorine in several instances (Sanekata 2010). Chlorine dioxide is an effective bactericidal agent producing fewer disinfectant by-products (DBPs) when compared to chlorine gas and hypochlorite. Monochloramines are another set of chlorine-based disinfectants that are employed; however, their effectiveness has been minimal, and they are generally used to prevent bacterial regrowth by maintaining stable disinfectant residues (Cromeans et al. 2010).

Ozone is another oxidizing agent which has the ability to deactivate many bacterial species, viruses, protozoa, and fungal spores. Applying ozone to drinking water is more expensive than chlorination, but has gained acceptance as a disinfectant because of no production of certain suspected carcinogens such as trihalomethanes or other chlorinated by-products (Voukkali and Zorpas 2015). However, ozonation can form aldehydes and bromates, which can pose health hazards to the general public. Its toxicity, limited life period with minimal residuals, and high running costs make it unsuitable for widespread application. Also, since ozone leaves no residuals in water after treatment, chlorination or the addition of chloramines typically follows next. This is essential because ozone breaks down complex organic compounds in water into simpler ones that can act as growth substrates in the water distribution system, to inhibit the regeneration of bacteria (Gerba 2015).

Other oxidizing agents like hydrogen peroxide, iodine and peracetic acid have also been utilized, but their application is constrained because of their impact on polymeric surfaces which reduces the efficiency and performance of the membranes (Nguyen et al. 2012b). Also, the impact of biocides is more on planktonic cells as compared to the biofilm due to the complex EPS-composed matrix (Leung et al. 2012). Quarternary ammonium compounds (QACs), formaldehyde, and glutaraldehyde are some of the non-oxidizing biocides used in biofouling control. However, they face the drawback of acclimatization and bacteria gaining resistance to the treatment method due to their continuous and long-term application (Baker and Dudley 1998).

Ultraviolet (UV) treatment is another physical method for controlling biofouling that generates hydroxyl radicals to prevent microbial growth. UV is an electromagnetic radiation with wavelengths between 10 and 400 nm. Out of the three UV waves, i.e., UV-A, UV-B, and UV-C with wavelength ranges 315–400 nm, 280–315 nm, and 200–280 nm, respectively, UV-C is considered to exhibit germicidal action for inactivating pathogenic microorganisms (Turtoi 2013). Simple operation, automated systems, and fewer harmful by-products make it an effective method however shorter contact time, and the development of UV-resistant strains limits its application (Carratalà et al. 2017).

The conventional anti-fouling method mentioned above faces many drawbacks as mentioned in Table 15.1 and does not have a direct impact on the biofouled surfaces. To overcome these limitations, other physical and chemical methods are discussed below that can effectively clean biofilm formation and eliminate the growth of microorganisms.

Table 15.1 Advantages and disadvantages of existing biofouling mitigation methods

Methods		Advantages	Disadvantages
Conventional methods	Chlorination	Presence of stable disinfection residues Prevent bacterial regrowth Odor minimization	Formation of DBPs like trihalomethane and haloacetic acids
	Ozone	Effective removal of bacteria and other microorganisms	High running cost Formation of aldehydes and bromates Difficulty in storage and transportation Limited life period
	UV	Simple operation Automated systems Fewer harmful by-products	Shorter contact time No disinfection residues Development of UV-resistant strains
Physical methods	Hydraulic cleaning	Reduces reversible fouling Effective removal on non-adhesive foulants	Periodic maintenance
	Pneumatic cleaning	Low maintenance cost Use of no chemicals Easy integration into the membrane systems	Reduced air sparging effectiveness High pumping cost
	Ultrasonic technology	Maintain higher permeate flux No generation of by-products	Membrane damage Scale up difficulties at the pilot and industrial level
Chemical methods	Sequestering agent, surfactants, disinfectants, and enzyme	Low risk of bacterial resistance Detachment of biofilms based on chemical interactions	Less effective Possibility of microbial regrowth Reduced membrane shelf life Use of toxic and expensive agents
Biological methods	Quorum sensing	Longer efficiency No physical damage to the membrane surface	Developmental phase Integration into large plants Parasitic properties of phages
	Phage therapy		

15.4.2 Physical Methods

Physical control methods possess the advantage of eliminating the usage of chemicals that could endanger human health or the environment in order to remove the foulants from the membrane surface by the implementation of mechanical forces. The techniques involve hydraulic cleaning, pneumatic cleaning, ultrasound technology, pulse flow, and many more (Gule et al. 2016a). Hydraulic cleaning is one of the most popularly used physical techniques for mitigating biofouling in filtration systems and MBRs with methods such as flushing (forward) and backwashing/backflushing (Fig. 15.3) (Hilal et al. 2007). In MBR, intermittent backwashing reduces the fouling rate by improving MBR operation and reducing reverse fouling (Lin et al. 2010a). This occurs due to the removal of the particles and microorganisms attached to the membrane surface, reducing the concentration polarization. Thus, backwashing of membranes has become a standard gold method for reducing fouling in MBRs and other crossflow systems. Yigi et al. (2009) had studied that rapid backwashing can highly impact the degree of membrane fouling in MBRs and crossflow systems and eliminate the reverse fouling phenomenon. Backwashing can also be combined with forward flushing during filtration to reduce particle accumulation.

Hydraulic cleaning can be combined with the pneumatic cleaning method by using air sparging, airlifting, air bubbling, and air scouring. In this, the air is supplied directly to the membrane surface during the filtration step, reducing the fouling rate. The foulants present on membranes are back transported from surfaces due to shear forces of liquid inducing detachment and higher permeate flux. This method is associated with a low maintenance cost, use of no chemicals, and easy integration into the membrane systems; however, reduced air sparging effectiveness and high pumping cost limits its application (Lin et al. 2010b).

Ultrasonic technology is a physicochemical method that influences fouling by applying continuous and intermittent waves. As depicted in Fig. 15.4, this technology includes phenomena such as microstreamers, microjets, acoustic streaming,

Fig. 15.3 Schematic of backwashing the membranes. Adapted with permission from Kim et al. (2018) Copyright (2018) American chemical society

and microstreaming. The cake formed on membrane surfaces is damaged using ultrasound-generated bubble cavities which remove the fouling deposits and disrupt microbial cells. They also maintain higher permeate flux where the continuous and intermittent waves are responsible for enhanced fluid flow through membrane systems. This technology doesn't generate any by-products, and the hydrogen peroxide and hydroxyl radicals that are produced add to the anti-fouling effect (Abdelrasoul and Doan 2020; Nguyen et al. 2012b).

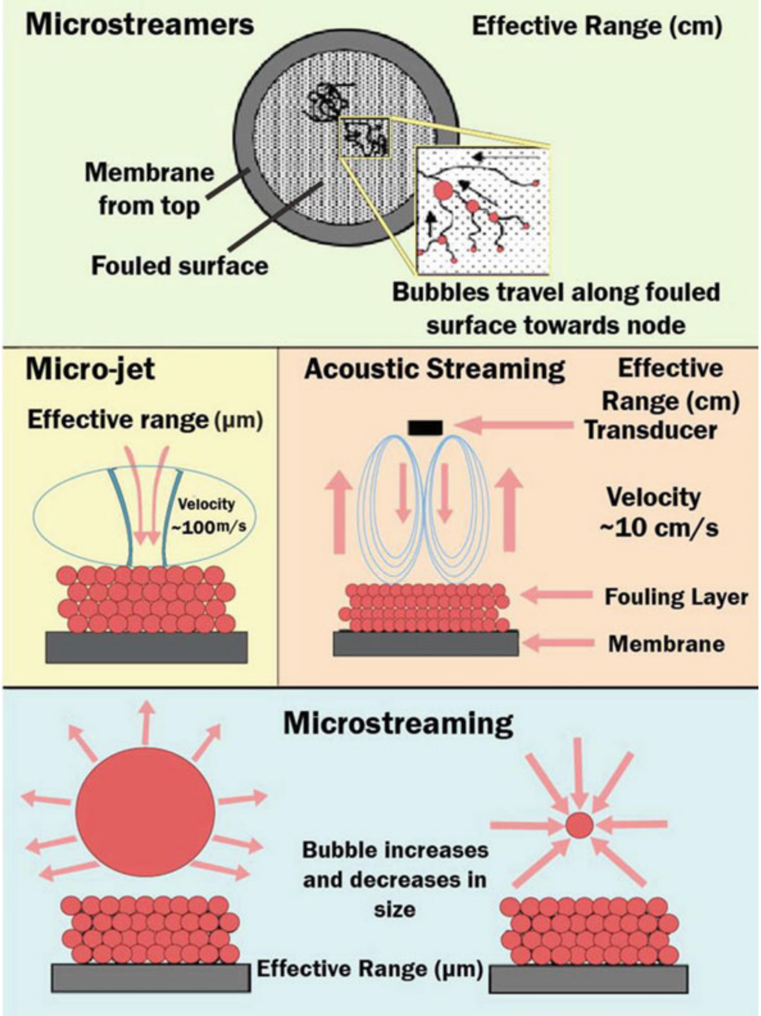

Fig. 15.4 Schematic of particle detachment from the fouled membrane on the influence of ultrasound. Adapted from Abdelrasoul and Doan (2020)

Electric fields or pulse surfaced polarization is considered to be another type of physical cleaning method to reduce membrane biofouling and has been traditionally involved in elevating the water transport through the membrane. Applying an electric field can reduce membrane fouling because of the vibration of the cake layer and act as a driving force for water flux (Visvanathan and Ben Aim 1989). Tarazaga et al. (2006) successfully reduced the biofouling mechanism and cleaned the UF membranes due to the influence of electric fields, thereby increasing the membrane flux. Similarly, Zumbusch et al. studied the effect of alternating current on the fouling rate in UF and reported that the electric field effect depends on the frequency, membrane material, conductivity, and applied field strength (Lin et al. 2010b).

15.4.3 Chemical Methods

Agents such as caustic (NaOH, KOH), EDTA (sequestering agent), surfactants (sodium dodecyl sulfate), disinfectants ($KMnO_4$, NaOCl, H_2O_2), and enzymes are the chemically induced cleaning agents for mitigating biofouling (Zondervan and Roffel 2007). These cleansing agents interfere and weaken the hydrophobic interactions and electrostatic interactions between bacteria and membranes. For example, caustic cleanses the membranes by hydrolysis and solubilizing the proteins and saccharides in the EPS. They are also involved in imparting a negative charge to weaken the interactions between the foulant layer and membrane (Nguyen et al. 2012a).

Enzymatic cleaning is another technology where the components of the EPS, such as polysaccharides and proteins, are degraded using enzymes like polysaccharases and proteases, respectively. For example, enzymes protease kinase A and trypsin are widely used to prevent biofilm formation (Leroy et al. 2008). These enzymes are also involved in degrading the organic matter and signaling molecules to disrupt microbial communication during biofilm formation (Fig. 15.5). These biocatalysts do not produce toxic by-products but are sensitive to variations in certain factors such as temperature and pH. Further, synthesizing enzymes is very expensive and since EPS is a complex consortium of many macromolecules, hence various different types of enzymes would be needed to remove them (Brady and Jordaan 2009).

Chemicals such as 2,4-dinitrophenol (DNP) can also be used, which interfere with the metabolic activities of the bacteria and reduce bacterial adhesion to the membrane surfaces. This is carried out by suppression of the autoinducer-2 (AI-2) production and thus inducing bacterial detachment (Xu and Liu 2011). Surfactants are another class of chemicals that can solubilize the foulants present on the membrane surface. They prevent biofilm formation by disturbing the hydrophobic interactions that exist between the bacteria and the membrane surfaces (Goldberg et al. 1990). For example, surfactants such as sodium dodecyl sulfate were instrumental in detaching *Pseudomonas fluorescens* biofilms from glass surfaces (Percival et al. 2019).

The above-mentioned chemical cleaning methods are not very effective and do not ensure the complete killing of organisms. Organisms are bound to regrow and

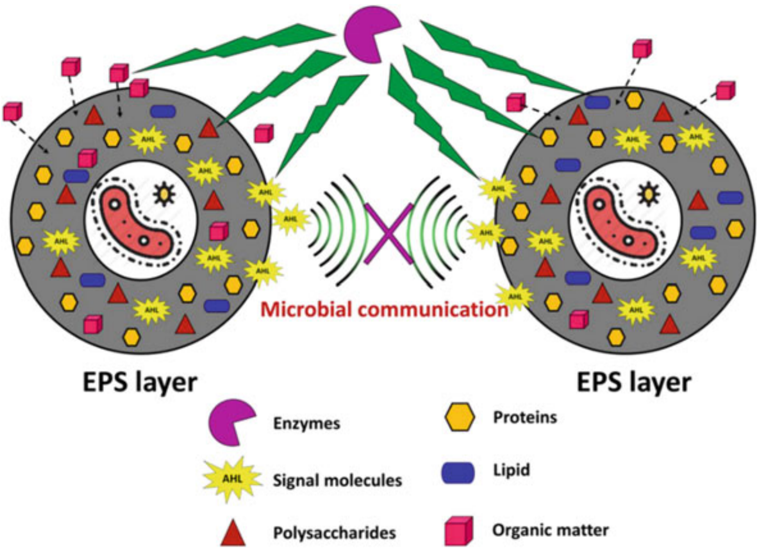

Fig. 15.5 Schematic of the mechanism of biofouling mitigation using enzyme-based methods. Adapted from Bachosz et al. (2022)

form multicellular complexes; thus, membranes must be cleaned frequently, reducing their shelf life.

15.4.4 Biological Methods

Biological-based methods for controlling biofouling employ the use of certain mechanisms that are a part of microorganisms found in the biofilm or use other microorganisms as weapons to eliminate the biofilm growth. Quorum sensing and phage therapy are the two most widely used biological control methods. However, these strategies are still in the developmental phase, and hence, the compatibility of these advanced methods on large-scale plants needs to be further investigated.

Quorum Sensing. One form of the cell-to-cell communication process is quorum sensing, where microorganisms communicate with each other by secreting signaling molecules like oligopeptides, autoinducer-2 (AI-2), and N-acylhomoserine lactones (AHL). This process is pivotal in the formation of biofilm and upregulation of genes regulating the synthesis of complex biofilm consortium. Microbial quorum quenching will be beneficial in disrupting this communication, and a number of such blockers have been developed with longer efficiency. The mechanism of biofilm inhibition in Quorum Quenching (QQ)-MBRs was studied by Oh and Lee. The synthesis of EPS which plays a crucial role in the creation of biofilms is regulated by reducing its production. This leads to the weaker architecture of biofilm as depicted in Fig. 15.6

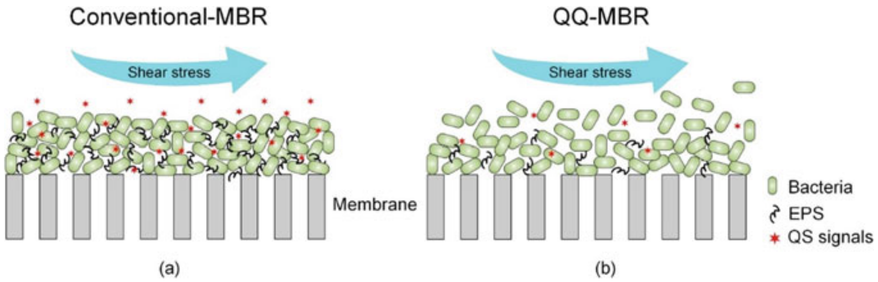

Fig. 15.6 Biofilm architecture in **a** conventional-MBRs and in **b** QQ-MBRs. Adapted from Oh and Lee (2018)

and the early separation of bacteria from the surfaces due to shear stress (Oh and Lee 2018).

Beads made of activated carbon-quorum quenching bacteria reduced MBR biofouling by 4.5 times when compared to control MBR, with a reduction in levels of 99.9% of AHLs in biocake and a lower rate of biofilm on membrane surfaces (Liu et al. 2021). Analogs of quorum sensing inhibitors also promote the quenching mechanism, with 6-gingerol analogs exhibiting inhibition of *Pseudomonas aeruginosa* biofilm formation with an increase in flux rate during the operation of the RO unit (Fig. 15.7) (Ham et al. 2019). Similarly, vanillin analogs have been instrumental in reducing the EPS content in the biofilm matrix by 64%, thereby weakening and degrading the biofilm formation (Kim et al. 2021). No modifications or physical damage to membrane surfaces were observed during the application of quorum quenchers. Furthermore, an optogenetic approach amalgamated with quorum quenchers has come to light during the forward osmosis of membranes in water purification systems (Mukherjee et al. 2018).

Phage Therapy. Phage therapy (lytic phage) where bacteriophages having the ability to infect bacteria is employed to solve the problem of membrane biofouling (Motlagh et al. 2016) The applied bacteriophages release certain virion-associated enzymes such as dispersin B or EPS depolymerases that can disrupt the EPS network and

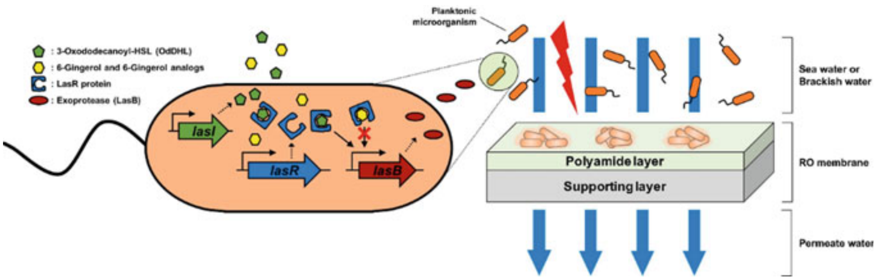

Fig. 15.7 Schematic illustration of biofouling mitigation using 6-Gingerol and its analogs in RO processes. Adapted from Ham et al. (2019)

disintegrate the biofilm. T4 bacteriophages are immobilized on membranes to form T4-immobilized membranes which eliminated the growth of bacteria, and only a 36% reduction in flux rate as compared to unfunctionalized membranes was observed (Ma et al. 2018). Bacteriophages engineered with enzymes that degrade biofilms are developed at a lab scale which showed a 4.5 magnitude reduction (99.99%) in bacterial biofilms which can be applied in industrial processes (Lu and Collins 2007). Phages isolated from wastewater units showed significance in restricting the growth of antibiotic-resistant bacteria in a prototype lab scale membrane bioreactor (Bhattacharjee et al. 2015). However, the use of bacteriophages in extensive wastewater treatment would eventually be complicated by their unique parasitic properties (Xiong and Liu 2010).

15.5 Current Advances in Biofouling Mitigation Strategies

The conventional approach for the prevention of biofouling involves the utilization of surfaces or materials with less bacterial attachment. However, recent advances in mitigation strategies involve the modification of membrane surfaces which can inhibit the growth of microorganisms. The following sections mention the techniques that are involved in surface modification during the manufacture of the membrane material.

15.5.1 Polymer Blending

Increasing the membrane surface's hydrophilicity and preventing microbes from adhering to the surface is the primary objective of blending polymers onto it. Blending has been proven to improve the permeability, mechanical strength, salt rejection, and antibiofouling properties, which enhances the performance of the membrane (Falath et al. 2017). Carretier et al. (2016) designed polyvinylidene fluoride (PVDF) membranes by blending them with a tri-block copolymer poly(styrene) and poly(ethylene glycol) methacrylate moieties which can be a promising material for water treatment. The process of vapor-induced phase separation was used to synthesize the membrane. The synthesized membrane had increased the hydrophilic capability and almost completely inhibited *Escherichia coli* and *Streptococcus mutans* growth. The modified membranes were thus instrumental in increasing the water flux recovery ratio in comparison with the commercial PVDF membranes. Another study by Falath et al. (2017) involved blending gum Arabic with polyvinyl alcohol (PVA) to increase the overall performance of RO membranes. The synthesized conjugated membrane played a key role in improving the membrane performance by providing mechanical strength, increasing the surface roughness, hydrophilicity, salt rejection, water permeability, and biofouling resistance.

Surface grafting has been another simple approach involved in introducing surface modifications in the membranes during the manufacturing process that can improve its properties. An example involves grafting ultrafiltration membranes with methoxy polyethylene glycol (PEO) and N-chloramine functional groups. Figure 15.8 illustrates the process of surface grafting, which reduced the protein adsorption and attachment of bacteria on the surface. These N-chloramine-modified membranes also showed antibacterial properties with 100% removal of *Staphylococcus aureus* and *Escherichia coli (E. coli)* which are Gram-positive and Gram-negative in nature, respectively, within 30 min of contact time (Hou et al. 2017). Another example of surface modification led to improved anti-fouling properties against the contaminants sodium alginate solution (SA), humic acid solution (HA), and bovine serum albumin (BSA) protein solution. A two-step surface modification was adopted as illustrated in Fig. 15.9. The two steps involved were membrane grafting with hydrophilic groups and low surface energy groups on a polyamide nanofiltration membrane (Ruan et al. 2018).

Polymer brushes are another class of membranes with functionalized surfaces for an antibiofouling property. The use of polymer brushes with fouling-resistant and antibacterial capabilities has been shown in a study by Ma et al. (2020). On polyamide (PA) covered with graphene oxide (GO), dual functional diblock copolymers were employed to produce forest-like polymer structures via the activators regenerated by the electron transfer-atom transfer radical polymerization (ARGET-ATRP) method. The study was able to unravel the different strategies employed by the Gram-negative and Gram-positive bacteria to reduce biofouling. With *Bacillus subtilis*, reduced biofouling was observed via the synergistic effect of bacteria-attacking and bacteria-defending groups present on the top. However, with *E. coli*, bacteria-defending groups played a significant role in reduced fouling. These membranes could mitigate biofouling by achieving the desired surface hydrophilicity, density, thickness, and architecture. Another study has shown polymer grafted surfaces wherein the perfluoroalkyl side chains present on the polymer brushes led to enhanced protein resistance performance (Wang et al. 2015).

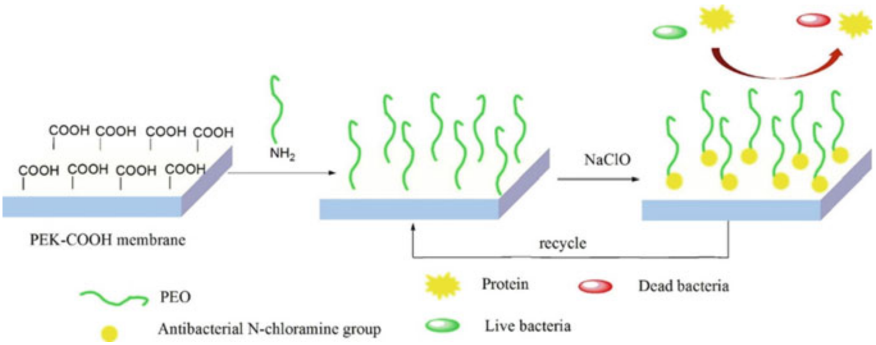

Fig. 15.8 Schematic illustration of the surface grafting of UF membranes with antimicrobial and anti-fouling properties. Adapted from Hou et al. (2017)

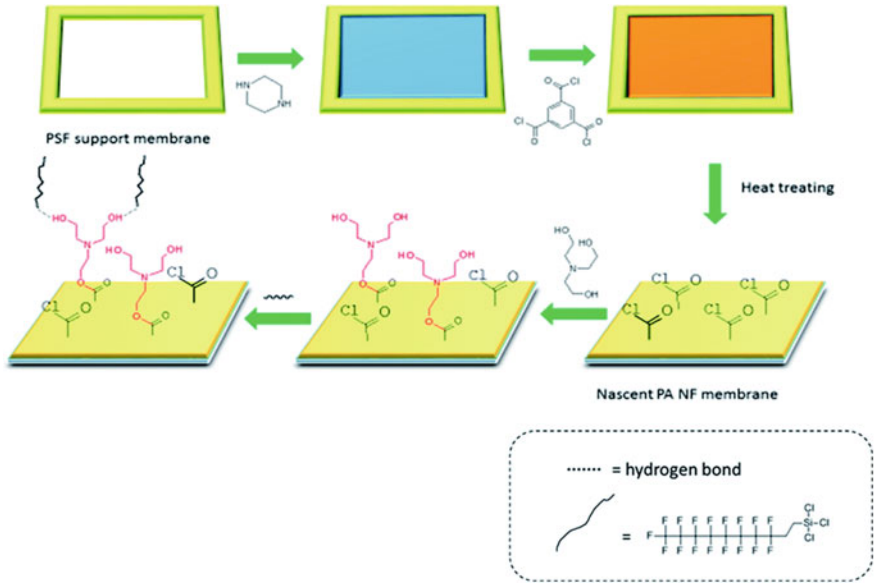

Fig. 15.9 Schematic diagram of the two-step process used to synthesize an amphiphilic NF membrane. Reproduced from Ruan et al. (2018) with permission from the royal society of chemistry, copyright 2018

15.5.2 Chemical Modifications

Chemical modification of membrane surfaces has been a desirable method for biofouling mitigation with the addition of certain chemical modifiers that form covalent bonding with the membrane surfaces. These modifications are imparted by techniques that involve sulfonation, carboxylation, amination, and epoxidation, with sulfonation being the most widely used method for the addition of hydrophilic groups (Upadhyaya et al. 2018). The sulfonic and carboxylic functional groups can be used for creating zwitterionic membranes with a positive and negative charge making the charge of the entire molecule zero. An example of zwitterionic membrane-modified surface is a PVDF membrane coated with the copolymers such as poly-(maleic anhydride-alt-1-octadecene-N,N-dimethylenediamine) (p(MAO–DMEA)) and poly-(maleic anhydride-alt-1-octadecene-3-(dimethylamino)-1-propylamine) (p(MAO–DMPA)) by an anchoring method that involves the process of ring-opening zwitterionization. These membranes exhibited increased hydrophilicity and resistance to proteins and bacteria (Venault et al. 2016). Further, Zhang et al. (2022) blended reduced GO-ZnO composite with PES ultrafiltration membrane. This was followed by surface grafting of the functionalized membrane with a zwitterionic hydrogel to impart dual functionality to the membrane surface. The antibiofouling ability of the synthesized dual functional membrane was investigated against

Pseudomonas aeruginosa, with the membranes showing low transmembrane pressure in comparison with the normal membranes, thus exhibiting low membrane fouling. Zwitterionic poly(carboxybetaine methacrylate) (pCBMA) grafted on the glass surface showed long-term resistance against biofilm-forming bacteria of *Pseudomonas* strains (Cheng et al. 2009). Dopamine-modified polymers on silicon wafers synthesized as mixed polymer brushes demonstrated long-term inhibition of *S. aureus* (He et al. 2019).

Another type of surface modification involved a two-step process of dip coating of the PES membrane in dopamine followed by the immobilization of D-tyrosine as depicted in Fig. 15.10, thereby enhancing the hydrophilicity and surface smoothness. The modified membrane showed a reduced fouling index, increased flux recovery ratio, and improved biofouling inhibition against *E. coli* (Jiang et al. 2017). Wibisono et al. (2015) have used an environmentally friendly method for biofouling mitigation by grafting certain neutral, anionic, and cationic hydrogels on feed spacers to reduce the attachment of *E. coli* and delay the formation of biofilm. Antimicrobial peptides are another class of modified membranes that are considered to be potential alternatives to conventional treatment technologies. The modification uses mimics of antimicrobial peptides to inhibit a wide range of microbes. Nisin, a polycyclic antimicrobial peptide made by Lactococcus lactis, is its example. Nisin proved efficient against a variety of bacteria, including *Pseudomonas aeruginosa* P60, *Bacillus* species, and mixed culture of the two species. The mode of action of Nisin is the removal of bacteria and EPS from the membrane surfaces, which showed a flux recovery rate of around 92% (Jung et al. 2018).

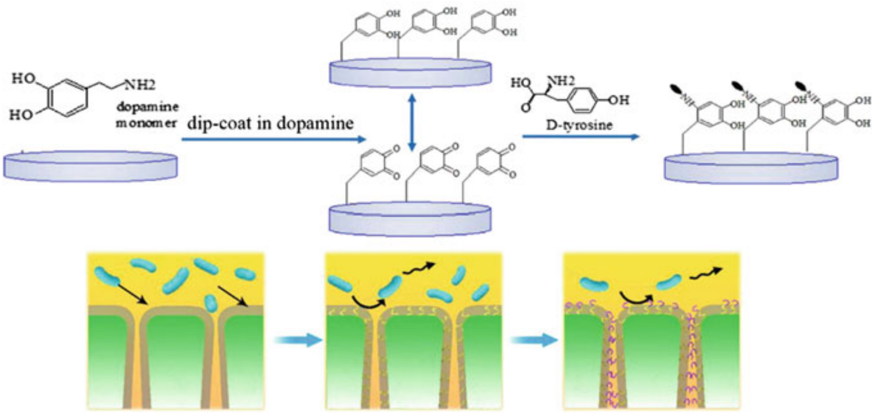

Fig. 15.10 Schematic diagram of the two-step modification process of membranes with antibiofouling capabilities. Adapted from Jiang et al. (2017)

15.5.3 Surface Hydrophobicity

The contact angle of a surface greater than 90 °C can be termed as hydrophobic surfaces and comprises of water repelling characteristics. However, surfaces with a contact angle greater than 150 °C are completely non-wettable and consist of a self-cleaning phenomenon which causes a hindrance to the attachment of bacteria to the surfaces. These surfaces are termed superhydrophobic surfaces (Gule et al. 2016b). Lotus leaf (*Nelumbo nucifera*) is an example of superhydrophobic surfaces which exist in our nature. Even though the surface of the leaf appears to be smooth, a scanning electron microscope has revealed surface roughness of varying scale lengths. Along with the surface roughness, the existence of epicuticular wax crystalloids, which are hydrophobic in nature, imparts superhydrophobicity to the leaf surfaces (Ganesh et al. 2011).

Because of the remarkable properties of superhydrophobic surfaces, researchers have been interested in developing surface materials with superhydrophobic characteristics to reduce biofouling. Lowered bacterial adhesion was observed against *S. aureus* (Fig. 15.11a, b) and *E. coli* (Fig. 15.11c, d) on the synthesis of nanoporous and nanopillars superhydrophobic surfaces (Hizal et al. 2017). These superhydrophobic surfaces were capable of preventing bacterial adhesion irrespective of the shape of the bacteria and flow conditions as illustrated in Fig. 15.11e–h. Yang & Deng adopted a straightforward, low-cost method for the synthesis of superhydrophobic surfaces (Yang and Deng 2008), wherein the synthesized superhydrophobic paper had higher tensile strength and resistance to bacterial adhesion. According to Hwang et al. (2018), the air-bubble layer's entrapment reduces the interaction between bacteria and the surface, which results in the antibiofouling feature of surfaces. However, the study has also shown that prolonged exposure to the superhydrophobic surfaces encourages bacterial attachment due to the air-bubble layer getting lost, limiting the usage of these surfaces for long-term performance (Hwang et al. 2018). Table 15.2 enlists some of the materials with superhydrophobic surfaces and their properties.

15.5.4 Nanotechnology

With the advancement in nanotechnology, nanomaterial-based membranes are an excellent class of membrane surfaces to mitigate biofouling. The effect is due to the synergism of the polymeric matrix and embedded nanomaterial. The polymer-nanomaterial complex can tune the membrane surface's characteristics which include hydrophilicity, mechanical strength, surface roughness, and porosity. The modified properties would be instrumental in increasing the membrane flux and reducing the biofouling phenomenon (Pichardo-Romero et al. 2020). An example of nanomaterial coated polymer membrane is polyurethane films with modified polyaniline-ZnO nanocomposites. These films showed exceptional chemical, mechanical, and antibiofouling properties (Mooss et al. 2019). Furthermore, using the chemical reduction

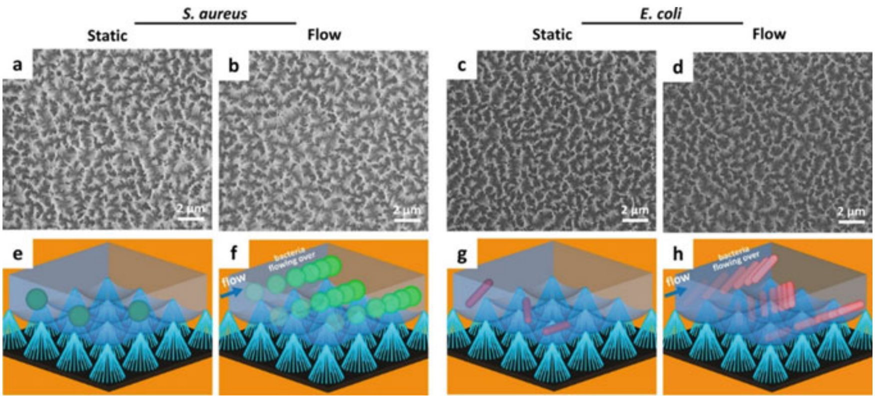

Fig. 15.11 FE-SEM image (**a–d**) and schematic (**e–h**) of bacterial adhesion on hydrophobic surfaces. Adapted from Hizal et al. (2017) Copyright (2017) American chemical society

Table 15.2 Examples of superhydrophobic surfaces with antibiofouling properties

Sr. No	Material	Properties	References
1	MnO_2 and Carbon Sphere (MCS) composite membranes	Surface roughness, stable structure, high separation flux, reusability, antibacterial properties	Chen et al. (2022)
2	ZnO-encapsulated mesoporous polydopamine microspheres	Self-healing capacity, superhydrophobic, antibiofouling, large area	Ni et al. (2021)
3	Nanostructured diamond films	Mechanical and chemical robustness, superhydrophobicity, antibacterial efficacy, marine antibiofouling	Wang et al. (2020)
4	Carbon nanomaterials impregnated on/powder activated carbon (CNMs/PAC)	Superhydrophobic, antibacterial, antibiofouling	Aljumaily et al. (2020)
5	iMglue-$SiO_2(TiO_2/SiO_2)_2$	Non-wetting capability, antibiofouling, tissue closure capabilities	Han et al. (2019)
6	Titanium and 9Cr-1Mo steel modified surfaces	Corrosion resistance and antibiofouling	Mahalakshmi et al. (2011)

method, microfiltration membranes can be coated with nanosilver for mitigating membrane biofouling with less reduction in flux rate for a 60-day operation period (Le et al. 2019). For long-term effect, silica was used as a carrier of silver nanoparticles on PVDF membranes, and thus, silica nanopollens were developed that produced a thinner biofilm layer which majorly comprised of dead cells (Zhang et al. 2020).

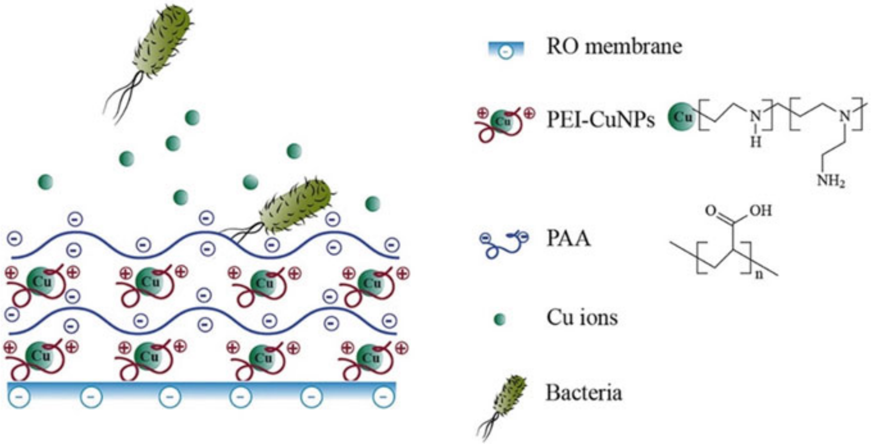

Fig. 15.12 Copper nanoparticles on thin-film composite RO membrane to reduce biofouling. Adapted from Ma et al. (2016)

Another example of a polymer-nanomaterial complex is that of polysulfone/alumina nanocomposite, which increased membrane hydrophilicity and surface roughness, and reduced the biofilm attachment onto the membrane surfaces. The separation efficiency of the membrane was also maintained because of the small membrane pore (Homayoonfal et al. 2015). Copper nanoparticles have been long considered to be an excellent biocide with antibacterial activity. Ma et al. (2016) implemented a layer-by-layer technique with spray and spin assistance to functionalize a thin-film composite polyamide RO membrane with copper nanoparticles, as depicted in Fig. 15.12. These functionalized membranes reduced permeate flux rejection and enhanced the polyamide membranes' ability to resist biofouling.

GO is another promising nanomaterial that can be applied to prevent bacterial attachment and biofilm growth. Faria et al. (2017) demonstrated the synthesis of a thin-film composite that was functionalized with GO and silver nanoparticles. These functionalized surfaces exhibited inhibition of *Pseudomonas aeruginosa* in both static and dynamic crossflow biofouling tests. Further, the functionalization of PVDF with GO and PVP improved the surface hydrophilicity and antibiofouling property due to the synergistic effect of GO and PVP, which is attributed to the formation of hydrogen bonds between them (Chang et al. 2014). PVDF membranes can also be incorporated with QACs for the fabrication of antibiofouling membranes. Zhang et al. (2017) used carbon carriers for the controlled release of QACs to maintain the antibiofouling properties. These modifications have improved the membrane's physicochemical properties, which have improved its porosity and permeability.

Metal–organic frameworks (MOF) are another emerging solution to biofouling in the membrane separation processes. MOFs consist of organic molecules blended with metals increasing the chemical functionalities and porosity of the membranes (Wang et al. 2018). The first study on biofouling control using MOFs was carried out

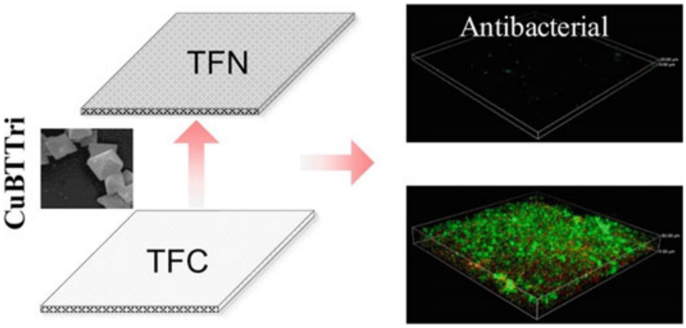

Fig. 15.13 Schematic diagram of the antibacterial activity of TFN membranes. Adapted from Wen et al. (2019)

by Zirehpour et al. (2017). In the study, MOF silver crystals were immobilized on the TFC membranes, thereby increasing the active layer on the membrane. This active layer increased membrane hydrophilicity which was empirical for improved antiadhesive and antimicrobial properties of membranes for biofilm inhibition (Zirehpour et al. 2017). The integration of MOF, CuBTTri, a copper-based active layer, led to the synthesis of an antibacterial thin-film nanocomposite (TFN) membrane. As depicted in Fig. 15.13, the TFN has a thinner biofilm layer in comparison with the TFC membrane, thereby increasing the membrane's flux and antibiofouling capabilities (Wen et al. 2019).

15.6 Conclusions

Biofouling is a complex process of biofilm formation which is the deposition and accumulation of unwanted microorganisms on surfaces. Biofouling of membranes affects the efficiency and cost-effectiveness of pressure-driven membrane processes, which has an impact on their large-scale operations. Thus, there is an immense need for antibiofouling surfaces which can combat this critical issue. This chapter focuses on highlighting the efforts that have been undertaken to reduce or eliminate the biofouling phenomenon.

Fouling mitigation approaches can be implemented at any point of the membrane processes, such as altering the membrane material, operating parameters, and system design. The existing conventional methods are found to be less effective for mitigating biofilm formation. The use of biocides, disinfectants, and other components can also damage our environment by polluting water resources. Moreover, the complex EPS matrix reduces the diffusion rate of disinfectants and antibiotics, conferring less exposure of microbes to these agents. High doses and delayed exposure of antimicrobial agents to microbial strains activate their drug-resistance genes, weakening the effect of agents. Membrane cleaning using physical methods is another widely used strategy at the treatment facility to reduce fouling. Monitoring the flow conditions with backwashing/backflushing, gas sparging, and adding electric fields is considered a versatile technology for biofouling mitigation. However, a complete paradigm shift has been observed in developing cost-effective and higher-efficiency anti-fouling agents that can be extrapolated at treatment sites. Novel techniques like quorum quenching and engineered bacteriophages have opened the horizons of exploring biological agents with anti-fouling properties.

Additionally, modification of membrane surfaces to develop fouling-resistant membranes has undergone much advancement. Majorly surface modifications are carried out using certain chemicals or nanoparticles mixed with the polymers to improve the membrane properties that support the detachment of bacteria or biofilm from surfaces. The enhancement of membrane characteristics, such as hydrophilicity, hydrophobicity, surface roughness, mechanical strength, and stability, is focused on reducing the adherence of bacteria to the membrane surfaces and increasing the shelf life of membranes. However, these developed membranes' compatibility with large-scale plants under harsh, varied parameters, and water conditions is still unanswered. Hence, more understanding needs to be developed using real wastewaters at a pilot scale to get better insights into the developed membrane strategies' potential.

Although a great deal of study has been done to examine the capability of these anti-fouling techniques, the fight against biofouling could be effectively solved using integrated approaches. Since biofouling is a vicious cycle, antifoulants should be incorporated which can not only prevent the adhesion of bacterial biomass but also inactivate them. An example of an integrated strategy is the utilization of superhydrophobic surfaces and antimicrobial coatings which can achieve both these effects. Simultaneously, limiting the concentration of nutrients in feed water would help to develop a fully functional system with optimum efficiency (Gule et al. 2016c). However, these integrated approaches can vary based on the application and duration of usage. Also, the challenge in these integrated management systems is to develop a cost-effective approach with an environmentally friendly strategy and sustainable solution, which calls for an immense amount of research and technical optimization.

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Chapter 16
Biomimetic Membranes for Effective Desalination and Emerging Contaminants (ECs) Removal

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Abstract Rapid growth and industrialization have increased water consumption and enhanced wastewater generation, thereby depleting surface water resources, decreasing groundwater tables, and the scarcity of drinkable water. In the last few years, water-related issues have become highly prominent. Moreover, the availability of freshwater resources is also limited, hence switching to sustainable alternatives such as seawater desalination and wastewater treatment has become essential. Treatment based on membrane separation is crucial for addressing environmental concerns and global water security issues. Due to better efficiency, lower footprint, reduced chemical use, and superior quality treatment, membrane separation becomes a viable solution. However, due to the inherent limitations of the membrane materials, there has been limited advancement in membrane technology for water treatment. With advances in material science and membrane filtration technologies, one can overcome the problems associated with conventional membrane treatment processes. Biomimetic membranes have emerged as a possible solution for membrane-based water purification and removing emerging pollutants in recent years. Bio-inspired technologies can master the challenges associated with existing membranes, including excessive energy consumption, very low selectivity, and limited permeability. Therefore, this chapter aims to briefly introduce different membrane-based separation technologies and compare membrane-deployed water purification and advancements for future development, mainly focusing on biomimetic membranes. Further, the last section deals with the scope of commercializing biomimetic membranes for emerging contaminants (ECs) removal and water purification.

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Keywords Membrane technology · Biomimetic membranes · Aquaporin proteins · Emerging contaminants (ECs)

16.1 Introduction

According to the Water Resources Group (WRG) report, about 40% of global water deficiency will be faced by 2030 (Malone 2022). Furthermore, according to the UN World water assessment, by 2025, around 2–2.5 billion people will face difficulties accessing consumable water (UNESDOC 2021). By 2050, at least 1/4th of the world's population will suffer from a freshwater shortage (Fuwad et al. 2019a). Increased emissions of greenhouse gases and escalating global warming are caused by increased urbanization, population growth, and extensive industrialization (Sharma et al. 2020). The constant release of complicated and untreated wastewater with a higher concentration of pollutants from agricultural production services, municipalities, local bodies, manufacturing, synthetic waste, textile hubs (Paul et al. 2019), and production industries causes lethal contamination of water resources like rivers, streams, lakes, ponds, etc. (Nations W.W.A.P 2022). Toxic contaminants in the environment have increased due to natural disasters and manmade activity. According to a report by UNESCOWWAP (2019), approximately 15–20 thousand people die daily from dumping ground 2–2.5 million tons of trash into water bodies (UNESCO 2022). As a result, one of the most critical research areas is the development of new and innovative methods for recovering freshwater from industrial and metropolitan wastewaters (Sharma et al. 2022). Therefore, a novel understanding of separation and purification methods is required to fully exploit the potential of these developing freshwater sources (Fuwad et al. 2019a). Since Loeb and Sourirajan in (1981), devised the cellulose acetate reverse osmosis desalination membrane about 50 years ago, synthetic membranes have covered a long journey (Loeb 1981). However, state-of-the-art synthetic membranes can now desalinate seawater under ideal circumstances with a 15–20% lower energy demand than RO membranes which is still 1.0–1.5 times the thermodynamic minimum energy (Barboiu 2012). As a result, there is a constant search for more efficient membranes with great separations and less energy. In the year 2006, Bowen went on to highlight how we might learn to construct membranes that are influenced by biomimicry to obtain better permeability and optimal selectivity (Bowen 2006).

Kumar et al. in the year 2020, presented a paper about adding aquaporin properties to desalination membranes (Suresh Kumar et al. 2020). Aquaporins are unique proteins found throughout living cells and have remarkable pore-forming capabilities. Under favorable conditions, they generate water channels that enable non-ionic yet polar water molecules to enter while excluding ionic species. Kumar et al. also showed aquaporins' excellent but distinct water permeability through characterization studies, extrapolating these findings to hypothesize a desalination membrane with increased activity (Suresh Kumar et al. 2020). In a recent review on bio-inspired membrane nanotechnologies, aquaporin-based membrane technologies have the most promising performance and efficiency but are far from commercialization (Ihsanullah et al. 2021). The potential efforts began in the previous ten years to fabricate realistic and commercial biomimetic desalination membranes assimilating aquaporin proteins. It is a good time to evolve into a new direction in desalination (Fuwad et al. 2019a; Müller et al. 2012).

In contrast with other traditional technologies for wastewater treatment, membrane-based technologies generate reliable quality freshwater with bare-minimum energy usage. For water desalination, numerous membrane techniques such as forward osmosis (FO), reverse osmosis (RO), electrodialysis (ED), and membrane distillation (MD) are currently employed (Hou et al. 2011). Out of all these, RO is the most extensively utilized and efficient separation process for water purification, with around 50–55% of desalination facilities worldwide using this technology (Zhan et al. 2020). Membrane materials, divided into two groups, are critical for the proper execution of membrane technology, and they are organic and inorganic materials (Fuwad et al. 2019a). Membranes with organic composition influence industries because of their low cost, higher efficiency, and excellent tunability. Further, the membranes are classified based on the force used to mobilize, temperature, concentration, power applied per unit area, or electric potential (Barboiu 2012). RO is a process that uses pressure as a driving force for water purification and needs specific unique membranes that can withstand a high-temperature and high-pressure environment.

On the other hand, FO utilizes natural energy for purification purposes and has multiple benefits over RO technology, such as low fouling, low energy requirement, and a lasting membrane lifespan (Kirschner and Brennan 2012). However, membrane fabrication and solution development require specialized membranes, restricting the application of FO for water purification. Some hybrid methods for water purification are developed to overcome the disadvantages of one process and optimally use the advantages of the other. ED is one among those in which electric potential is used as a driving force to separate ions from the input, and the solution acts as a driven solvent (Wang et al. 2021). For low salt concentrations in the water, RO-based technologies become uneconomical compared to ED, exhibiting higher separation and excellent performance. Another process in the same hybrid membrane technology series is MD (Jovanovic-Talisman et al. 2009; Shen et al. 2014). It is a membrane-based water sweetening technology that uses the partial vapor pressure difference across a hydrophobic but previous membrane using temperature as a driving force. This hydrophobic but previous membrane permits the water vapors to percolate through the membrane, excluding the water molecules or liquid (Duong et al. 2012). MD has several advantages over other filtration processes, including more efficiency and minimum operating charges. Moreover, quality is free of the concentration (ions) in the input solution (Nations W.W.A.P 2022; Wang et al. 2015).

So, this chapter aims to lay out an understanding of different forms of membrane technologies, such as RO, FO, MD, and electrodialysis. The technological applications of these membranes, the materials used, and the obstacles that each membrane technology presents are examined. Further, biomimetic membranes, particularly aquaporin-based membranes for water purification, are discussed, emphasizing using these membranes to remove ECs.

16.2 Membrane Technologies

16.2.1 Forward Osmosis (FO)

Water can transmit across a semipermeable membrane under natural flow in forward osmosis; this is comparatively less energy-consuming than reverse osmosis (Chun et al. 2018). Moreover, this property is utilized on a larger scale in food and drug preparation, desalination, and wastewater treatment processes (Yanar et al. 2021).

Technology in use. In the long run, FO systems can overcome the RO-based technology with less energy, lower fouling, and better efficiency, making it a good-to-go approach (Engelhardt et al. 2020). The continuous action of water across the membrane causes the fouling, but backwashing without chemicals easily yields about 90–92% water flux (Nikbakht Fini et al. 2020).

Membrane material. FO membranes are synthesized in almost the same way as RO membranes. A thin layer with high selectivity is chosen, further supported by porous support to provide the membrane's physical stability. Whereas, some recent research in this field abstracted that the osmotic force of the membrane decreases because the (Chun et al. 2018) perviousness and thickness of the support leads to the internal concentration polarization (ICP). And this, ICP can be increased further if:

(i) The membrane is dry, and air spaces are present in the membrane structure, which hinders the pore space and also accelerate the ICP, thereby decreasing its water flow and resulting perviousity (Munshi et al. 2018)
(ii) Membranes are less prone to degradation due to their strong chlorine resistance, but their poor ability to permeate and pH range limit their large-scale use (Engelhardt et al. 2020).

Challenges. FO has several advantages, with the exceptions such as in evaluating reverse solute diffusion, tedious process, concentration polarization, and solute recovery. Table 16.1 depicts some of the advantages and challenges of FO technology (Lee et al. 2020). For example, the drawer can influence polarization by its atomic diameter, diffusibility coefficient, and viscosity. In the same fashion, poor selectivity and less porosity elevate solute diffusion in a reverse direction, increasing the chances of membrane fouling (Engelhardt et al. 2020; Zhang et al. 2020). Continuous work is done to improve material synthesis for FO membrane to increase its selectivity, porosity, and efficiency.

16.2.2 Reverse Osmosis (RO)

Water is allowed to flow through a semipermeable membrane (SPM) under applied pressure, such movement of water is referred to as reverse osmosis (RO). Due to advancements in membrane materials, feed pre-treatments, and optimal filtering, this approach is gaining popularity (Zhan et al. 2020). Although nowadays, due to the development of recent technologies, the practice of RO is decreasing, and people are switching to less energy and more sustainable technologies. So, some new technologies may soon overcome RO technology (Garudachari et al. 2020) which is currently the most well-known and widely used technology compared to other technologies for water filtration and treatment.

Recent technology. Cross filtration is used in the RO method, where the input flows across the conduit in two directions. The permeate in one direction, and the impurities in the other (Zhao et al. 2012). RO technique can quickly remove about 95–99% of solid particles, dissolved salts, and biological contaminants. The reject stream concentration depends on two factors: the size and charge of the species (Nikbakht Fini et al. 2020). With an increase in these factors, the removal potential also increases. However, due to the lack of ionization in the solution, this technique cannot remove gases such as CO_2. A simple RO system comprises four components: pre-treatment, flow unit, assemblage, and post-treatment. To reduce fouling, the feed is pre-treated to eliminate unwanted materials such as suspended solids, macromolecules, and bio-contaminants. The pressured pre-treated sample is then transported to membrane assembly for additional treatment. Water can pass through an SPM, but salts cannot (Engelhardt et al. 2018).

Membrane materials. Pressure is the essential requirement for reverse osmosis to happen, and to sustain such a high-pressure, polymer-based membrane is employed; these membranes are broadly classified as cellulose acetate (CA) or non-cellulose acetate (NCA) (Bhojwani et al. 2019). Durability, high permeability, and low fouling are the utmost parameters for choosing a RO membrane. Non-cellulose polyamide is the most common material used for RO membranes because of its characteristics, as mentioned above (Werber et al. 2016). NCA membranes consist of an active thin polyamide layer which helps in higher salt rejection and more permeability to water. The various polymeric membranes can be divided into two types depending on the material, as in Table 16.2 (Fig. 16.1).

Challenges. Although RO technology has a lot of advantages (Table 16.1), including pure water extraction, salt rejection, and high permeate flux, still its performance is compromised in high energy requirements (Fuwad et al. 2019a; Chen et al. 2021). Even though RO technology is widely utilized, the scientific community is still looking for alternatives or energy-efficient systems because of its high energy demands, fouling, and difficulty synthesizing new membrane material. In addition, expensive pre-treatment processes, high pumping costs, and vast membrane areas often multiply the cost and make it expensive (Li 2021).

Table 16.1 Applications, advantages, and shortcomings of various membrane technologies

Separation process	Driving force	Energy consumption	Application	Advantages	Shortcomings	References
FO	Concentration gradient	0.5–5 bar	Water purification, power generation	Low energy consumption, lower cleaning cost, low fouling	Slow as compared to RO; sometimes leakage problem is also faced	Schaep and Vandecasteele (2001), Schneider and Gassel (1984)
RO	Pressure gradient	2.3–12.5 kWh/m^3	Micro solute and desalination and filtration technologies	High mechanical strength, ultrapure water	Lifespan short, fouling common problem, high cost and lower permeability	Castellana and Cremer (2006)
Distillation	Temperature gradient	0.5–1.3 kWh/m^3	The concentration of the solution, water purification	Complete removal of dissolved non-volatile solutes, low operating pressure	Comparatively more temperature, low flux rate	Lawson and Lloyd (1997), Calabrò et al. (1994)
ED	Electric potential gradient	1.0–3.0 kWh/m^3	Desalting of ionic solutions, the concentration of solutions	Ionic solutes, ultrapure water	Smaller life span, expensive, and fouling common problems	Strathmann (2010)
Biomimetic membranes	Pressure/concentration gradient	N/A	Ion filtration, organic solvent filtration	Low energy consumption. High rejection and better flux	Difficult for scale-up applications, difficult to handle	Atkinson (2020), Wang et al. (1862)

Table 16.2 Examples of polymeric-type materials (Fuwad et al. 2019a; Shen et al. 2014)

Polymer	Example
Natural or Cellulose (CA)	Diacetate, triacetate
Non-cellulose (NCA)	Nylon, polyethersulfone (PES), polyacrylonitrile (PA), polyurea, polyvinylidene fluoride (PVDF)

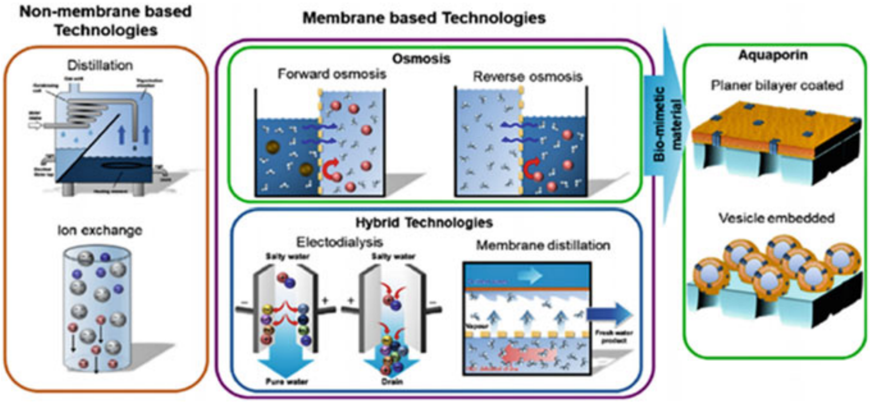

Fig. 16.1 Thermal-based desalination, mainly temperature-driven, and membrane-based technologies for desalination, which are generally pressure-driven. Reproduced with permission from Fuwad et al. (2019a)

16.2.3 Membrane-Based Distillation (MD)

MD is a separation method that is thermally driven, and separation happens because of a vapor pressure gradient (VPG) over a hydrophobic micro-pervious membrane (Calabrò et al. 1994). This water-repellent surface permits only vapors to pass across and not the liquid. Membrane distillation works on thermal evaporation as the driving force and is considered a non-membrane-based technology (Calabrò et al. 1994; Lawson and Lloyd 1997). Based on the method of vapor collection, the membrane distillation is divided into four major configurations, i.e., (i) Direct contact-based membrane distillation (DCMD), (ii) Vacuum-based membrane distillation (VMD), (iii) Air gap membrane distillation (AGMD), (iv) Sweeping gas membrane distillation (SGMD) (Fuwad et al. 2019a; Shen et al. 2014; Lawson and Lloyd 1997). The difference between the methods mentioned above is tabulated in Table 16.3.

Nowadays, the hybrid configuration has been designed to overcome the challenges associated with traditional methods of membrane distillation. These hybrid methods are designed in such a way to increase the thermal efficiency of the process so that they can be further used for industrial applications (Fuwad et al. 2019a; Lawson and Lloyd 1997). These include multi-effect membrane distillation (MEMD), where permeate vapors heat the feed so that heat is recovered and vapors are condensed. To enhance the vapor rate, MEMD replaces the air gaps with a mesh. For almost

Table 16.3 Methods for membrane distillation and their significance (Zhao et al. 2012)

Methods	Significance
Direct contact	Generally useful in food industries for edible food distillation, heat losses are majorly due to conduction losses
Vacuum distillation	Added cost due to vacuum pumps and condensers, generally used for components with high volatility and water purification and filtration
Air gap distillation	It works by introducing air spaces between the final extract and membrane, decreasing the loss by heating and increasing the mass transfer resistance
Sweeping gas distillation	Cost is expensive as adding a vacuum between the permeate and membrane layer makes it costly, which helps reduce the thermal polarization
Multistage multi-effect distillation	Generally known to achieve good thermal efficiency and performance, a mixed configuration helps recover heat and vapors that recompense

identical to MEMD, V-MEMD only differs in an efficient vacuum, which makes it more cost-effective (Fuwad et al. 2019a; Calabrò et al. 1994).

Technology in use. MD being a hybrid technique, has several benefits over different non-hybrid technologies. MD requires a minimum working temperature and pressure, significant efficiency for desalting, and extraction of ions just like nitrates and other organic solvents (Shen et al. 2014) (Fig. 16.2).

Membrane material. Unlike other approaches, MD membranes are designed to hold water while permitting only vapors to pass through effectively (Fuwad et al. 2019a). In MD, the membrane's selectivity is influenced by several factors, including

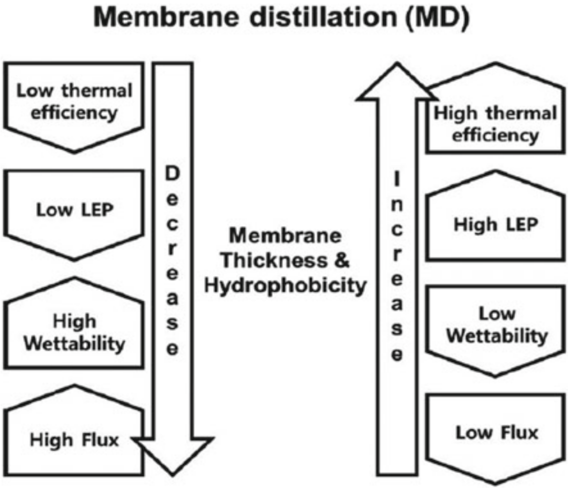

Fig. 16.2 Illustration of the performance of MD based on various factors. Reproduced with permission from Fuwad et al. (2019a)

electrical polarity, diffusion coefficient, pore size, etc. Water can cause membrane wetting during operation, which causes the membrane to lose selectivity (Calabrò et al. 1994). So, to achieve complete selectivity and efficient operation, hydrophobic membranes are used. Polyvinylidene fluoride (PVDF, MP 170 °C), polyethylene (PE), polytetrafluoroethylene (PTFE, MP 327 °C), and polypropylene (PP, MP 130–170 °C) are hydrophobic and thermally stable, hence commonly preferred for use in MD applications (Li 2021). Some current studies show that the performance of MD was improved with polytetrafluoroethylene (PTFE) membranes because of the high mass transfer coefficient and non-wettability nature of PTFE membranes as compared with membranes consisting of other materials such as polyethylene (PE) and polyvinylidene fluoride (PVDF), etc. (Fuwad et al. 2019a).

Challenges. The challenge that most scientific community faces in applying membrane distillation technology at a commercial scale is expensive membrane synthesis and wetting of membrane pores that ultimately removes the membrane's selectivity property and decreases flux and lifetime of the membrane due to internal polarization (Fang et al. 2020). The other challenges in MD processes are temperature, concentration polarization, and contaminants fouling the membrane surface.

16.2.4 Electrodialysis (ED)

Electrodialysis is a slightly different technology for filtration than the other two (RO and FO) technologies. An electric current is the driving potential for separating ions from water in electrodialysis. ED consists of a selective ion exchange membrane that separates different cell compartments. When the electricity is applied, the charges move toward the electrodes by passing through an SPM (Strathmann 2010). These processes happen within a cell boundary called an electrodialysis cell (ED cell) (Müller et al. 2012). This ED cell consists of:

(i) Electrodes–that push the ions/solute to separate.
(ii) A semipermeable membrane for ions selectivity.
(iii) An electrolyte that fills the gap among the electrodes to permit the current flow.

Technology in use. In ED process, ions are removed from an aqueous solution using electrically charged membrane viz, cation exchange membrane (CEM) and anion exchange membrane (AEM) and an electrically potential driving force. CEM allows the flow of cations and restrict the movement of anions and other charged neutral species; similarly, AEM allows only anions to pass through the membrane and blocks the cations and other uncharged species. The performance of ED depends on a number of parameters, including its ability to permeate membranes, its selectivity, the concentration of feed and effluent, amount of charge/electric, flow rate, etc. If the cost comparison is made between ED and RO technology, then ED is about 25% cheaper than RO and removes more ions, including nitrates and uncharged materials, e.g., silica (Zhang et al. 2021a). The most critical use of ED for water treatment is its fouling resistive properties. Fouling can be eliminated easily by polarity reversal of electrodes. This process is known as electro-dialysis reversal (EDR) (Strathmann 2010).

Membrane materials. The following conditions must be satisfied for a membrane to function as an ion exchange membrane (IEM).: (i) Stability-mechanical stability of the membrane should be maintained when the solution concentration changes; with a change in concentration, the membrane must not either expand or collapse. (ii) Chemical stability—the membrane should be chemically stable, i.e., withstand high temperature, accommodate increased pH levels, and show resistivity against oxidizing agents' addition. (iii) Perm-selectivity—the membrane must possess the ability to be permeable to counter-ions (referred to as a cation or an anion) and almost impervious to co-ions. (iv) Resistance—when the resistance is low, the membrane permeability should be high, therefore supporting the movement. IEM primarily consists of carbonless materials, a fixed cationic group (e.g., NH_3^+, NR_2H^+, and NR_3^+) that hinder cations movement (Müller et al. 2012). IEMs are divided into two main groups: (A) homogenous charged species that are chemically bonded; and (B) heterogeneous groups in association with the matrix of the membrane (Fuwad et al. 2019a).

The membranes can be classified as organic and inorganic. When polymers and copolymers with the ionic groups combine to form a membrane, such membranes are called organic membranes, e.g., PE, PP, PVDF, etc., and ionic groups are, e.g., acrylic, methacrylic, and acrylonitrile. Zeolite and phosphate salts result in inorganic membranes, but inorganic membranes have certain limitations over organics as, unlike organic, inorganic membranes have poor electrochemical properties and are more expensive (Müller et al. 2012).

Challenges. Unlike FO, ED requires a driving force for the purification action, as in the case of RO technology. Still, the difference is that in RO, pressure-driven power is needed, while in ED, electric current-driven action is required. However, more energy is consumed in both cases than in FO (Fuwad et al. 2019a). Other challenges include membrane manufacturing and costing, short lifespan, scaling, and sometimes, undesired reactions due to the chemical reactions yielding poor results (Table 16.1) (Strathmann 2010). Moreover, increased salt concentration has positive feedback on the energy consumption of ED. It was also observed that when the salt concentration of feed goes beyond 3 g/L, the reaction becomes almost non-feasible. In natural conditions, the salinity of seawater is approximately in the range of 32–35 g/L (Shen et al. 2014).

16.2.5 Bio-Inspired Membranes

As the name suggests, bio-inspired membranes are membranes inspired by biological principles and bio-natural phenomena (Kirschner and Brennan 2012). Bio-inspired membranes are a much broader term when a comparison is drawn between biomimetic membranes. So, sometimes we can also classify biomimetic membranes as a subtype of bio-inspired membranes. In recent studies, biomimetic membranes have acquired utmost importance due to their efficient salt rejection and superior water flux compared to other traditional membranes. Concurrently, with the development of research in this field via supramolecular chemistry of molecules (Fuwad et al. 2019a; Li et al. 2020), sophisticated instrumentation and characterization with high-resolution techniques have enhanced our potential to imitate the biostructures with more accuracy. Such breakthroughs generate the potential for further research in biomembranes. Membranes around the cell provide a passage to selective solvents and substrates with high selective diffusion and fast transportation rates that is almost uncommon in artificial membrane systems (Fuwad et al. 2019a).

16.3 Bio-mimetic Membranes: Separation Paradigms for a Bio-membranes

Biological membranes or bio-membranes (BMs), based on their internal structures and complex mechanisms, adopt effective separations to maintain the general metabolism and efficient working of the body (Shen et al. 2014; Tu et al. 2021). Thus, these BMs act as an excellent model that inspires the synthesis of synthetic bio-mimic membranes (Fuwad et al. 2019a; Tu et al. 2021). The sections below discuss these paradigms in detail.

16.3.1 Surface Proteins

Continuous layered proteins collected on the outer side of the walls in the prokaryotic cells are referred to as layer proteins or surface proteins (S-layer) (Shen et al. 2014). These protein molecules are non-covalently attached to lipid bilayers such as lipoglycans and peptidoglycans. These surface proteins are organized in either hexagonal or oblique fashion and form porous (30–70%) and thin (~2–8 nm) layers of surface protein (Fuwad et al. 2019a). Being lean and spongy, these are visible under a high-resolution scanning microscope (Shen et al. 2014). The protection of cells, adhesion properties, molecular sieving, ion traps, and surface recognition are functions of this thin layer in a cell. Although S-layer serves as a way for surface changes, modifications, purification, and antifouling properties, they have yet to be introduced on larger scales (Tu et al. 2021) (Figs. 16.3 and 16.4).

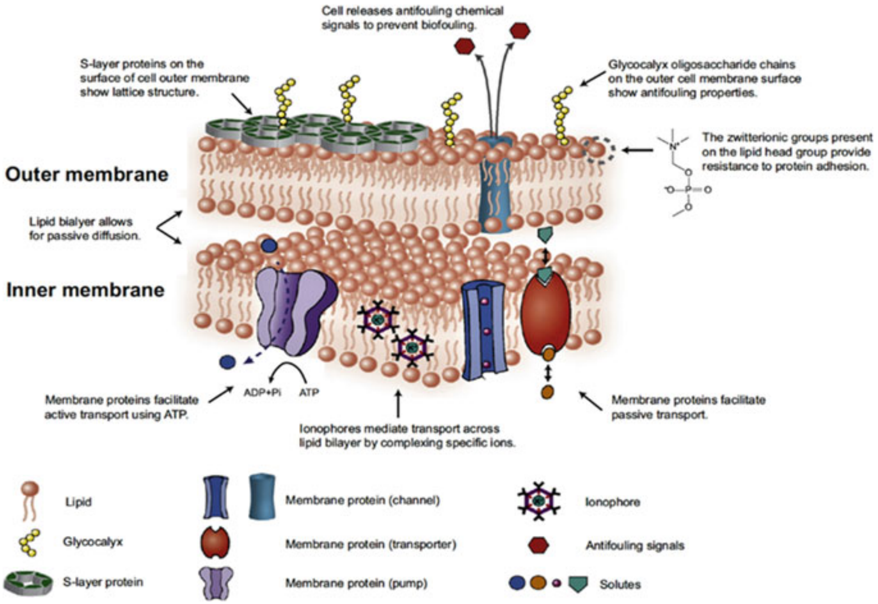

Fig. 16.3 Illustration of a gram-negative bacterium and biological membrane separation with fouling resistive properties. Reproduced and modified with permission from Shen et al. (2014)

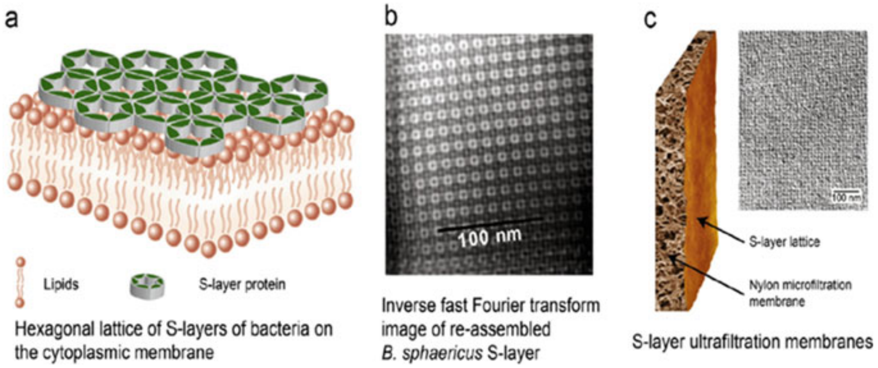

Fig. 16.4 S-layer membranes **a** Hexagonal lattice protein in bacterial membranes. Reproduced with permission from Shen et al. (2014) **b** Re-assembled FTIR image for bacterium S-layer. Reproduced with permission from Keizer et al. (2008) **c** UF membrane electron micrograph of S-layer. Reproduced with permission from Schuster et al. (2001).

16.3.2 Phospholipid Membrane Layer

The lipid bilayer is a vital but persistent barrier that separates the outside and inside cell compartments of a biological cell and permits small charged neutral molecules to pass across it using the solution diffusion model (Tu et al. 2021). The solution diffusion model is a two-step transport mechanism where molecules first enter the cell membrane and pass via the hydrocarbon portion of the cell membrane (Shen et al. 2014). This movement across the membrane is due to a potential gradient generated chemically, and therefore the permeability of the phospholipid bilayer is given as:

$$\boldsymbol{P = \frac{KD}{d}} \tag{16.1}$$

where K = partition coefficient for solute between hydrocarbon section and water of the lipid bilayer, D = solute diffusivity, and d = thickness of the hydrocarbon section of the lipid bilayer.

Overton’s rule is the relationship between the solute’s partition coefficient and the membrane’s permeability (Shen et al. 2014). The primary mode of passage across bilayer membrane include solution diffusion-based transport of water, nutrients, and gas molecules and progression through bio-membranes. Ions are also allowed to pass slowly across the lipid bilayer, whereas reasonable control is maintained by protein-based bio channels, transporters, and pumps. The cell volume that expands or shrinks is based upon osmotic pressure across cell walls mediated through channel transport (Fuwad et al. 2019a; Shen et al. 2014). These osmotic and water permeation principles, applied to all-natural membranes, helped us understand and design membrane technologies for FO and RO systems (Fuwad et al. 2019b).

16.3.3 Transport Across Bio-Membranes: A Transporter Conciliate Approach

Ionophores (special transporters) located in the water-repellent interior of the lipid bilayer can aid the movement of molecules across bio-membranes (Fuwad et al. 2019a). These transporters were initially found to help transfer ions such as K^+, Na^+, and Cl^- in the mitochondria (referred to as the cell’s powerhouse) of microorganisms, catalyzing energy processes. Ionophores are halichondrin peptides (molecules and ions with twelve or more than twelve membered rings) containing O_2 atoms or other suitable ligands. These ligands facilitate a joining space for an appropriate ion. (Shen et al. 2014).

A well-established fact is that the K^+ ionophore, which has a high affinity for potassium over other cations, is used in the ion-selective electrode (ISE). A classic representation of ISE is depicted in Fig. 16.5 as mentioned below (Schuster et al. 2001).

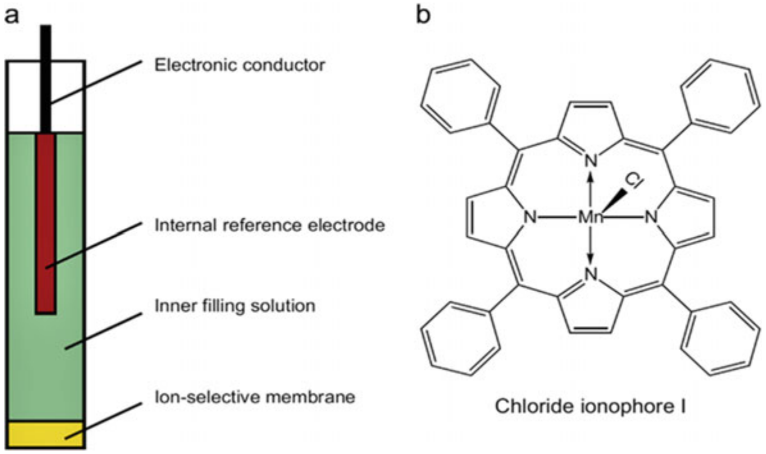

Fig. 16.5 Ionophore-based membrane: **a** Shows conventional electrode with ion-selective nature. ISMs are made of particular polymers, additives, ionophores, and substitutes. **b** Shows the Cl ionosphere, and the core Mn binds efficiently to Cl. Reproduced with permission from Shen et al. (2014)

16.4 Membrane Protein-Mediated Separation

The material movement through the membrane is regulated by unique membrane-based proteins that facilitate all active and passive activities, making biological membranes highly efficient at transporting materials (Chen et al. 2005). Proteins are categorized into three main types based on the transport mechanism: channels, pumps, and transporters. The details about channels, pumps, and transporters are provided in Table 16.4.

16.5 Biological Antifouling Approaches

Fouling resistive characteristics are very common to natural biological membranes. This resistive nature of natural foulant, which varies from micropeptides to macro-cells, makes these membranes highly selective (Hardie and Heurlier 2008). Most biological membranes have specific functional groups such as lipid head groups on the outer side of the membrane and prevent exterior foulant from adhesion (Zwaal et al. 1977). The zwitterion's negative or positive charges generate hydration due to electrostatic charges, resulting in a considerable proportion of water molecules tightly attached to zwitterions, reducing protein adsorption (Zhu and Marchant 2006). This vital characteristic impacts the formation of zwitterion polymeric coverings for fouling resistance applications. Intrusion with bacterial quorum signaling (QS) is one of the most straightforward approaches for creating an anti-biofouling impact.

Table 16.4 Classification of proteins based on the transport mechanism

Transport mechanism type	Specification	References
Channels	Pores facilitate the movement across the membrane passively The nature of selection depends on the charge, size, and underlayer interactions Usual channels are ion channels, gap channels, and water junctions Force for movement: Concentration potential Movement rate: highest Conformational change: not required	Lodish (2013)
Transporters	Based on transport mechanism is divided into three types: 1. Uniporters—used for the movement of only a single solute across potential differences generated by concentration 2. Symporters—used a gradient potential generated by an electrochemical means and facilitated solute movement in the same direction as upstream 3. Antiporters—used a gradient potential generated by an electrochemical means and facilitates upstream solute movement in the opposite direction Conformational change: required Transport rate: medium	Lodish (2013)
Transmembrane proteins	Have combining areas for particular ions or under layers The change in the shape of macromolecules is done via consuming ATP (ATP to ADP) or by absorbing photons Conformational change: required Transport rate: slowest	Lodish (2013)

Bacterial populations use the QS approach to control the progression and biofilm production. The adhesion of cells to the surface is aided by surface topography (Hardie and Heurlier 2008).

16.6 Aquaporin Membrane

Although several experiments are performed on biomimetic membranes, upscaling this technology and reaching the total capacity is still challenging (Zwaal et al. 1977). A typical biomimetic aquaporin membrane comprises three essential parts: aquaporin, membrane proteins (MPs) that operate as a water facilitator; an amphiphilic housing, which contains the reconstituted aquaporin proteins; and a porous solid underlayer, which gives physical strength (Fuwad et al. 2019a) (Fig. 16.6).

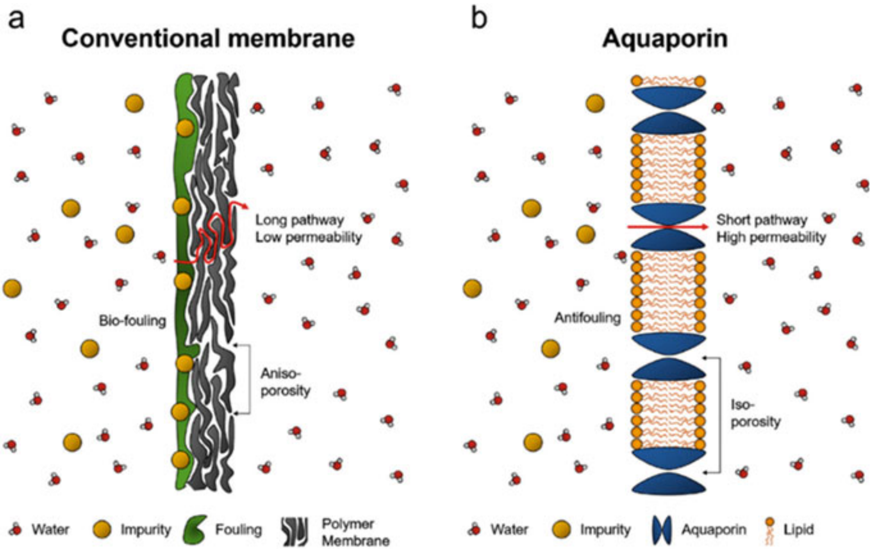

Fig. 16.6 **a** Drawbacks of traditional membranes, high fouling, and poor flux; **b** The advantage of aquaporin membranes over traditional membranes. Reproduced with permission from Fuwad et al. (2019a)

16.6.1 Transport Proteins (Aquaporins)

Aquaporins are the essential membrane proteins that act as channel for the flow of water by forming pores in the membrane. The presence of this pore is responsible for the selective permeability of the water molecules. Aquaporin proteins are a particular class of proteins found in all three kingdoms of life: bacteria, archaea, and eukaryotes (Tu et al. 2021). The primary function of these proteins is to maintain a water balance in the cells and permit water movement through the membrane.

Firstly, aquaporin proteins were discovered in red blood cells; later on, they were found in microorganisms, plants, and animal cells. Based on the structure and function, aquaporin proteins are divided into three major groups: (i) Orthodox aquaporin (allows water permeation only); (ii) Aquaglyceroporins (allows some molecules like CO_2, $CO(NH_2)_2$, NH_3, and $C_3H_8O_3$ to pass); (iii) Subcellular aquaporins (consists of unusual amino acid sequence and function which are still unknown) (Vadgama 2005).

The aquaporin monomer unit comprises six chains, which pass over alpha-helical domains with $-NH_2$ and –RCOOH terminal oriented towards the cell's cytoplasm. These helices are shown by H1-H6 terminology as represented in Fig. 16.7b; the extracellular and cytoplasmic vestibules form five interhelical loop regions characterized by A-E (Dingwell et al. 2019). The water-repellent chains B & E overlap with the water-repellent layer of the membrane and result in a sandglass formation (two inverted pyramids connected by a narrow tube), which permits water movement by

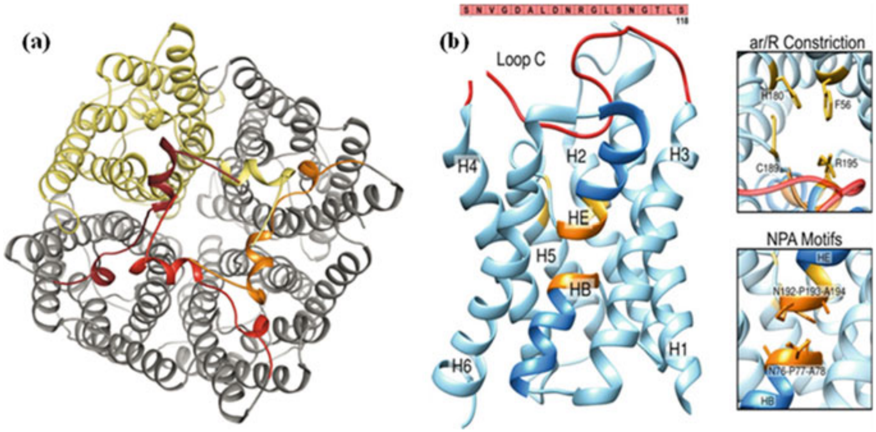

Fig. 16.7 Aquaporin model; **a** Overview of aquaporin structure. Reproduced with permission from Fischer et al. (2009); **b** The structural view showing the small chains parallel to the membrane. Reproduced with permission from Dingwell et al. (2019)

creating small helices, represented by HB and HE. These overlying results create channels within the monomers (Vadgama 2005). The top portion of the protein is connected by H2 and H5 chains, and the second portion is created by the C-side of the H1 and H4 chains, respectively. This setup ultimately results in making the pervious pores as narrow as 3 Å in size, which is a few points larger than the size of a water molecule, i.e., 2.8 Å, thereby restricting the movement of any other ion or particle greater than the water (Shen et al. 2014; Vadgama 2005).

16.7 Emerging Contaminants (ECs) Removal

ECs are majorly synthetic carbon-containing compounds that are nowadays detected in natural environments. ECs include primarily personal care products (PCPs), pharmaceutical organic contaminants (POCs), compounds disrupting endocrine systems (EDCs), surface-active agents, weedicides and pesticides, flame resistance, and additives manufacturing, etc. (Salamanca et al. 2021). The familiar sources of ECs include drugs and additives used in feed. Although certain impurities can be eliminated in WWTPs, ECs are frequently left behind. For rearing cattle and livestock, pesticides are used in agriculture, pharmaceutical, and other personal care products (PCPs), which, if not absorbed inside the body, can be removed from the body through urine and feces. These contaminants periodically reach the wastewater treatment plants (WWTP) and, in due course, enter the water streams (Rivera-Utrilla et al. 2020). Other contributors include hospital discharge, urban manufacturing plants, and WWTPs. The existence of ECs in the aquatic system results in causing a potential effect on marine species and leads to alterations that endanger the liveability and existence of marine life. Although some contaminants can be removed in WWTPs, the removal of ECs is often insufficient. The type of ECs compounds and their harmful effects on the environment and health are provided in Table 16.5 (Rivera-Utrilla et al. 2020; Shabani et al. 2021).

It is self-explanatory from Table 16.5 that ECs can cause various environmental and health-associated hazards. Treating them using sustainable and effective technology becomes the need of the hour. The biological treatment setup is a breakthrough in the recent ECs removal technologies. Therefore, there has been continuous growth in the scientific methods for synthesizing bio-membrane in the last decade, using simple and effective ways to be used at an industrial scale (Rivera-Utrilla et al. 2020; Zhao et al. 2012).

Table 16.5 Type of ECs, compounds present, and their effects on environment and health (Shabani et al. 2021)

S. No.	Type of ECs	Compound's present	Effects
1	PCPs	Analgesics, lipid regulators, antibiotics, diuretics, non-steroid anti-inflammatory drugs (NSAIDs), stimulant drugs, antiseptics, beta-blockers, antimicrobials, pharmaceutics, and cosmetics, SPF sunlight protecting cosmetics, food additives, perfumes, and metabolites	Environment—water quality parameters affected and most likely affects the potable water supply. Human health—abnormal hormonal control causing reproduction impairments, decreased fecundity, increased incidence of breast and testosterone cancers, and persistent antibiotic resistance
2	EDCs	Changes in the endocrinal system's activities result in adverse health effects on an entire organism, its offspring, and communities	Ecology and humans—the pre-mature breakage of eggs leads to neo-natal deaths in fishes, other marine organisms, and aquatic mammals. Reproductive and immune-suppressive changes in the aquatic species. Endocrinal hormone imbalance in humans
3	Pesticides	DDT, carbamate, pyrethroid, chlordane, malathion, dieldrin, and other derivatives of the same compound	Immuno-suppressive effects in the chordate phylum, aquatic mammals, and modify kidney tissues in mammals
4	Surfactants	Fatty acid esters of sorbitol Sorbitol monolaurate, phosphatidylcholines	It causes the physical instability of human growth hormones (HGH) and is accountable for disturbing endocrine processes

16.7.1 Treatment Technologies

Biological treatment technologies have become the most frequently utilized technology for ECs removal in the last few years. Some commonly used bio-methods include high-microbial sludge, artificial wetland, membrane bio-reactors (MBRs), aerobic/anaerobic bioreactors, etc. Recent studies revealed imperishable carbon-containing micro-pollutants which cannot be adequately remediated using biological treatment processes. So, supporting treatment technologies such as chemical treatment are also complementary for effective and efficient removal of ECs; such new technologies are also referred to as hybrid EC removal technologies that use a combination of biological and chemical treatment technology methods. Table 16.6 shows some biochemical treatment technologies (Rivera-Utrilla et al. 2020).

When complex and sizeable molecular weight ECs are broken down by microbes like algae, bacteria, and fungi into non-complex smaller structures, the process is known as biodegradation. On further mineralization, they tend to convert into simple and degradable inorganic molecules such as carbon dioxide and water (Rivera-Utrilla et al. 2020; Shabani et al. 2021). Some ECs are even hazardous and highly resistive to the growth of microbes, thereby resisting biological degradation; in such a case, a development regulator is required to regulate the growth of microbes for proper bio-degradation. Such a process is called co-metabolism. Biodegradation methods have been conventionally used in WWTPs for the extraction of ECs. Further, they can be divided into aerobic and anaerobic methods, where aerobic methods consist of activated sludge, membrane bioreactor, and sequence batch reactor processes; on the other hand, anaerobic methods include sludge and film reactor processes.

Although there is a lot of talk about bio-methods in the preceding part, along with the benefits, bio-methods have certain drawbacks, just like any other technology. However, we may describe it as different because it has fewer drawbacks than any other method of ECs removal. Some of the challenges associated with bio-methods include removal efficiencies affected by the seasonal variations resulting in reliability issues. In some methods, ECs are partially or almost not removed efficiently, resulting in the generation of many other waste products such as sludge. So, to cope

Table 16.6 Different biological and chemical treatment technologies

Treatment technologies	Category	Examples
Biological treatment technologies	N/A	High microbial sludge, artificial wetland, membrane bio-reactors (MBRs), aerobic/anaerobic bioreactors, etc.
Chemical treatment technologies	Conventional	Fenton, Ozonation, Photolysis
	Advanced oxidation	Ferrate (VI), reduction of Fe^{3+} to Fe^{2+} using UV irradiation (Fenton process), catalysis in visible and UV light, solar energy driven techniques, photo, and electro-fenton methods

with these challenges and address the issues of sustainability and reliability, an alternative technology called bio-mimetic or, more particularly, aquaporin membranes (AqP) came to light. And with the recent advancement, bio-mimetic or aquaporin membranes have become a successful method for ECs removal (Bolong et al. 2009).

16.7.2 Comparison Between Different Treatment Technologies

Traditionally, chemical technologies are favored for the removal of ECs. Still, with the understanding of challenges and demerits associated with chemical methods becoming clearer, treatment technologies started to switch to bio-methods. Nowadays, a hybrid combination is used for better removal and efficiency. Table 16.7 illustrates the advantages and challenges of the chemical and biological membranes, which helps us comprehend why we need to switch to more affordable, efficient, and sustainable technology to remove ECs (Zhao et al. 2021). And that alternative approach is nowadays provided by bio-mimetic membranes that mimic the biological setup and help in efficient ECs removal. Although such treatment technologies are in the niche stages of development, once developed, they can save tons of energy and resources, making EC removal highly efficient and sustainable (Zhao et al. 2012).

Table 16.7 presents a picture of each technology and its associated advantages and drawbacks, so we can infer that each technology has some beneficial outcomes but is restricted by some disadvantages. As a result, new advancements in the field are highly appreciated to eliminate such weaknesses and minimize the cost of scaling up. One such novel method for ECs removal has been using membranes, particularly Aquaporin membranes, because of their high specificity, efficient working, and porous channels with selective permeability. The section below will briefly discuss biomimetic aquaporin membranes for ECs removal.

16.7.3 Aquaporin (AqP) Membranes as a Tool for ECs Removal

Membrane research is not a new field, but advances in terms of changing characteristics, membrane synthesis, and membrane development have made it a different subject for further research and exploration. The membrane's ability to reject or remove ECs, and its rejection efficiency, are based on molecular dimensions, membrane adsorption behavior, and loading of organic contaminants to be evaluated. It is usually believed for a membrane system with a unique type of pore arrangement and chemical behavior that the standoff on this type of material is associated with its molecular weight, presence of a charge, and water-attracting or repelling properties of the passing solutes (Rivera-Utrilla et al. 2020). As a result, we can conclude

Table 16.7 Comparison between conventional, non-conventional, and physio-chemical methods

Treatment methods	Treatment process	Advantages	Challenges	References
Conventional treatment methods	Bio-activated carbon	High efficiency for EC removal Effective removal of oxidative residuary products No hazardous waste emissions	Somewhat expensive to maintain because of the high OPEX cost Effective disposal of high concentration sludge Furthermore, the total cost increases by almost 60% when sludge processing is also considered	Bolong et al. (2009)
	Microalgae bioreactor	Biomass from algae is used as a fertilizer, helping maintain efficient resource utilization Waste quality is comparatively good, and no toxicity risk is found	Low temperature reduces the efficiency of the system Improper degradation of EDCs is a big problem	Bolong et al. (2009); Zhong et al. (2020)
	Activated Sludge	Effectively less CAPEX and OPEX cost Eco-friendly and less emission of toxic waste	Low efficiency for pharmaceuticals and beta-blockers Sludge quantity is more compared to other processes Chemical oxygen demand for waste is high, effectively in the range of 4000–4200 mg/L; the process is almost unfeasible	Zhao et al. (2021); Tang et al. (2013)
Non-conventional methods	Constructed wetland	Power efficiency is high and inexpensive maintenance and working costs Shows an outstanding performance with emerging compounds like estrogen, pharma products, and cosmetics waste	Solid entrapments and sediment waste generation Need more space, a large effective area, and potentially more significant time	Zhang et al. (2021b)

(continued)

Table 16.7 (continued)

Treatment methods	Treatment process	Advantages	Challenges	References
	MBR	Generally, consider efficient removal of ECs and substances of biological nature that remain even after treating effluent The release of toxic emissions is significantly less	One of the significant areas of limitation is fouling and high energy demand The cost further adds on if aeration cost is also considered	Zhang et al. (2021b)
Chemical processes	Coagulation	It helps in turbidity removal, which generally arises from suspended particles	One of the major disadvantages is producing a large amount of sludge Secondly, it is considered almost none of the use technology when removing micropollutants	Ahmed et al. (2017)
	Ozonation	It shows more excellent combining potential with ECs in the presence of H_2O_2 (oxidizing agent)	Energy utilization is more and release of oxidation products as waste	Ahmed et al. (2017)
	Advanced oxidation processes (AOPs)	AOPs are considered to be selective treatment. It favors decontamination and disinfection of selective oxidants Significant ancillary effects on removing ECs such as EDCs, pharmaceuticals, PCPs, and pesticides short degradation rate	High CAPEX and OPEX costs Release of toxic by-products	Ahmed et al. (2017)

(continued)

Table 16.7 (continued)

Treatment methods	Treatment process	Advantages	Challenges	References
	Fenton and photo-Fenton	Degradation and mineralization of ECs	Decrease of OH formation chloro and sulfate-Fe (III) complexes	Ahmed et al. (2017); Rivera-Utrilla et al. (2013)
	Photocatalysis (TiO_2)	Use intense solar radiation in place of UV rays for effective product formation Degrading carbon-rich sustained compounds for effective removal High reaction rates upon using catalysts	Complex to consider the large volume of wastewaters for treatment	Rivera-Utrilla et al. (2020); Ahmed et al. (2017); Rivera-Utrilla et al. (2013)
Physical process	MF/UF	The main advantage of this physical process is the effective removal of heavy metals, which are helpful for desalting activities and useful for effluent removal in WWTPs	High cost of operation, high energy demand, membrane fouling, and disposal issues	Rivera-Utrilla et al. (2020)
	NF	Helps in the easy removal of textile effluents, dissolved dye, and other inorganic compounds	Limited application in pharmaceutical extraction, other fouling, and high energy demands are also there	Rivera-Utrilla et al. (2020)
	RO	Highly effective in the removal of pharmaceutical and cosmetic waste and EDCs	Nature of permeate—corrosive Lower efficiency in removal of pharmaceutical waste	Rivera-Utrilla et al. (2020); Bolong et al. (2009)

that aquaporin's porous membrane is brilliant in rejecting contaminants. However, as per the global mass balance, the portion of ECs is confined due to adsorption across the previous matrix space of the membrane (Bolong et al. 2009). To overcome this problem, Salamanca et al. (Salamanca et al. 2021) suggested multiple rinses to recover ECs fully; however, for some contaminants, they extracted in a single rinse, but for some other pollutants, it takes a much longer time to remove. Hence, multiple runs are performed. The tendency of a contaminant to be filtered out in a single run or numerous runs is usually based on its nature, impurity characteristics, filtration ratio, pore sizes of the membrane and movement rate, etc. These factors contribute to the efficiency of aquaporin membranes in filtering out most of the ECs in a single run with an efficiency of about 95%, which is relatively good compared to other methods for potential separation.

16.8 Future with Aquaporin Membranes as Potential ECs Removal

Escalating pollution is one of the most pressing issues confronting our ecology, including terrestrial and marine ecosystems. Pollutants are substances that alter the normal or optimal condition of air, water, or soil. Cosmetics, chemical products, textile and plastic pollutants, herbicides, pesticides, pharmaceuticals, and personal care goods are some significant sources of such polluting agents (Ahmed et al. 2017). The pollutants that are synthetic and organic are referred to as emerging pollutants. Biologically inspired porous aquaporin membranes have a unique ability for almost all organic chemicals and analytes to follow a highly selective approach (Bolong et al. 2009). Such characteristics of permeable aquaporin membrane also contribute effectively to the eco-favorable development of the environment and an effective way of ECs removal. Additional benefits of aquaporin separation and purification technology include high specific porosity, precise selectivity, efficient activity, controlled and accurate water channels, and others. The features mentioned above are of uttermost significance for the separation, extraction, and cost-effective remediation of ECs.

16.9 Conclusion

The current advancement in membrane technology, including biomimetic membranes, has reached a favorable stage (Zhao et al. 2021). Several technologies have been developed in the last few decades that undertake membrane technology to the next level. However, there are many challenges to overcome before these technologies are up-streamed. As per the literature, three significant challenges have been identified for biomimetic membranes (Shen et al. 2014):

1. The shortage of clear and elementary understanding of the interactions between the functional components and the materials used for the matrix.
2. High cost for the synthesis of biomimetic membranes.
3. Scalability issues of present systems for the amalgamation of bio-membranes.

Basic understanding of materials, such as artificial water passages that are synthetic transmembrane molecules, bio-material synthetic coating, membrane protein synthesis, and their interactions with frequently used and suggested membrane matrix materials like silicon and polymeric substrate, is yet a widely unexplored area of scientific research (Shen et al. 2014). Like membrane-based proteins, aquaporin must be combined with amphiphilic substances such as BCPs. Recently, most research applications have been focused on studying the interplay between the proteins (membrane proteins) and the amphiphilic housing (lipid/BCPs), e.g., the different interactions observed during lipid movement and their effects on the proper functioning of proteins. The length of the hydrophobic region that matches the aquaporin protein is a significant hindrance to aquaporins' stability, sustainability, and functionality.

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Chapter 17

Synthesis of Ceramic Membranes and Their Application in Wastewater Treatment and Emerging Contaminants Removal

Nainsi Chauhan, Rishabh Sharma, and Swatantra P. Singh

Abstract Due to its many advantages over other conventional treatment processes, membrane technology has been successfully used in wastewater treatment and desalination. Smaller footprint, higher efficiency, ease of operation & lower chemical consumption with optimum output are some of the inherent benefits of membrane-based treatment processes. However, some challenges associated with membrane technology, such as selectivity-permeability trade-off, fouling, specificity for uncharged contaminants in pressure-driven membranes, and energy consumption, led the scientific community to look for some improvements in membrane systems. These necessitate a new generation membrane with better selectivity & antifouling capability. Membrane technologies have broad applications in the removal of contaminants from drinking water and wastewater. The ceramic membrane has made rapid progress in industrial/municipal wastewater as well as drinking water treatment owing to its advantageous properties over the conventional polymeric membrane in recent decades. The beneficial characteristics of ceramic membranes include fouling resistance, high permeability, good recoverability, chemical stability, long shelf life, and self-cleaning properties and contaminants degradations which have found applications with the recent innovations in both fabrication methods and nanotechnology. Therefore, ceramic membranes hold great promise for potential applications in water treatment. Porous ceramic membranes have gained a commercial foothold in microfiltration (MF) & ultrafiltration (UF) applications in wastewater treatment. Ceramic-based membranes are promising and will soon become key players in water technology. This chapter mainly highlights the research and progress of fabrication methods to synthesize ceramic membranes. Furthermore, wastewater treatment

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applications of ceramic membranes, including oily wastewater treatment, heavy metal ion removal, industrial wastewater treatment, bacteria and viruses removal, and removal of emerging contaminants from wastewater are presented. Finally, future scope and challenges for further improving low-cost ceramic membranes are also emphasized in this chapter.

Keywords Ceramic membranes · Desalination · Wastewater treatment · Microfiltration · Ultrafiltration

Abbreviations

BOD	Biological oxygen demand
COD	Chemical oxygen demand
FO	Forward osmosis
MF	Microfiltration
MB	Methylene blue
MBR	Microbial Bioreactor
NF	Nanofiltration
RO	Reverse osmosis
UF	Ultrafiltration

17.1 Introduction

17.1.1 Water Crisis

Water is one of the essential resources and almost mandatory for the survival of all living forms on earth, whether plants, animals, or developed beings such as humans. Water availability is not limited but is somehow restricted to pure water sources that are significantly available for human consumption. About 97.5% of total available water is in the form of salt water that is directly non-consumable, and about 2.5% is only available for human use (Administrd Bb, n.d.). Water is also necessary for many aspects of the economy. According to the State of Climate Services 2021, approximately 3.6 billion people were without potable water for at least 30 days per year in 2018. This situation is expected to worsen by 2050 when the global population reaches more than 5 billion people. Furthermore almost 2.6 billion people reside in areas with penurious sanitation, and millions of people die each year—3800 children every day—from diseases spread by impaired water or human waste. Many others have been sick due to illness and contamination (Shannon et al. 2008). Fast industrialization, exponential urbanization, and increasing population have all significantly increased the need for water filtering capacity. Moreover, the wastewater generated by textile industries (Sharma et al. 2021), dye-effluent-based clothing plants, and other synthetic waste hubs further exaggerated the situation (Paul et al. 2019). Environmental disasters & various anthropogenic activities contributed to the increase of toxic pollutants in the environment (Erukhimovich and Cruz 2004). Water consumption has risen at more than twice the pace of human population increases in the last century, leaving water scarcity one of the most globally critical issues. The need for increased water filtration and desalination capacity has been exacerbated by increasing industrialization in developing countries and the resulting contamination of freshwater resources. Water prices will exceed as freshwater resources become limited, fueling the operating cost (Abdullayev et al. 2019). These data are likely to get worsen due to the rapid increase of water contamination by various pollutants such as pesticides, heavy metals, pharmaceutical compounds, & endocrine disrupting chemicals (Bohn et al. 2009; Shannon et al. 2008).

Additionally, regulations governing the quality of pure drinking water, surface water, and wastewater/municipal sewage are becoming increasingly stringent, making appropriate water management more critical than ever (Abdullayev et al. 2019). As a result, water contamination is a significant threat to water usage. This means that introducing any undesired element into the water, which pollutes and degrades the water's quality, makes it unsafe not just for drinking but for agricultural and industrial use. As a result, removing contaminants from water is critical for it to be suitable for use. So, clean and safe drinking water necessitates the evolution of reliable, inexpensive, and dependable methods for purifying local raw water resources.

Over the last few decades, the efficacy of traditional water treatment technologies has declined. The current high-water quality rules and regulations are incompatible with the conventional treatment system. Wastewater reuse is also becoming highly significant, particularly in desert and semi-desert regions where water is imported at a large expense. The need to reuse municipal and industrial wastewater, which contains many harmful elements that conventional treatment techniques cannot eliminate, has arisen due to the rising population and increasing water scarcity (Inyinbor et al. 2018). As a result, membrane therapy will be the best alternative. Furthermore, improvements in membrane quality and an ever-increasing demand for membrane processes are opening the way for membrane treatment in terms of their cost. For modest facilities (up to 20,000 m^3 /day capacity) (Wiesner et al. 1994), the cost of novel membrane filtration is predicted to be more or less than that of conventional treatment procedures, according to specific estimates. Membranes can be used to better various separate contaminants without needing chemicals. Emerging contaminants such as medicines and personal care products have raised concerns about their removal from water due to their potentially detrimental effects at low concentrations, necessitating modern treatments such as membrane technology (Inyinbor et al. 2018). According to Hamingerova et al. (2015) conventional treatment plants are insufficient against these new pollutants. Membrane technology can thus be instrumental in eliminating these pollutants. In comparison to traditional treatment, membrane-based treatment plants have a lower footprint. Membrane technology's automatic controls and alarms can ensure trouble-free operation with minimal operator attention, making it easier to operate than conventional treatments (Cui and Muralidhara 2010).

17.1.2 Membrane Technology

Membrane technologies are known to be one of the most effective desalination and wastewater treatment. Membrane water filtration has various advantages, including a small footprint, low operating temperature, ease of operation, high removal efficiency, and low sludge production (Haque Barbhuiya and Singh). Membranes are classified on the basis of operational modes (1) cross-flow filtration (2) dead-end filtration. Membrane technology is classified based on driven forces such as (1) Pressure-driven process includes UF, MF, NF, RO, and MBR applications, (2) Thermally driven process includes MD applications, (3) Chemically potential driven process includes FO applications, and (4) Electro potential driven process includes ED applications (Moattari and Mohammadi 2020).

Membranes are divided into two types based on the substance; they are made of polymeric and ceramic membranes. Wastewater treatment and desalination have long relied on polymeric membranes (Arumugham et al. 2021). Ceramic membranes, on the other hand, are a relatively recent technology. Membrane bioreactors (MBRs) (Fard et al. 2018), microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) all used ceramic membranes (Kim and Bruggen 2010) as shown in Table 17.1.

17.1.2.1 Polymeric Membranes Versus Ceramic Membranes

Membranes are separated into organic (polymeric) and inorganic (ceramic) membranes based on the material used in their construction. Inorganic membranes include ceramics, zeolites, amorphous silica, nonporous carbon, carbon molecular sieves, mixed conducting perovskites, and palladium alloys, while organic membranes include polysulfone, polyether sulfone, polymethyl pentene, cellulose acetate, polyphenylene oxide, and polydimethylsiloxane. Membranes made of polymers (Arumugham et al. 2021) and ceramic materials (Fard et al. 2018) have been

Table 17.1 Classification of pressure-driven membranes

Separation process	Category	Pore size	Applications
Microfiltration	Microporous	50 nm–5 um	Bacteria, fine solids
Ultrafiltration	Mesoporous	5–100 nm	Proteins, viruses, total suspended solids, natural organic matter
Nanofiltration	Microporous	1–5 nm	Dye, divalent ions dissolved solids
Reverse osmosis	Dense	–	Monovalent ions

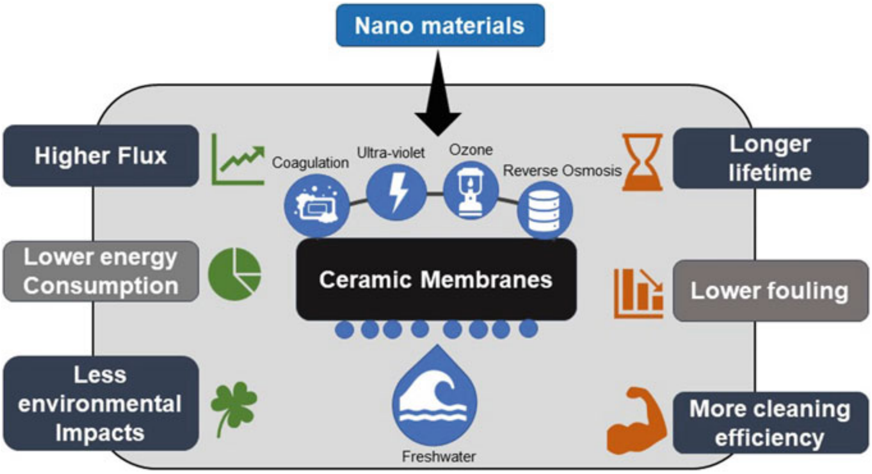

Fig. 17.1 Ceramic membrane advantages over the polymeric membrane

widely used in a variety of applications. Polymeric membranes, on the other hand, have mostly dominated the market as commercial filters for industrial and domestic applications. Regardless of their ubiquitous utilization, the polymers used to make membranes are fouling, have long-term negative environmental consequences, and are non-biodegradable. Ceramic membranes, like polymeric membranes, become contaminated during a standard separation process (Kim and Bruggen 2010). Compared to polymeric membranes, ceramic membranes offer a (Fig. 17.1) lower fouling proclivity, more mechanical strength, a longer lifetime and, higher chemical and thermal stabilities, cheaper operational costs, according to Lee and Kim (2014) (Sheikh et al. 2020) as shown in Table 17.2.

With the rapid development in technology, ceramic membranes can be seen as a filtration technology for the coming future. As with the emerging population, the need for freshwater resources also increases, and it leads to a water-scarce condition in the coming future so a reliable, efficient, and sustainable water treatment technology serves as an inoculum for developing technologies in the future. Ceramic membranes' intriguing characteristics have enticed academics to investigate their use in desalination and wastewater treatment. Several studies are now being conducted to improve the performance of ceramic membranes. Furthermore, many researchers are investigating new methods for fabricating ceramic membranes with low-cost materials (Hubadillah et al. 2018). Ceramic membranes should be considered a superior option for overcoming these issues. (Ben-Ali et al. 2018).

Table 17.2 Comparison between polymeric and inorganic membranes (Ben-Ali et al. 2018; Fard et al. 2018)

Properties	Organic membranes	Inorganic membranes
Material	Depending on the operating temperature, rubbery or brittle type membranes	Inorganic materials, i.e., glass, ceramic, silica, etc.
Characteristic	Rubbery state when flexible and glassy state when in rigid form	Mechanically, thermally, and chemically stable operational under harsh feed condition
Advantages	Good selectivity, cost-effectiveness, easy processability	Withstand harsh chemical cleaning, be sterilized and autoclaved, withstand high temperatures (up to 500 °C), be resistant to wear, have a well-defined and consistent pore structure, have a high level of chemical stability, and have a longer life span
Disadvantages	Fouling, limited operating temperature, chemically nonresistant and pressure, the short lifetime	Fragile, rigid

Table 17.3 The main advantage and disadvantage of each fabrication method used to produce ceramic membranes (Ewis et al. 2021)

Method	Inexpensive	Simple operation	Environmentally friendly	Multiple configurations can be produced	Produce relatively high membrane strength	Other
Paste casting	✓	✓	X	✓	X	Difficult to control the membrane thickness
Tape casting	✓	✓	X	X	X	Low production rate and easy control on membrane thickness
Pressing method	X	✓	✓	X	✓	Produce only flat disc shape
Extrusion	✓	X	✓	X	X	Produce only flat disc shape
Freeze casting	✓	✓	✓	✓	X	Produce tubular shape

17.1.2.2 Disadvantage of Ceramic Membrane

Ceramic membranes have several drawbacks that make their production and fabrication complex, including their high cost, incompatibility with alkalis, and brittleness. The higher density of ceramic membranes compared to polymers is one of their key drawbacks. Low membrane surface area per unit volume is another issue with ceramic membranes, but a long service life typically overcomes this. Reduce the labor expenses involved with coating the surface membrane layer of each carrier. In order to produce a greater filtration surface area, the porous multichannel monomer membrane component can be more expensive than the polymer membrane. One of the major aspects of the ceramic membrane is membrane sealing membrane technology, especially for ceramic membranes that operate at high temperatures (over 900 °C) and pressure (above 10 atm). So to overcome this, the seal technology must be able to deliver a gas-tight membrane for applications without completely altering the mechanical and chemical properties of the ceramic membranes (Drain membrane sealing applications ceramic membranes for power plant oxygen transport membranes: dense).

This chapter aims to know the basic principle of ceramic membrane technology, its advantages over polymeric membranes, its applications in wastewater treatment applications, and its great advancement in the industrial field. It also reviews the fabrication methods to synthesize ceramic membranes and emphasizes using these membranes to remove ECs. Finally, market prospects and future research goals are described for extensive ceramic membrane applications in the water and wastewater industry.

17.2 Ceramic Membrane Technology

The ceramic membrane is a ceramic-based inorganic separation membrane having a separating function. It's a product made by consistently blending inorganic raw material additives following reaction molding and high-temperature calcination. Generally, the porosity of the membrane is more than 30%, with an average pore size of 110 μm (Tai et al. 2020). Ceramic membranes have a multi-layered structure (Fig. 17.2) that includes a macroporous support layer, an intermediate layer, and a selective microporous top layer (Arumugham et al. 2021). The active (top) layer plays a key role in the better separation of contaminates and also determines the membrane's porosity & contributes to the membrane's mechanical and thermal properties. Since low-cost ceramic membranes have relatively wide pores in the micro range, an intermediate layer can reduce the membrane's pore size and provide advanced functionalities, such as hydrophobicity, to enhance the membrane's performance. The support layer provides mechanical strength & also increases permeability by providing a smooth membrane surface (Asif and Zhang 2021).

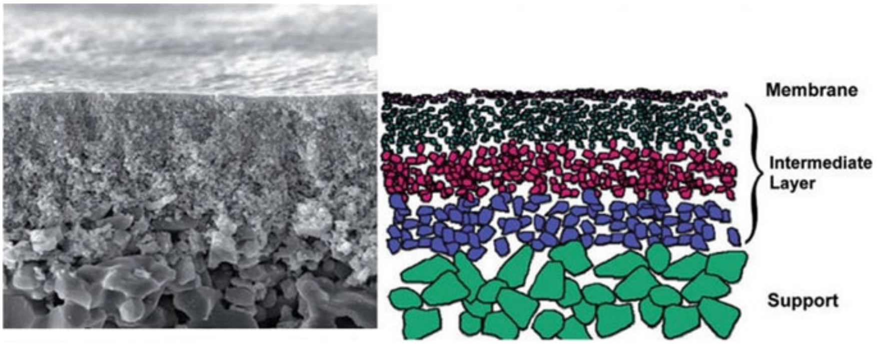

Fig. 17.2 Schematic representation of ceramic membrane structure; **a** Represents the SEM analysis for ceramic membrane, **b** Diagrammatic sketch for ceramic membrane (Liquid filtration through ceramic membranes 2017)

The most prominent inorganic substances used to form ceramic membranes are alumina (Al_2O_3), zirconia (ZrO_2), titanium (TiO_2), and silicon carbide (SiC). Additionally, zeolite, fly ash, and kaolinite have reportedly been investigated as ceramic membrane preparation alternatives. These ceramic precursors have outstanding mechanical strength, thermal stability, and pH tolerance across a broad range. An integrated membrane is one in which the same substance composes all three layers of the ceramic membrane. Composite ceramic membranes are defined as those in which the materials utilized for each layer differ. Ceramic membranes are categorized according to their pore size, membrane nature (hydrophobic or hydrophilic), and uses. The ceramic membrane's pore size is critical in deciding its applicability. Numerous MF and UF applications, for instance, involve the study of ceramic membranes (Fig. 17.3) with macropores (>50 nm) and mesopores (2–50 nm). A novel class of pollutants known as micropollutants can be eliminated by NF membranes (pore size 0.2–2 nm). Membrane distillation (MD) applications can benefit from hydrophobic macroporous membranes (0.1–0.5 m) (Arumugham et al. 2021). Ceramic membranes provide the porosity required for microfiltration/ultrafiltration (MF/UF) separation, as well as durability, chemical, temperature, and pressure resistance (Goh and Ismail 2018).

17.3 Fabrication Methods of Ceramic Membranes

Ceramic membranes are made using a variety of manufacturing techniques. Depending on the application and membrane structure, each method is different. The membrane manufacture process is divided into four stages: (1) particle or powder dispersion, (2) membrane structure shape (flat or tubular), (3) heat treatment (calcination or sintering), and (4) surface modification (additional layer deposition) (Shurygin et al. 2021).

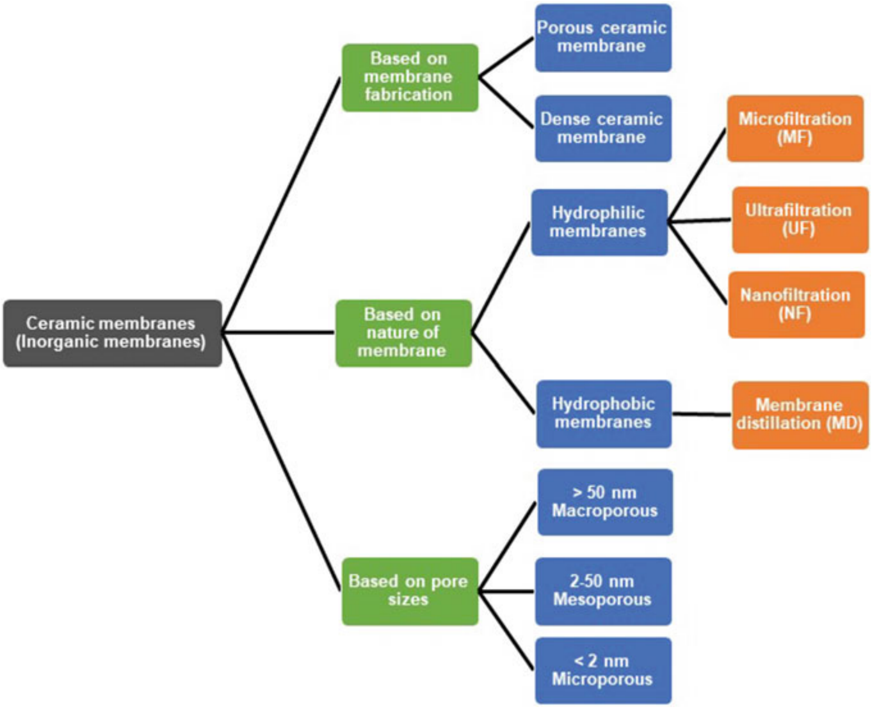

Fig. 17.3 Classification based on ceramic membrane pore characteristics, nature and fabrication membrane

17.3.1 Preparation of Powder Suspension

Ceramic membranes are produced in the first step of production from a slip-like dispersion of tiny particles. In which the raw materials or ceramic materials are blended with some additives like polymeric binders or plasticizers, or pore formers to retain the membrane's microstructure and quality (Azaman et al. 2021). Example: Raw materials like kaolin, quartz, clay, etc. are mixed with a binder like polyvinyl alcohol (Samhari et al. 2020) or starch (Elomari et al. 2017) in a ball mill for a specific amount of time to form a powder suspension.

17.3.2 Shaping Techniques

During the second step of fabrication, i.e., shaping technique, obtaining a green membrane with the desired geometry by molding the membrane using the appropriate fabrication method. The slip is deposited on to the porous mold which is used to get desired shapes, such as flat, tubular, and multichannel monoliths. Using the capillary action principle, the solvents are removed from the pores of the material, leaving behind only ceramic particles on the porous support of the membrane (Azaman et al. 2021). The type of fabrication procedure determines the geometry of the produced ceramic support or membrane. As a result, the membrane's microstructure and morphological characteristics differ depending on the synthesis method. Ceramic membranes are typically manufactured in either a flat or tubular shape. There are many more intricate configurations that are variations of tubular-shaped membranes, such as multichannel monoliths and hollow fiber membranes. While extrusion is frequently used to create tubular-shaped membranes, pressing, paste casting, and tape casting are typically used to create flat-shaped (circular) membranes. Several studies described ceramic membranes' production utilizing slip casting, freeze casting, and phase inversion (Yu et al. 2020) (Gaudillere and Serra 2016). Slip casting is generally used to form a hollow fiber membrane. Pressing, paste, and tape casting used to form flat ceramic membranes, and the extrusion method is used to prepare tubular membranes (Amin et al. 2016a).

17.3.2.1 Pressing Method

It is the most common and effective method for the fabrication of flat ceramic membranes. This method is categorized into two techniques that aid in the dry compaction of ceramic powder: (1) Axial pressing (uniaxial/biaxial) and (2) Isotactic pressing. In uniaxial die compaction, the powder material is compressed and shaped simultaneously in a rigid die (Hubadillah et al. 2017). Uniaxial die compaction can be divided into cold and hot processes. For the cold pressing method, a die is filled with a powder material mixture, then uniaxially pressed to a green body (compacted powder). After that, take out the sample. The hot method is nearly identical to the cold process, except that the green body is heated by induction in a vacuum or inert gas atmospheric (Perez-Moreno et al. 2012). The isostatic pressing technique uses multiple pressure to produce a more even and precisely formed compact. Compared to the paste casting procedure, the pressing process gave better coverage for manufacturing ceramic membranes. The pressing technique could result in a high-mechanical-strength ceramic membrane that could be used in high-pressure applications (Vasanth et al. 2011a). Uniaxial pressing, however, is more affordable and suitable for high-volume production (Monash et al. 2013). This approach involves properly combining the basic ingredients with the additives (binders, pore-forming agents, etc.) to create a homogeneous mixture. In order to obtain a flat membrane with the necessary shape, the resulting mix is then uniaxially compressed into a mold with the aid of a pressing machine, as shown in Fig. 17.4b–i. As a result, as uniaxial pressure is applied, the green membrane's strength increases, and the final membrane's pore size decreases. However, there is a maximum pressure beyond which there are no structural alterations (Issaoui and Limousy 2019). Subsequently, the membranes are dried and sintered at the optimal temperature to produce a membrane that is mechanically stable and free of cracks (Azaman et al. 2021) (Sandhya Rani and Kumar 2021).

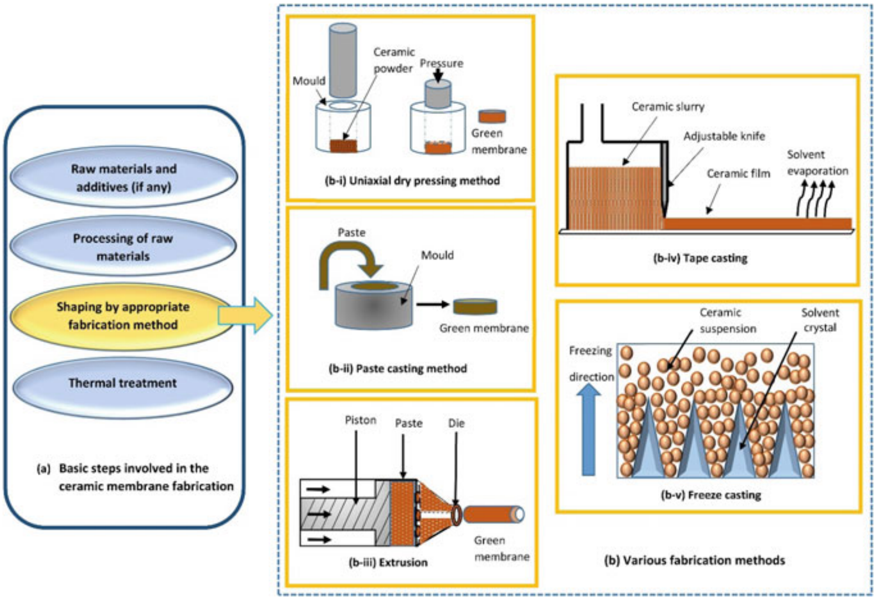

Fig. 17.4 Various fabrication methods to prepare ceramic supports (Sandhya Rani and Kumar 2021)

17.3.2.2 Paste Casting Method

Due to its simple approach and economic viability, it is the most widely used method. It is used to make intricate, irregular, and non-concentric shapes. It doesn't need any specific equipment, unlike other techniques. This process involves combining the raw components with the appropriate quantities of deionized water to create a thick and uniform paste. The paste is then aged, put into a porous or nonporous mold, and manually squeezed to create a green membrane with the required shape (Fig. 17.4b–ii). The membrane is then dried naturally at room temperature for nearly to 24 h, followed by oven drying and sintering. Furthermore, the wall thickness is difficult to manage during the drying stage's consolidation and is typically thick. According toLi et al. (2020), the thickness of a ceramic membrane cast using the paste casting process varies depending on the casting time and slurry condition (Amin et al. 2016a; Azaman et al. 2021). The fundamental problem with the paste casting method is the low ceramic membrane strength caused by high porosity and low molds toughness. Controlling the sintering temperature is also important for controlling membrane strength and porosity. To effectively fabricate the membrane, however, takes a qualified person because it is difficult to control the microstructure and obtain a membrane that is free from cracks (Monash et al. 2013).

17.3.2.3 Extrusion Method

It's commonly used to make tubular-shaped ceramic membranes. This process is simple, essential, and mass-producible. Instead of using a mold, a die exhaust is used here. Blending, pugging, extrusion, cutting and drying, and sintering are the five processes in the extrusion process (Zereffa and Desalegn 2019). In this technique, the paste is made by combining the ceramic powder with deflocculants, plasticizers, surfactants, and additives like binders to create the desired characteristics. Additionally, binders are selected in a way that enables their removal from the final product during sintering. In order to create a viscous paste, the raw components were first combined with the necessary additions and vigorously kneaded. To create membranes with the correct shapes, the paste will be extruded using a piston, and a suitable geometric die after getting, as shown in Fig. 17.4b–iii. The membrane is cut with a sharp blade to the correct length, and it is then dried for a long time. The membranes then go through various heat treatments (Ren et al. 2015).

However, only this method provides a strong membrane structure; nevertheless, it needs a long preparation process and the production of sufficient pressure to run the mixture. It is generally suggested that the extrusion process be carried out at high temperatures and at a slow pace to avoid crack formation. Ceramic membranes can also be made from low-cost materials like apatite powder and kaolin using the extrusion method (Sun et al. 2020).

17.3.2.4 Tape Casting Method

In general, tape casting is used to create flat, thin ceramic sheets as well as insulated and dielectric plates. The raw material slurry or powder suspension is spread into the reservoir in this operation. A casting knife lies behind this reservoir, controlling the thickness of the gel layer (membrane) generated between the blade and the moving carrier (Nishihora et al. 2018). The membrane is then dried by evaporating the solvent off the membrane surface and burning it, which comprises vaporization, disintegration, and oxidation processes. Finally, the membrane sintering procedure is performed Fig. 17.4b–iv. This process produces ceramic membranes that are usually only a few millimeters thick (Samhari et al. 2020).

The main drawback of the tape casting technique is the uneven shape of the membrane that is produced by the erosion of the plaster mold, particularly when using inexpensive components in the slurry mixture, like kaolin. Of the tape casting method is the uneven shape of membrane created as a result of plaster mold erosion, especially when employing low-cost elements in the slurry combination such as kaolin. The organic de-binding and sintering processes, as well as the long processing time for the slurry containing small particles, cause crack formation. Organic solvents such as xylene, benzene, and other poisonous, dangerous, and expensive organic solvents should be utilized as binders, flocculants, and plasticizers in some slurry types (Nishihora et al. 2018; Samhari et al. 2020).

17.3.2.5 Freeze Casting Method

A innovative and promising fabrication method for creating highly porous ceramic membranes with vertical and hierarchical pores is called freeze casting, also known as ice templating (Huang et al. 2021). In this technique, physical interaction is used in place of chemical reactions. This method is utilized to develop membranes that are useful in both health and energy applications. Preparing a stable colloidal solution (combination of ceramic powder, surfactants, and binders), putting it into a mold, freezing the molded suspension, sublimation of the frozen suspension at low pressure and temperature, and lastly, sintering the membrane are all part of the process. This process involves freezing a liquid suspension for several hours, then sublimating the frozen liquid medium under reduced pressure. This process can be carried out with water, which is an environmentally benign solvent (Liu et al. 2017). In the process of freezing, the formation of solvent crystals rejects ceramic particles in the suspension, which shapes the pores (Fig. 17.4b–v). Additionally, the green compact is carefully sintered to enhance mechanical stability. With this technique, pores' size, shape, and distribution can be controlled (Khalili et al. 2015). Finally, unlike the extrusion method, the support layer's resistance to gas diffusion is negligible, decreasing the chance of pressure loss through the porous support (Fard et al. 2018).

17.3.3 Heat Treatment

The precursors for ceramic membranes are generated after the shape-forming stage. Then they are heated and dried. This is a very crucial step after shaping; the sintering process provides mechanical robustness and porous structure to the membrane. It occurs at a temperature below the melting point of the raw materials. It consists of three main steps:

1. **Pre-sintering**, occurs at a temperature of about 200 °C. Water may be chemically attached to the ceramic particle surfaces or crystallized water within the inorganic phases; hence pre-sintering is performed to remove it from the membrane precursors Guo et al. (2018)
2. **The thermolysis** or the calcination stage involves removing all organic components from the membrane precursor Azaman et al. (2021).
3. **In the sintering stage, the ceramic membrane's final shape** is stabilized, the porosity and pore size undergo significant modifications and the mechanical strength increases Ben-Ali et al. (2018). The mechanical strength of the finished membrane increases as the sintering temperature rises while the porosity decreases. Sintering activity and phase change of the membrane material and the support are important elements that determine the thermal stability of ceramic membranes Elomari et al. (2017). The ceramic material is held at a specific temperature for long enough for it to approach its equilibrium structure during sintering. The membrane structure may be maintained at temperatures as low as

100–150 °C below the sintering temperature, which is typically around 1000 °C Samhari et al. (2020).

17.3.4 Additional Deposition Layer Methods

The properties of the ceramic membrane, such as selectivity, conductivity, permeability, porosity, mechanical strength, hydrophilicity, biocompatibility, and so on, can be altered or improved by adding additional layer deposition. In order to build composite membranes, layer deposition techniques must be used to add layers to the asymmetric substrate. To create a gradient pore structure throughout the cross-section of the membrane, each layer is typically made up of ceramic particles of various sizes. To get the requisite selectivity at the end, multiple layers are usually required. Membrane technologies for water treatment advances the most typical method for layer deposition onto the support is a dip or spin coating (Ewis et al. 2021).

17.3.4.1 Sol–Gel Process

It is a relatively low-temperature chemical method to produce glassy or ceramic membrane material, especially metal alkoxide nanoparticles. It's utilized to make membranes with pores ranging from 10 to 100 microns. It supports the control of pore size and pre-size distribution. Ceramic UF membranes with good selectivity and pores that range from 100 nm to a few nanometers. Dip coating is used to deposit a colloidal (alkoxide) or polymeric solution onto a membrane substrate, which is then transformed into a gel by hydrolysis, condensation, or polymerization. It is then heat-treated to generate a thin, homogeneous skin on top of the membrane. Chemical vapor deposition and neutron sputtering are two alternative coating processes (Ewis et al. 2021).

There are two main routes for the sol–gel technique–(1) the colloidal gel route (2) the polymeric route.

(1) **Colloidal route**

The colloidal procedure is in which an excess acid or water is used to hydrolyze a metal alkoxide that has been dissolved in alcohol. When the resultant precipitate is heated for a lengthy period, it forms a stable colloidal solution of dense oxide particles. The resulting A stable colloidal solution of dense oxide particles occurs when the resulting precipitate is heated for a prolonged period of time. The colloidal solution is chilled before being coated on the support membrane's surface. This causes a metal oxide layer to develop, which is sintered at temperatures ranging from 500 to 800 °C. The colloidal technique for preparing alumina membranes is shown in the equations below (Monash et al. 2013).

$$\text{Precipitation}: \mathrm{Al(OR)_3} + \mathrm{H_2O} \rightarrow \mathrm{Al\ (OH)_2}$$

$$\text{Peptization}: \mathrm{Al(OH)_2} \rightarrow \gamma - \mathrm{Al_2O_3} \cdot \mathrm{H_2O}(\text{Boehmite})$$
$$\text{Sintering}: \gamma - \mathrm{Al_2O_3.H_2O} \rightarrow \mathrm{Al_2O_3} + \mathrm{H_2O}$$

(2) **Polymeric route**

It involves partially hydrolyzing a metal alkoxide that has been dissolved in alcohol with a small amount of water. The active hydroxyl groups on the alkoxides react to produce the inorganic polymer molecule, and the resulting polymer layer is deposited on the surface of membrane supports. During the drying and sintering processes, a metal oxide coating formed. The produced gels are powdered and then calcined after the drying stage. The sol–gel method is a feasible method, and the products' chemical composition could be well controlled because of the low reaction temperature (Amin et al. 2016a; Bokov et al. 2021).

The sol–gel process can be used to create ceramics as a molding material and as a bridge between thin metal oxide layers in a variety of applications (Khalili et al. 2015). The materials produced by the sol–gel process are employed in a variety of technologies, including separation, surface engineering, energy, optical and electrical (such as chromatography). For the manufacture of nanoparticles with various chemical compositions, the conventional and industrial sol–gel process is used (Qiu et al. 2010). Industries, including surface coating, building insulation, and the manufacture of specialized garments, all utilize dried gels in various ways. It is noteworthy that nanoparticles can be produced by grinding the gel in specific mills. Figure 17.5 depicts the production of a slurry or gel for the fabrication of a ceramic membrane using the five processes of hydrolysis, condensation, aging, drying, and calcination (Bokov et al. 2021).

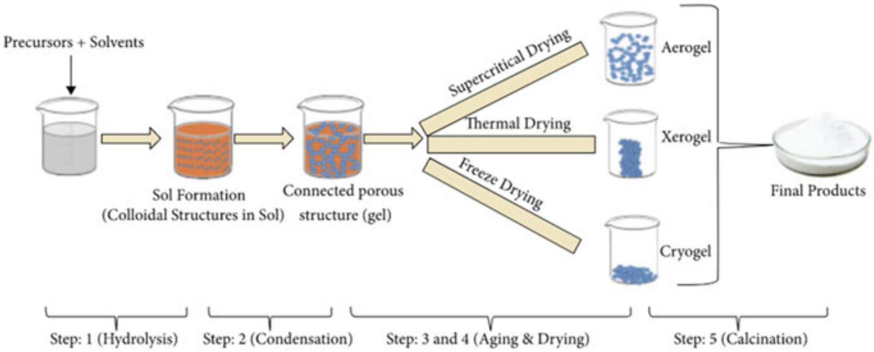

Fig. 17.5 Different stages of the sol–gel process: from precursor to final product (Bokov et al. 2021)

17.3.4.2 Dip Coating

Dip coating is a method of applying paint to a surface. As soon as the dip-coated substrate comes into touch with the air, it quickly dries up. Usually, a calcination phase follows. Coatings that are extremely thin can be made by this technique (Amin et al. 2016a).

17.3.4.3 Chemical Vapor Deposition (CVD) Method

CVD stands for chemical vapor deposition. The deposition of exceedingly thin and homogenous layers on a substrate is the goal of this approach. These layers might have comparable or dissimilar compositions, resulting in changes to the membrane's surface properties. A gas-phase chemical process at a high temperature can be used to deposit this material (Amin et al. 2016b).

17.4 Application of Ceramic Membranes

Due to polymeric membranes' inferior chemical and thermal stability and lifetime, ceramic membranes have been commonly used in applications where they are not acceptable. For example, ceramics can resist high temperatures, powerful chemicals (solvents, extremely acidic or caustic solutions), and oily water (Gopinath et al. 2021). In contrast to polymeric membranes, ceramic membranes can withstand high backwashing pressures, strong cleaning agents, and high-temperature sterilization without swelling in a solvent. Due to all of these advantages, ceramic membranes are now used commercially to maintain flux stability (El-Aswar et al. 2022). Ceramic membrane's efficacy in a variety of industrial uses, including the use of microfiltration to remove bacteria from food and dairy products (Tomasula et al. 2011), hot gas filtration (Li et al. 2011), juice clarification (Emani et al. 2013), and the biotechnology and pharmaceutical applications in the filtration of fermentation broths (Waszak and Gryta 2016) receives a lot of attention these days in the development of membrane technology. Also of great interest are alternate wastewater treatment methods, pollution control in industrial areas, the separation of oily wastewater (Madaeni et al. 2012), the treatment of textile mills (Barredo-Damas et al. 2012), removal of heavy metal content in industrial effluent (Noor et al. 2017) (Fig. 17.6). Table 17.4 describes the use of ceramic membrane technology in removal of various pollutants in wastewater treatment.

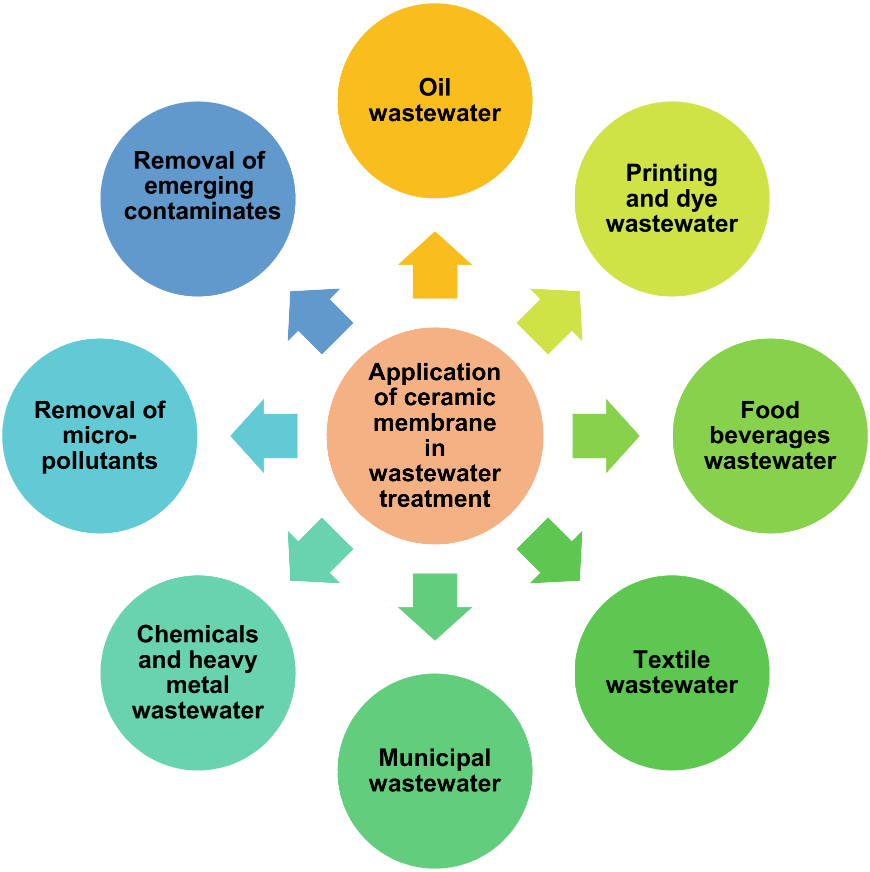

Fig. 17.6 Application of ceramic membrane in wastewater treatment

17.4.1 Drinking Water Production

Membranes such as MF and UF are widely employed in the production of drinking water, and they can handle both micro and large-scale capacities. Portable membrane systems are employed in small-scale MF/UF applications, while MF/UF membranes can be used as stand-alone or hybrid systems in a water treatment process train in large-scale applications. Polymeric membranes have controlled this industry for a long time and continue to do so, although the use of ceramic membranes to create drinking water has gradually increased. Drinking water can come from a variety of sources, including groundwater, lakes, and rivers, as well as municipal wastewater and the ocean (Meng et al. 2606). Huge systems are necessary to produce drinking water from surface water for a large community, i.e., for municipal usage. The water purification process will be broken down into several steps. Preparing drinking water from surface water is significantly more expensive since it involves more purification

Table 17.4 Pollutants removal by ceramic membrane water filtration technology

Process	Pollutant removal	Rejection %	References
UF	Oil emulsion water	97.8	Lu et al. (2016)
MF	Dye (red 80, acid orange 74, and methylene blue	98%, 85%, and 94%, respectively	Bouazizi et al. (2017)
UF	Ciprofloxacin	99.5	Bhattacharya et al. (2019)
NF	Radioactive uranium	91	Shannon et al. (2008)
UF	Pb (II)	99.6	RoyChoudhury et al. (2019)
UF	Fe (II), Fe (III), Cu(II), Cr(III)	86–98	Ouammou et al. (2018)
UF	Hg (II) and As (III)	99.9	Jana et al. (2011)
MF	BSA	91	Vasanth et al. (2017)
UF	Ni (II)	88.87	Noor et al. (2017)
MF	*E.coil*	94	Kumar et al. (2019)
	Humic acid	82	Zhang et al. (2020)
UF	Direct black DB	99	Majewska-Nowak and Kawiecka-Skowron (2011)
UF	Dye (MB, rhodamine WT)	88.3 & 99.1	Isanejad et al. (2017)
UF	EBT	99.4	Chen et al. (2017)

steps because the process design is dependent on the feed quality and the final water quality (Asif and Zhang 2021). A typical surface water purification process train includes a pre-filter unit, chemical addition, natural filtration, disinfection, coarse filtration, preservation, and storage. Conventional pollutant removal units like as coagulation and sedimentation, as well as disinfection units, may be replaced by ceramic MF/UF membrane units (s) (Li et al. 2017; Lin et al. 2018). Furthermore, the ability to reject microorganisms, bacteria, and viruses can reduce the number of chemicals that must be added to drinking water, preserving a large amount of space in the process. In order to make drinking water from the seawater, pre-treatment to reverse osmosis is being provided by ceramic MF/UF units (Asif and Zhang 2021; Issaoui and Limousy 2019; Li et al. 2017; Advanced Ceramic Membranes and Applications).

17.4.2 Municipal Wastewater Treatment

Ceramic membranes are typically employed in the water treatment process for increased products, and their cost is greater than conventional procedures (Meng et al. 2606). The fact that no chemical agents are introduced, and the effluent water quality is stable causes people to gradually become aware of it. Domestic water purifiers using ceramic membranes have also become more popular recently. They can filter water while retaining useful minerals, eliminating bacteria, rust, heavy metal ions, etc., and they don't generate secondary pollution. They have wide market potential and can be consumed promptly. Domestic wastewater contains a lot of water but is less contaminated than industrial wastewater. If it is not treated properly, it will contaminate the water body adversely. As a result, adequate treatment of urban sewage is required (Lin et al. 2018).

Using ceramic membranes to treat domestic sewage, (Huang et al. 2022) investigated the disinfection capacity of different cleaning agents for membrane tubes, and the results indicated that membrane fouling was primarily caused by colloidal substances, biological, organic matter, and other substances and that using 0.5% NaOH and 7.5% H_2O_2 had a good clean treating effect on the membrane tube (Lin et al. 2018).

In the application for treating domestic water, (Fatimah et al. 2015) presented the development and characterization of a new TiO_2-modified kaolinite ceramic membrane that was made using a tubular support structure and natural kaolinite. TiO_2 coatings with various compositions were studied on ceramic surfaces. The created membrane was then used to evaluate the levels of bacteria, iron (Fe), manganese (Mn), nitrate (NO^-), total dissolved solids (TDS), and total suspended solid (TSS) both before and after filtering. It has been demonstrated beyond a reasonable doubt that COD, TSS, and TDS are not considerably impacted, but Fe, Mn, NO^-, and bacteria reduction are. Similarly, (Ajayi and Lamidi 2015) ball clay has been used as the primary precursor for ceramic water filters in research on heavy metals (such as zinc (Zn), nickel (Ni), manganese (Mn), lead (Pb), chromium (Cr), and copper (Cu) in water used for in-home use. With respect to all of the parameter studies, their manufacturer's ceramic membrane exhibits excellent performance (Lee et al. 2015).

17.4.3 Industrial Wastewater Treatment

17.4.3.1 Oil and Lipids Treatment from Oily Wastewater

Oily wastewater comes from a variety of sources, including oily emulsion, water produced from oil fields, cleansing agents, wastewater produced from food and beverage waste, and other sources. Water oil emulsion is hard to degrade, pollutes the environment and also emulsifies easily (Huang et al. 2022). Large amounts of oily wastewater are produced by petrochemical industries and petroleum refineries, which poses a serious threat to the aquatic environment. As a result, disposing of oily wastewater in an environmentally responsible manner is getting more difficult. It's difficult to work with traditional methods (e.g., adsorption, chemical precipitation, and dissolved air flotation) (Yang et al. 2022). Ceramic membranes have a remarkable impact on the treatment of free and emulsified oily wastewater (Meng et al. 2606). In the Colorado oil field in the United States, used nanofiltration membranes (NF270 and NF90) to treat produced oily wastewater. The results reveal that the NF270 membrane significantly extract the fresh water when the recovery rate is high

(>62%) (Mondal and Wickramasinghe 2008) The oil presence is below the findable limit, with a median particle size of less than 1.5 μm. Currently, inexpensive ceramic membranes are widely employed for the treatment of wastewater contaminated with oils and lipids. As depicted by few research (Sandhya Rani and Kumar 2021; Abbasi et al. 2012) that kaolin clay from the Zenooz mine in Marand, Iran, was used to create the tubular mullite ceramic microfiltration membrane. Approximately 9% of the total organic carbon was rejected for synthetic feeds, according to the results.

Furthermore, a great number of researches conducted both at domestically and abroad have proved that ceramic technology has a superior filtration effect, and it is progressively demonstrating its competitiveness in the treatment of wastewater (Sandhya Rani and Kumar 2021).

17.4.3.2 Textile and Synthetic Fiber Wastewater Treatment

The cloth and fabric industry uses a lot of water, and the water it produces as waste includes suspended particles, chemicals, heavy metals, pulp, and other contaminants. Almost all dyes are firm, stable, chemically oxidizing, light-resistant, and non-biodegradable (Saikia et al. 2019) (Bouazizi et al. 2017). As a result, responsible for developing environmental toxins resulting in genetic mutations and cancer-causing effects in both aquatic and human lives (Chaturvedi et al. 2021). Therefore, it is required to treat waste before dumping them into freshwater resources. There are various types of pollution, and dealing with them using conventional practice is challenging. Ceramic membrane technology is found to be excellent for water treatment (Lin et al. 2018). To remediate textile wastewater, (Ananthashankar and A.G. 2013) employed alumina microfiltration membranes. The study reveals that the elimination of suspended particles and organic material was excellent. Insoluble dyes were removed at a rate of above 98%. Surfactants could be used to remove soluble dyes of approximately 97% simultaneously (Meng et al. 2606).

17.4.3.3 Application in Printing and Synthetic Dye Wastewater Treatment

Mixed concentrations, organic-rich content in water, dark color, and significant changes in acidity and alkalinity make printing and dyeing effluent extremely challenging to treat. Currently, the standard treatment approach combines physicochemical and biological methods; however, the treatment impact is insufficient (Issaoui and Limousy 2019). The inorganic ceramic membrane, with its high permeability and superior mechanical qualities, can efficiently separate pollutants in printing (Singh et al. 2019) and synthetic wastewater (Sharma et al. 2021), which has attracted increasing interest. To treat printing and dyeing wastewater, (Lee et al. 2015) employed membranes with a pore size of 50, 200, and 800 nm, a 200 nm operating pressure differential of 0.2 MPa, a temperature of 30 °C, and a membrane pore diameter of 50, 200, and 800 nm. The COD removal rate before treatment was 65% and after using ceramic UF membranes was 87.6% (Lin et al. 2018).

17.4.3.4 Industrial Wastewater Treatment

The effluent from chemical industries has a complex chemical makeup and typically comprises both strong acids and alkalis. The ceramic membrane technology has the upper hand in treating this type of wastewater over the traditional methods since they are more difficult to handle. Sludge and water were separated using an inorganic ceramic membrane distributing device in the primary sedimentation tank of the caprolactam production wastewater treatment process (Abbasi et al. 2012). According to the findings, the inorganic membrane method can successfully remove suspended solids (SS) and COD from water, with an SS removal rate of about 90%. Chemical wastewater has a complex composition, and the wastewater produced frequently comprises strong acids and alkalis (Radeva et al. 2021). The conventional process is tough to handle, while ceramic membrane technology treats this type of wastewater more effectively. Additionally, industries including tanneries, mining, fertilizers, metal plating, and paper production produce wastewater that contains heavy metal isotopes. These are poisonous, cancer-causing, and non-biodegradable. Even at very small concentrations, metal ions such as Zn (Zinc), Pb (lead), Cu (Copper), Hg (Mercury), Cd (Cadmium), Cr (Chromium), and Ni (Nickel) are hazardous. In order to reduce environmental and health risks, these heavy metal isotopes must be removed from water sources. In 2017, Hubadillah reported a methodology to eliminate Zn, Ni, and Pb ions from water with the help of ceramic membranes by phase inversion technique (Hubadillah et al. 2017). They inferred that at pH 5 achieved 99% removal of metal ions. In 2017, Noor et al., conducted Ni removal from industrial wastewater using a saying ball clay membrane and achieved a rejection of 88.87% (Noor et al. 2017).

17.4.3.5 Cellulose and Paper Industry Wastewater Treatment

The cellulose and paper industry produces a large amount of water during its manufacturing steps, such as pulping, bleaching, de-inking recycled paper. BOD, COD, chlorine-containing compounds, organic halides, and the quantity of total suspended and dissolved solids are also high in industrial wastewater. As a result, before disposal, the pollutants should be mitigated to environmentally acceptable levels using proper treatment processes. Goswami et al. (2019) showcased integrated biodegradation followed by the MF to treat wastewater from the cellulose and paper industries (Goswami et al. 2019). An inexpensive ceramic membrane with a 1.01 m pore size and a porosity of 44% was used for MF. As a result, pollutants should be lowered to levels that are acceptable to the environment before being disposed of using approved treatment methods. It was revealed that the combined approach had attained 87.6%

removal of COD and 94.5% toxicity reduction (Goswami et al. 2019) ((Issaoui and Limousy 2019; Liu et al. 2018)).

17.4.3.6 Wastewater Treatment of Dairy Waste

The dairy industry suffered from a big challenge of remediating dairy wastewater because each liter of milk produced approximately 2.5 L of wastewater. Dairy effluent must be treated because it has a major demand for oxygen while degrading. Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) are some of the methods to measure the amount of oxygen used and the degradation efficiency of the solution. Membrane-based treatment is one of the best ways to handle various amounts of contaminants in the feed while taking up a small area than traditional water treatment plants. Using low-cost ceramic membranes, a few scientists focused on dairy wastewater management and efficient treatment. (Goswami et al. 2019) (Vinoth Kumar et al. 2016), for example, use a cheap and inexpensive tube-shaped ceramic membrane for the effective treatment of dairy effluents. As a result, the COD concentration was lowered from 1462 mg/L to 135 mg/L, which was the acceptable limit. Another study used a natural clay-based flat membrane to treat dairy effluent and achieved 100% turbidity rejection (Goswami et al. 2019). Furthermore, an input content of 150 mg/L resulted in a 94% reduction in oil and fat (Mehrotra et al. 2021).

17.4.3.7 Bacteria and Virus Removal from Wastewater

To produce safe drinking water, microorganisms such as pathogenic bacteria and viruses must be removed. Membrane-based separation methods are becoming increasingly significant. (Vasanth et al. 2011a) used uniaxial dry compaction and sintering to produce a flat ceramic membrane with approximately 1.3 m of pore size. At a feed concentration of about 105 CFU/mL, the membrane was used to isolate bacteria from contaminated water, and the obtained rejection was close to 99% (Goswami et al. 2019). In another study, the kaolin-based raw material was used for ceramic membrane preparation, and these prepared membranes were used to isolate *E. coli* from a synthetic waste solution. Using the prepared inexpensive, thin ceramic membrane, a 99.9% bacterial rejection efficiency was obtained. Further Kumar et al., (Kumar et al. 2019) developed an inexpensive clay-based membrane with a 180 nm of pore size. The efficacy of a previous ceramic membrane constructed of natural clay and rice husk is used for removing bacteria and viruses from actual drinking water sources, such as rainwater and surface water. They found that *E. coli* and bacteriophage MS2 were rejected 99% of the time from polluted water (Vasanth et al. 2011b) (Abdullayev et al. 2019).

17.4.4 *Food and Food Products Industries*

In the food and food product sectors, filtration using membranes are significant process. MF and UF filtration systems mainly dominate this sector. They can be utilized instead of many typical process units to provide final product clarity, sterilization, concentration, and purification. MF can be used to clear cheese whey, milk defatting, and pasteurize it by removing microorganisms (Sandhya Rani and Kumar 2021). MF and UF membranes are also utilized to purify liquids such as wine, juice, beer, and other beverages in the sugar refining and beverage industries (Emani et al. 2013). To reduce operational expenses (OPEX), wastewater produced in these sectors can be reused by recycling using MF/UF membranes. Ceramic-based membranes for MF/UF have proven to be successful in the food and allied sectors, providing improved longevity than polymeric membranes in various applications. Ceramic membranes have been employed in a wide range of beverage production for many years (Lee et al. 2015) (Sandhya Rani and Kumar 2021).

17.4.5 *Removal of Biological Macromolecules and Organic Micropollutants*

Due to their unavoidable adsorption to the pores, bio-molecules such as polysaccharides, polypeptide chains, and humic acid compounds continue to cause a significant problem in the membrane filtration process. Deposition of bio-macromolecules such as tannic acid, humic acid, sodium alginate, and others causes the membrane's performance to decrease and imparts hindrance to better flux during filtration. To treat this polluted water, surface modification on the membrane is done. An effective way to introduce a selective layer that can also increase membrane longevity and toughness is by vacuum-based deposition of diamine functionalized graphene oxide (graphene oxide frameworks, or GOFs) over the surface of alumina membranes. The sieve-like GOF structure of the GOF/alumina modified by butylene diamine (BDA) had a small gap between the layers that increased freshwater flux while restricting the protein molecule channel. The electrostatic repulsion of the enhanced membrane surfaces may explain the better rejection of polypeptides or humic acids as well as a good flux recovery ratio (94.86% for Lysozyme and 95.21% for humic acid) (Vasanth et al. 2011b).

17.4.6 *Removal of Emerging Contaminants (EC)*

In the last decade, international associations have made significant attempts to define and characterize ECs. The term "emerging" contributes to new contaminants discovered in water bodies, aquatic species and, nowadays in human beings (Bilal et al.

2019). The word emerging further contributes to new properties and effects of compounds that turn toxic with time, which initially exists in the environment in non-toxic forms (Rivera-Utrilla et al. 2013). ECs were defined as substances found in the background but not currently considered in regular environmental performance programs. Due to their adverse effects and persistence, these may be the candidates for future legislation (Bolong et al. 2009). On a broad scale, more than 1000 substances were named as ECs, divided into 16 major categories that are algal biomass growth, fusing, and antifoaming agents, antioxidants, synthetic washing powders, waste from disinfection, rubbering and plasticizers, flame controllers, diffusive wastes, additive compounds from petrol, diesel and natural gas, nanomaterial by-products, perfluoro alkylated compounds, personal care, and beauty products, pharmaceuticals and drug waste, pesticides, pesticides, insecticides, and antibacterial agents (Bilal et al. 2019; Ahmed et al. 2017). According to a report presented by the Europe-based Environment agency group', the ECs are also considered substances and chemicals that are hazardous and toxic, and they are closely monitoring the increased concentrations and effects of these ECs, since they are increasingly found in European water bodies nowadays (Alcock et al. 1999).

Similarly, almost the same condition is observed globally, including in India (Ewis et al. 2021). Although a number of techniques are used to get rid of these emerging pollutants, some new methods, including the use of ceramic membranes, are discussed here. Ceramic membranes are fabricated by consistent blending and defined separation with regular mixing of different inorganic raw materials (Azaman et al. 2021). Further high calcination temperature and exact molding are some conditions for efficient fabrication and synthesis of these membranes (Vasanth et al. 2011a). After preparation, the membrane material can be directly used for desalination, ECs removal, and wastewater treatment. Moreover, the multilayer structure and macroporous support substrate further add to the separation efficiency of the ceramic membrane filters. As a whole, ceramic membranes are an efficient method for emerging pollutants removal and wastewater remediation. Further, the discussion about the emerging contaminants, their effects, and the role of membrane filtration with special emphasis on ceramic membranes is discussed in Table 17.5.

17.5 Challenges of Ceramic Membrane

The potential challenge in ceramic technology is the cost factor, which can be addressed either by lowering the steps involved in the fabrication process or lowering the sintering temperature. The introduction of cheap synthesis technologies, such as the mixed phase inversion and sintering approach, minimizes ceramic membrane fabrication costs (Fard et al. 2018; Goh and Ismail 2018). However, more development and efforts are needed to lower the sintering temperature and perpetuate a consistently excellent membrane. The overall quality of these membranes must be improved in order to attain the desired mechanical strength and potential permeation. Enhanced basic knowledge of the synthesis process of these membranes facilitates

Table 17.5 Showing the major sources, pollutants, targeted contamination, and emission compounds for common ECs

S.No	Sources	Pollutants	Contamination target	Emission compounds	References
1	Pharmaceutical waste	Anti-depressants	Terrestrial and aquatic contaminants	• Amitriptyline • Fluoxetine	Rivera-Utrilla et al. 2013)
		Analgesics	Soil and marine environment	• Diclofenac • Paracetamol • Ibuprofen • Acetaminophen (Tylenol)	Ahmed et al. 2017)
		Antibiotic	Terrestrial and marine systems	• Amoxicillin • Erythromycin • Oxyfloxacin	Salamanca et al. 2021)
		Antineoplastic	Soil and marine environment	• Cyclophosphamide • Busulfan • Carmustine • Melphalan • Streptozocin	Chaturvedi et al. 2021)
2	Veterinary industry	Antibiotics for livestock	Soil, water and air contamination	• Polymixins • Chloramphenicol • Lincosamides • Macrolides • Tetracyclins • Streptogramins	Mo et al. 2017)
3	Agricultural contaminants	Pesticides and Insecticides	Soil and Aqueous	• Neonicotinoid • Carbamates • Pyrethroids • Organochlorine • Carbamates • Dinitrophenols • Organotins	Bilal et al. 2019)

(continued)

Table 17.5 (continued)

S.No	Sources	Pollutants	Contamination target	Emission compounds	References
4	Household and Industrial contaminants	Brominated Flame Retardants (BFRs)	Soil, aqueous and atmosphere	• Polybrominated diphenyl ethers (PBDEs) – textile waste, electronic waste and plastic components • Tetra-bromobisphenol A (TBBPA) – thermoplastics, circuit boards • Polybrominated biphenyls (PBBs) – plastic foam materials, tarpaulin material and textile fibres • Hexabromocyclododecanes (HBCDDs) – heat insulation in construction industries	Sharma et al. 2021; Chen et al. 2022)
		Polycyclic Aromatic Hydrocarbons (PAHs)	Soil, aqueous and atmosphere	• Naphthalene • Dibenzo anthracene • Benzopyrene	Ouyang et al. 2022)
		Perfluorochemicals (PFCs)	Soil, aqueous and atmosphere	• Perfluoroalkenes • Perfluoroamines • Perfluorocarboxylic acids • Perfluorinated aryl borates • Perfluoroalcohols • Fluorosurfactants	Bello et al. 2021)

(continued)

Table 17.5 (continued)

S.No	Sources	Pollutants	Contamination target	Emission compounds	References
5	Beauty and cosmetic products	Organic filters	Soil and aqueous	• Ethylhexyl methoxycinnamte (EHMC) • Octocrylene (OC) • Butylmethoxydibenzoylmethane (BMDM) • Benzophenonone derivatives	Bilal et al. 2019)
		Inorganic filters	Soil and aqueous	• TiO_2 • ZnO • H_2O_2	Bilal et al. 2019)
		Parabens	Soil and aqueous	• Methylparaben • Propylparaben • Ethylparaben • Halogenated parabens	Ouyang et al. 2022)
		Triclosan (TCS)	Soil and aqueous	• 5-chloro-2-(2,4 dichlorophenoxy) phenol	Wilkinson et al. 2017)
		Microbeads	Soil and aqueous	• Polyethylene • Terephthalate • Polymethyl methacrylate • Polyethylene terephthalate	Wilkinson et al. 2017)

the improvised dependency and reproducibility of manufacturing and scaling-up processes. Growing a non-stop fabrication and sintering system is also a challenging condition when it comes to up-scaling the sintering and mixed phase inversion process (Lee et al. 2015). To satisfy the demand for up-scale treatment capacity, less area modules and basic designs may be necessary to lower housing material costs while also increasing productivity. Whenever it comes to fouling, the mechanism varies based on its characteristics and uses. Although a physio-chemical cleansing of ceramic membranes can be accomplished without difficulty, resulting in auxiliary waste products that must be dealt with and disposed of; thus, more ecologically friendly membrane cleansing methods are required. In the near future, more enormous efforts will be essential to utilize ceramic materials and membranes as a cost-effective and environmentally friendly water treatment and desalination method (Arumugham et al. 2021) (Goh and Ismail 2018).

17.6 Conclusion

This chapter presents an overview of ceramic membrane fabrication, synthesis, and application. Based on these studies, mainly ultrafiltration (UF) and microfiltration (MF) ceramic membranes are used for municipal and industrial wastewater treatment. According to the existing literature studies, the ceramic membrane is a better performer in terms of fouling control, longevity of life, permeates intensity, efficient cleaning, and environmental sustainability as compared to polymeric ones. However, the synthesis and fabrication of ceramic membranes are costlier as compared to polymeric membranes, but these innate advantages overcome the cost factor. However, the cost of ceramic membranes can be minimized by using inexpensive raw materials like quartz, clay, kaolin, felspar, etc. In the present time, multiple attempts have been made by industrialists, scientific communities, and other concerned stakeholders to modify the technique in such a way as to prepare cheap but effective ceramic membranes for treatment applications. These membranes are fabricated using cheap raw materials, as mentioned above. Ceramic membranes with minimal cost have been widely used in a variety of wastewater treatment and remediation. These membranes are widely used in oil and water treatment applications and have achieved rejection rates of up to 99%. Improved membrane performance has also been observed for industrial wastewater from the abattoir, synthetic fibers, and dairy industries. All of the applications, however, are predominantly on a micro-scale. Mechanization of these processes will necessitate extensive research. Modeling of the entire production and application processes is required to achieve optimal conditions with relatively little effort.

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Chapter 18
Near-Zero Liquid Discharge for Wastewater Through Membrane Technology

Avinash Kumar, A. Sudharshan Reddy, and Swatantra P. Singh

Abstract Regulatory authorities are making effluent disposal standards more stringent to minimize the effect of pollution load on natural streams and protect the environment. Industries producing wastewater with a high pollution load and refractory organics are forced to have a near-zero liquid discharge (NZLD) system to meet the effluent standards for disposal. In the NZLD process, solids are separated from wastewater, and recovered water is again used in the process. Thermal methods were used to achieve zero liquid discharge (ZLD), but they are not feasible for diluting wastewater streams due to high energy consumption. At present, membrane processes such as reverse osmosis (RO), forward osmosis (FO), membrane distillation (MD), membrane electrodialysis (MED), and capacitive deionization (CDI) are being used for preconcentration of wastewater before feeding to the thermal units to reduce operational and capital cost. The use of RO and NF reduced energy consumption in conventional ZLD systems by replacing the brine concentrator. RO has high feed TDS limitation and is more prone to fouling due to operation at high pressure. Therefore, FO, MD, or CDI can be used for handling the rejection from 1st stage RO. CDI and EDR are applicable for relatively lower feed concentrations and can replace 1st stage RO in the ZLD system. The crystallizer requires a lot of energy and can be replaced with a solar crystallizer or evaporation pond to reduce energy consumption in the NZLD system. This chapter aims to give insight into the application of membrane technology in achieving ZLD and making it economically feasible. The application of recently developed membranes and modifications can improve the efficiency and applicability of membrane-based ZLD systems.

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Keywords Desalination · Wastewater treatment · Solid recovery · Membrane processes · ZLD

18.1 Introduction

At the present time, every country in the world is running in the race for development by utilizing the maximum amount of natural resources. Water is also one of the most important natural resources without which life cannot exist. But population increase and the limitless desires of humans have increased water consumption. Most of the water after use is discharged without or with minimal treatment in the running water streams, i.e., rivers and oceans, due to its self-purification characteristics (Chen et al. 2022). Again raw water is extracted from natural resources due to the admissible characteristics of water. To protect natural water resources, national and international organizations such as WHO (World health organization), CPCB (Central pollution control board), and BIS (Bureau of Indian Standards) have given wastewater disposal standards for effluents from various industrial and domestic sources, which should meet before disposal in water streams. As a result, industries adopted several treatment processes, such as sedimentation, coagulation, flocculation, biological treatment, adsorption, filtration, oxidation, and membrane processes, for the safe disposal of effluent wastewater. But with time, effluent standards are becoming quite stringent to reduce freshwater consumption and enhance the use of reclaimed water. So, industries are focusing on advanced treatment technologies to recycle the generated wastewater and reuse it in some industrial processes. This concept also helps achieve some sustainable development goals given by United Nations (Yaqub and Lee 2019).

The concept of zero liquid discharge (ZLD) is also a wastewater treatment and recycling process which rose in the USA, in the 1970s when the salinity level in the Colorado River increased to a greater extent (Tong and Elimelech 2016). Regulatory bodies mandated the nearby power plants to adopt ZLD technology and ease the approval of new projects with ZLD technology. ZLD refers to the installation of facilities that will allow industrial effluent for complete recycling/reuse and convert solute into residue in solid form utilizing concentration and evaporation, and solid residues should be recovered and reused or should be stored safely. The treated water can be used in industrial processes or domestic use but cannot be discharged in the ambient environment, even on the industry premises. In essence, the concept of ZLD emerged from a place where industries could not meet the discharge limits of regulatory agencies. Industries with high organic load and other refractory pollutants will require adopting the ZLD system. The major drivers and benefits of adopting ZLD are shown in Fig. 18.1.

To achieve ZLD, conventional treatment processes such as primary and secondary treatment are essential before tertiary treatment. In tertiary treatment, mainly filtration, concentration, and evaporation are adopted. Evaporation of concentrated streams is quite more economical than dilute streams. In an ideal ZLD system, a

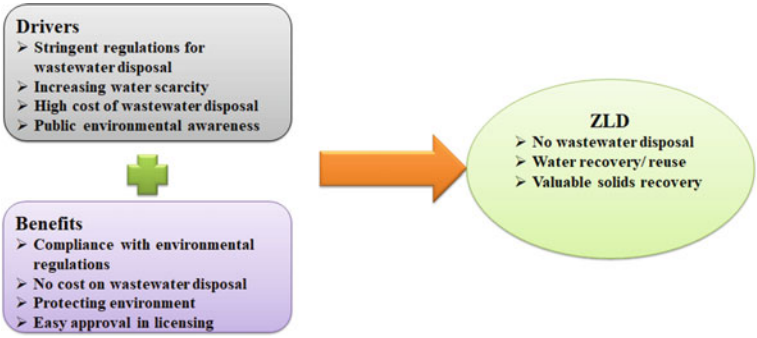


Fig. 18.1 Drivers and benefits of ZLD

closed water cycle is used, as shown in Fig. 18.2, and no water is discharged from the system. However, it looks quite unrealistic without the availability of advanced treatment units and funds. Additionally, in achieving ZLD, there is a critical role of water minimization hierarchy, as shown in Fig. 18.3. Freshwater use can be minimized by giving preference to source elimination and reduction, direct use of produced wastewater, and reusing treated wastewater (Wan Alwi et al. 2008). Water audit around the industrial process provides an idea about the required water quality and volume for different processes, and the potential to apply water minimization hierarchy (WMH) in the industrial process (Yaqub and Lee 2019).

This chapter highlights the principle and needs of the ZLD system. It also summarizes conventional thermal ZLD systems used in industries with their limitations. The potential of modern membrane-based technologies in achieving ZLD with minimal cost and effectiveness is also evaluated, including their respective limitations. Possible solutions and research needed for the application of membrane-based ZLD in the real environment are also highlighted in this chapter.

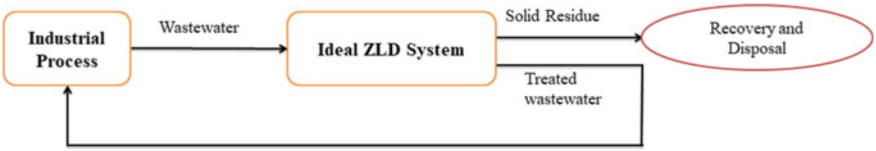


Fig. 18.2 Concept of ideal ZLD system

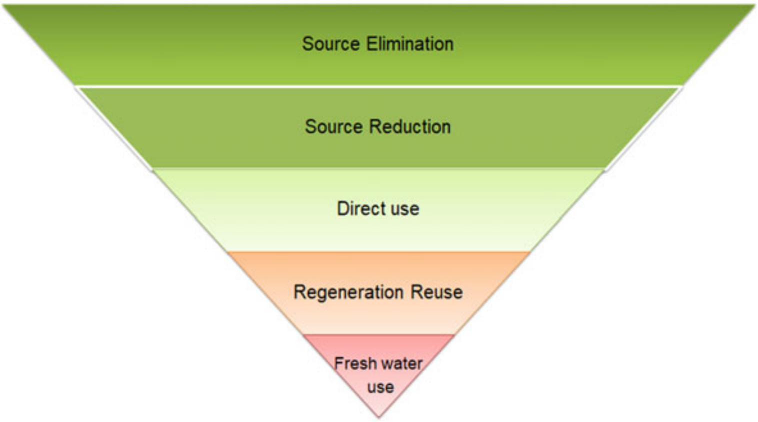


Fig. 18.3 Water minimization hierarchy pyramid

18.2 Conventional ZLD Systems and Major Concerns

18.2.1 Thermal ZLD System

At their early stage, ZLD systems mostly comprise thermal units to evaporate water from the wastewater streams and separate residual solids. A schematic diagram for the thermal ZLD system is shown in Fig. 18.4. The first pretreatment is given to influent wastewater to reduce its scaling and fouling potential in further treatment units (Semblante et al. 2018). Based on influent wastewater characteristics, several processes, such as pH adjustment, coagulation, precipitation, filtration, and ion exchange, can be used for the pretreatment of wastewater. After pretreatment, wastewater is fed into the brine concentrator unit to evaporate water and concentrate the wastewater stream. Mechanical vapor compressors (MVC), multi-effect desalination (MED), and multistage flash (MSF) are available options for brine concentration. MVC is the commonly used unit for concentrating wastewater (Shaffer et al. 2013). Preheated wastewater is fed from the top in MVC and passes through several small-diameter heat exchanger tubes, forming a thin film at its inner surface. After passing to the tubes, the slurry is collected in the sump, whereas superheated compressed water vapor is circulated back to the outer surface of heat exchanger tubes to transfer its latent heat in evaporating falling wastewater. Condensed vapor is circulated back to the industrial process, whereas concentrated slurry is sent to the crystallizer for further concentration (Shaffer et al. 2013). Even after utilizing the waste heat in MVC through heat exchangers, this process is highly energy-intensive and typically requires 20-25 kW-h/ m^3 of treated water (Tong and Elimelech 2016). Using MVC, brine can be concentrated up to 250,000 mg/l with 90- 98% water recovery (Tong and Elimelech 2016). However, titanium and stainless steel are used to manufacture MVC to avoid corrosion, which causes high capital costs.

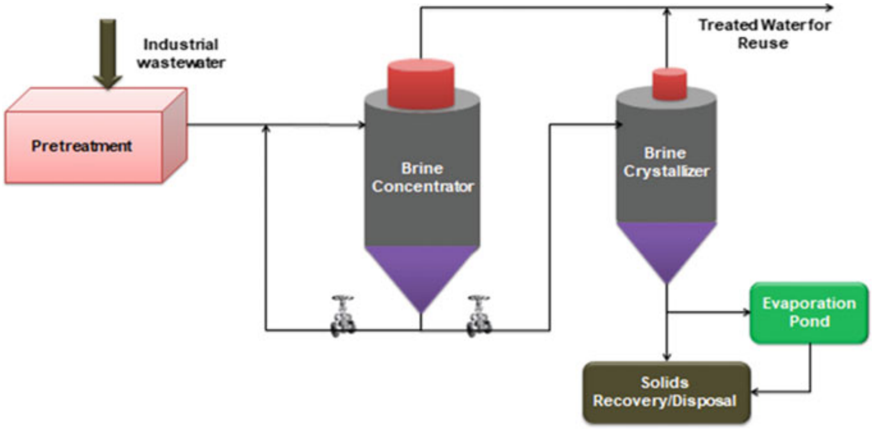


Fig. 18.4 Schematic diagrams for thermal ZLD system

Concentrated wastewater slurry is fed into the crystallizer after passing through the heat exchanger tubes. Water vapor from the crystallizer circulated back over the heat exchanger tubes after compression to utilize sensible heat and condense the vapor. Energy consumption by the crystallizer is almost three times of the concentrator unit, i.e., around 52–66 kW-h/m^3 of treated water (Tong and Elimelech 2016). Evaporation ponds can be used as an alternative to crystallizer units in the availability of cheap land and high atmospheric temperature, but the overall system will deviate from the principle of the ideal ZLD system. Based on the characteristics of recovered solids, they can be used as a fertilizer or stored for the recovery of valuable materials (Yaqub and Lee 2019; Tong and Elimelech 2016).

18.2.2 Major Concerns with Thermal ZLD Systems

Thermal ZLD systems have very high capital and operation cost. The use of titanium and stainless steel in concentrators and crystallizers to avoid the corrosion of heat exchanger tubes and chamber increases its capital cost (Shaffer et al. 2013). A lot of energy is required to heat the feed wastewater, which increases its operational cost. This energy comes from fossil fuels directly or indirectly and releases greenhouse gases into the environment leading to global temperature increases and other environmental issues. Recovered solids are very heterogeneous and may contain heavy metals and other harmful compounds, making their handling and disposal difficult (Yaqub and Lee 2019).

18.2.3 Possible Solutions for a Feasible ZLD System

Increasing interest and research in the field of ZLD systems have resulted in the application of membrane technology in combination with thermal methods. The use of reverse osmosis (RO) and nanofiltration (NF) membranes in ZLD for concentrating the wastewater reduced its energy consumption by up to 2 kW-h/m^3 of treated water for 50% recovery (Tong and Elimelech 2016). Other membrane processes such as forward osmosis (FO), membrane distillation (MD), electrodialysis (ED), and electrodialysis metathesis (EDM) have shown their capability to achieve ZLD in an environmentally sound way. Using these advanced membrane processes, it is possible to increase the purity of recovered solids and enhance recovered water quality at feasible capital and operational cost as compared to a thermal ZLD system (Yaqub and Lee 2019; Tong and Elimelech 2016).

18.3 Basics of Membrane Technology

18.3.1 Definition and Working Principle

The membrane functions as a selective barrier between two phases, permitting some chemicals to pass through while preventing others from doing so. The ability of membranes to allow specific molecules is called selectivity, and the rate at which it allows molecules to pass is called permeability. Influent water applied to the membrane is called feed, and the pure water which passes through the membranes is called permeate (Saleh and Gupta 2016). Stream having a concentration of molecules rejected by membranes is called retentate, as shown in Fig. 18.5.

18.3.2 Membrane Classification for Water and Wastewater Treatment

Membranes have gained their applicability in various fields due to their effectiveness, performance over time, easy fabrication, and upscaling. Several methods and materials are available to fabricate membranes with desired characteristics (Saleh and Gupta 2016). Membranes are typically classified based on nature, structure, material, mode of operation, surface morphology, charge, driving force, and geometry, as shown in Fig. 18.6.

Based on the nature of membranes, they can be classified as natural and synthetic membranes. Natural membranes use materials from plants and animals for their fabrication, whereas synthetic membranes are prepared with several synthetic chemicals. Membranes can be porous and non-porous in structure. The porous membrane contains interconnecting voids to transport water molecules through convection

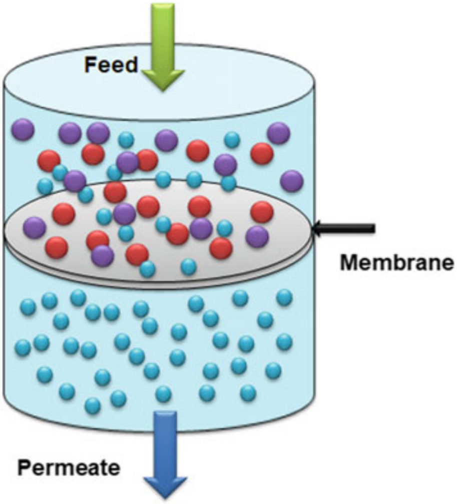


Fig. 18.5 Membrane filtration process

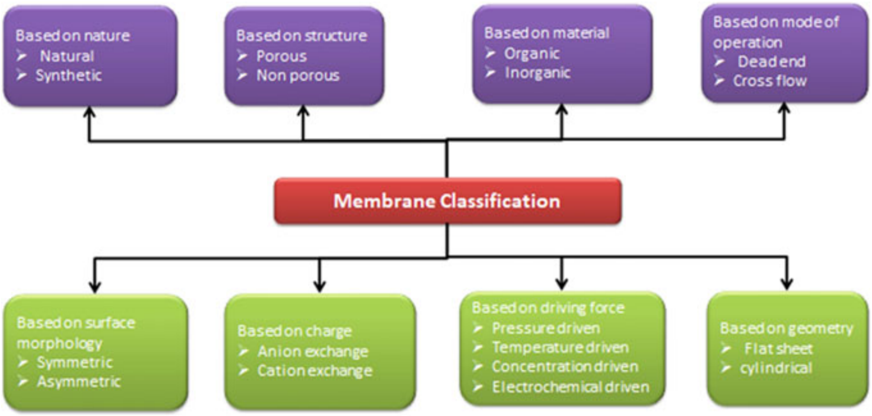


Fig. 18.6 Membrane classifications for water and wastewater treatment

and/or diffusion mechanism (Saleh and Gupta 2016). Examples of porous membranes include polymeric films, where the void spaces and polymer matrices are continuous. Porous membranes are used for separating solid and colloidal particles, large molecules, and cells from the feed utilizing MF and UF. Non-porous membranes are formed by the continuous phase of a dense and thin layer of polymer to have a closely packed uniform packing. These membranes are majorly used in gas separation and RO applications in which transport is governed by diffusion. Dense (non-porous) membrane fabrication can be done by melt extrusion, compression molding, and solution casting methods (Saleh and Gupta 2016).

Organic and inorganic materials are used for the fabrication of membranes as per desired characteristics and applications. Polymeric materials are common for the fabrication of membranes due to their low cost, easy tuning of pores and fabrication, flexibility, and applicability. Polymeric materials such as cellulose acetate (CA), polyamide (PA), polysulfone (PS), polyacrylonitrile (PAN), polyethersulfone (PES), polyvinylidene fluoride (PVDF), polyphenylsulfone (PPS), and polyetherimide (PEI) are most common in organic membrane fabrication (Koyuncu et al. 2015). Inorganic membranes can work in harsh operating conditions such as high temperature, pressure, and wide pH range, which make them suitable for industrial chemical processes. Inorganic membranes have added advantages of well-defined pore size, long life, non-biodegradability, and applicability for stronger cleaning agents such as steam sterilization, backflushing, and ultrasonic cleaning (Koyuncu et al. 2015). These inorganic membranes can be further classified based on their porous and non-porous characteristics. Membranes can be operated in dead-end mode or cross-flow mode. But cross-flow mode is more common due to its less fouling chances and constant permeate flux with time after the initial stage (Kayvani Fard et al. 2018). In dead-end operation, feed and permeate streams are parallel to each other, whereas in cross-flow mode, permeate stream is orthogonal to the feed and retentate stream, as shown in Fig. 18.7.

Membranes can have symmetrical or asymmetrical surface morphology. Symmetrical membranes have uniform pores throughout the structure, just like a sponge, and can be produced by irradiation etching, precipitation from the vapor phase, stretching, and vapor and temperature-induced phase separation methods (Saleh and Gupta 2016). But asymmetric membranes have channel-like pores, and their size varies from top to bottom. Asymmetric membranes have better selectivity, but low permeate flux, whereas symmetric membranes have poor selectivity but better permeate flux. Membranes are fabricated in the form of flat sheets or cylindrical

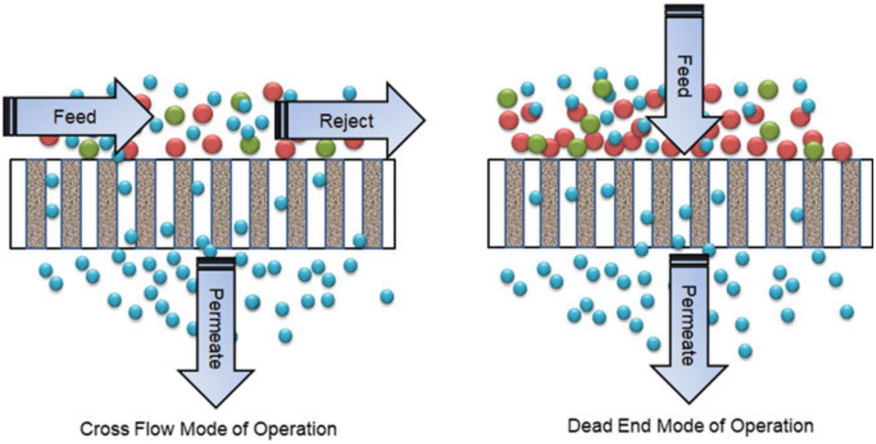


Fig. 18.7 Schematic for dead-end and cross-flow mode of operation

shapes. Flat sheet membranes are used on a porous support frame or spiral wound to increase the surface area for a given volume. Spiral wounds are more common due to their easy operation and strength against high pressure. Cylindrical membranes (hollow fibers) are used in casing during their application (Koyuncu et al. 2015). Anion exchange membranes have fixed cations and mobile anions, whereas cation exchange membranes have fixed anions and mobile cations. These membranes are semipermeable and less prone to fouling and are majorly used in electrodialysis and related applications (Saleh and Gupta 2016).

Feed water is forced to flow through membranes to get a pure permeate stream and a highly concentrated retentate stream. Required force can be applied through pressure, temperature, electrochemical, or concentration gradient. Membrane processes such as MF, UF, NF, and RO are based on pressure-driven force (Koyuncu et al. 2015). Dialysis and forward osmosis are governed by the concentration gradient. The temperature gradient is the driving force in the case of the MD process, whereas electrochemical forces govern the ED, EDR, and CDI processes. Table 18.1 gives information about various membrane processes based on different driving forces and mechanisms of separation. Feed and permeate phases affect different membrane processes' driving forces and separation mechanisms.

18.4 Membrane Fouling and Factors Affecting the Membrane Fouling

Membrane fouling. Attachment or deposition of any material at the membrane surface or inside the pores due to which flux is reduced is called fouling of membranes. Material that causes fouling is called foulant. The feed may contain several types of chemical compounds, particulates, and microorganisms, which can foul the membranes through pore-clogging, pore-narrowing, or gel formation (Behroozi and Ataabadi 2021). The fouling type depends on the foulant's nature and characteristics, as shown in Fig. 18.8.

Colloidal and particulate foulant can clog the pores by forming a cake layer at the membrane surface. Scaling occurs due to the precipitation of inorganic salts such as carbonates, bicarbonates, sulfates, hydroxides, and oxides of metallic ions (i.e., calcium, magnesium, aluminum, and silica) over the membrane surface (Saleh and Gupta 2016). Organic molecules such as oils, macromolecules, proteins, antifoaming agents, fulvic acid, polysaccharides, and polyacrylic polymers also can clog membrane pores due to their larger size and hydrophobic nature of the membrane surface. But biofouling is the most studied and common fouling in membranes when it is used for water and wastewater treatment. In initial conditions, only a few microorganisms attach to the membrane surface and generate extracellular polymeric substances (EPS) by utilizing food and nutrients available in the feed. This EPS is a gel kind of substance, which protects the attached microorganisms against turbulence and increases their population very rapidly to clog the whole membrane

Table 18.1 Classification of membrane processes based on driving force (Saleh and Gupta 2016)

Driving force	Feed phase	Permeate phase	Membrane process	Separation mechanism
Pressure difference (ΔP)	Liquid	Liquid	Microfiltration (MF)	Size
	Liquid	Liquid	Ultrafiltration (UF)	Size
	Liquid	Liquid	Nanofiltration (NF)	Size and affinity
	Liquid	Liquid	Reverse osmosis (RO)	Size and affinity
	Gas	Gas	Gas separation (GS)	Affinity and size
	Gas	Gas	Vapor permeation	Affinity and size
Concentration difference (ΔC)	Liquid	Liquid	Dialysis	Size
	Liquid	Liquid	Forward osmosis (FO)	Affinity
Electrical potential difference (ΔE)	Liquid	Liquid	Electrodialysis	Charge
	Liquid	Liquid	Membrane electrodialysis	Charge
Temperature difference (ΔT) and ΔP	Liquid	Liquid	Membrane distillation	Vapor pressure
ΔC and ΔP	Gas	Liquid	Membrane contactor	Affinity
	Liquid	Gas	Membrane contactor	Affinity

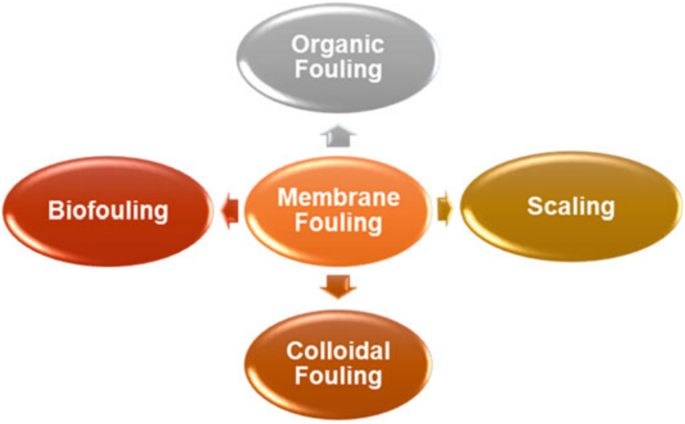


Fig. 18.8 Types of membrane fouling

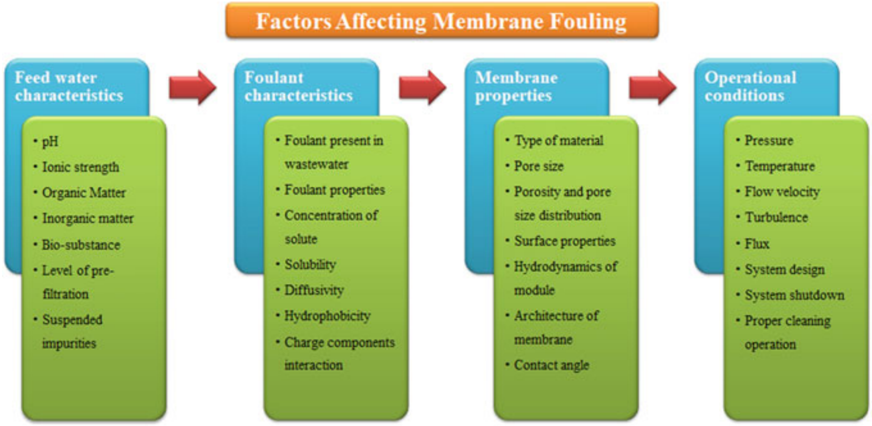


Fig. 18.9 Factors affecting fouling of membranes

module. To avoid biofouling of membranes, it is desirable to prevent their attachment in the initial stages; otherwise, it becomes very difficult to remove microorganisms from membrane surfaces and pores when they have produced a sufficient amount of EPS (Saleh and Gupta 2016).

Factors affecting membrane fouling. Membrane fouling is mostly affected by feed water characteristics, foulant characteristics, membrane properties, and operational conditions during the filtration process, as shown in Fig. 18.9. Feed water characteristics such as pH, organic and inorganic solids, and ionic strength decide the initial fouling of membranes. By giving proper pretreatment to feed water, membrane fouling can be reduced to a great extent. Foulant characteristics such as concentration of solutes, solubility, charge, molecular size, hydrophobicity, and diffusivity decide the interaction between membrane and foulant. High concentration of solutes, opposite charge as of membrane surface, and hydrophobicity of foulant favor the fouling of membranes.

Membrane properties such as pore size and their distribution, roughness, hydrophobicity, porosity, and surface charge also significantly impact membrane fouling. Several modifications have been investigated to improve membrane properties and reduce the fouling of membranes. Early fouling of membranes causes low membrane life, which increases its overall operational cost. Operating conditions can be optimized to reduce membrane fouling to a greater extent. Fouling can be reduced to a certain extent if cross-flow velocity is increased and flux is reduced.

18.5 Popular Membrane-Based Technologies for the Treatment of Water and Wastewater

18.5.1 Pressure-Based Membrane Technologies

The solution is forced to pass through membranes to get pure permeate while the membrane retains impurities. These pressure-based membrane processes can be classified into microfiltration, ultrafiltration, nanofiltration, and RO based on their pore size range and pressure requirement, as shown in Fig. 18.10.

Microfiltration (MF) and ultrafiltration (UF). Microfiltration is a sieving process in which membranes have a pore size in the range of 0.1 μm to 10 μm, and it requires comparatively less pressure (i.e., 0.2–5 bar) due to less resistance (Kayvani Fard et al. 2018). Microfiltration is used as a pretreatment during water and wastewater treatment to avoid scaling and fouling further treatment units. MF is capable of rejecting particulates, proteins, bacteria cells, oil, and colloidal particles. Ultrafiltration (UF) refers to the filtrated separation of particles. UF membranes have a pore size in the range of 1 nm to 100 nm and reject solute molecules through adsorption, size exclusion, and deposition of pollutants on the membrane surface, leading to the caking formation (Koyuncu et al. 2015). UF membrane is capable of removing macromolecules, viruses, and suspended particles. UF membrane is operated at lower pressure (typically 1–10 bar) with cross-flow mode to reduce fouling (Selatile et al. 2018). The filtration of suspended colloids, the treatment of product water streams in the food and beverage industry, the recovery of valuable resources from coating or dyeing baths in the automotive and textile industries, and the treatment of wastewater in various industries are all applications of UF technology. Osmotic pressure is less

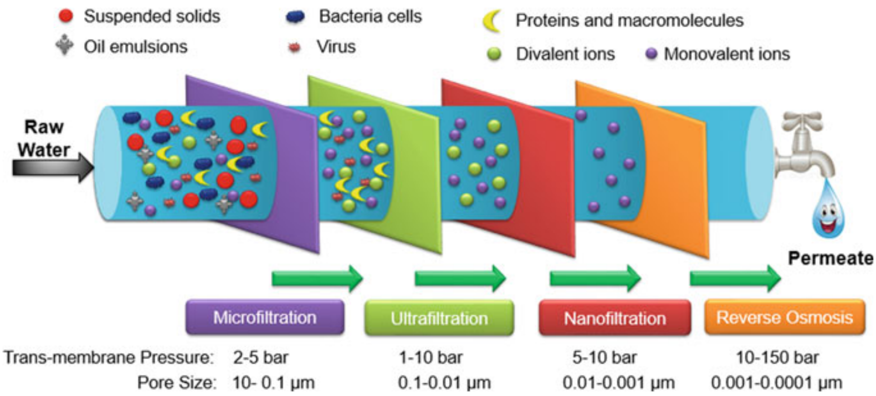


Fig. 18.10 Pressure-driven membrane processes

significant in the case of MF and UF due to the larger pore size of membranes. Polysulfone, PVDF, and cellulose acetate are generally used for MF and UF membrane fabrication (Koyuncu et al. 2015).

Nanofiltration (NF) and Reverse Osmosis (RO). NF membranes have their pore size in the range of 10 nm to 1 nm, due to which pressure requirement is increased (i.e., 5–10 bar) in comparison with UF membranes. RO membranes stand somewhere between porous and dense membranes due to their pore size of less than 1 nm (Loganathan et al. 2016). Solvent molecules are forced against osmotic pressure through a semipermeable membrane to get pure permeate. Solution diffusion governs the permeation through NF and RO membranes. NF membranes have high rejections (>99%) for multivalent ions and low to moderate rejections (i.e., up to 70%) for monovalent ions (Saleh and Gupta, 2016). RO membranes have a very thin active layer over the substrate layer. These membranes operate in cross-flow mode and have higher chances of scaling when the salt concentration exceeds its solubility limit. Operation at high pressure increases the cost of operation and chances of fouling. To sustain high pressure, steel casing and strong membrane material are required. Fouling tendency increases with an increase in the recovery rate. NF and RO are the core elements of desalination plants these days and are also applied in industries for achieving ZLD. Polyamide membranes are commonly used as RO and NF membranes due to their high crosslinking and other beneficial properties. Application of the RO membrane process is not economically feasible if the salinity level exceeds 75,000 ppm (Subramani and Jacangelo 2014).

18.5.2 Forward Osmosis (FO)

The movement of solvent molecules from low solute concentration to high solute concentration is called forward osmosis. On one side of the semipermeable membrane, feed water is passed, and concentrated draw solution is on the other side. When solvent molecules move from wastewater to the draw solution, then a concentrated wastewater stream and diluted draw solution are obtained. Concentrated wastewater is further sent to thermal or anaerobic units for treatment and solid recovery, whereas draw solution is recovered from diluted draw solution for reusing the FO process (Achilli et al. 2010). A schematic of the FO process is shown in Fig. 18.11. FO works under natural osmotic pressure, requiring very little or no external pressure. But separation of permeate from the diluted draw solution stream is a major concern with this process due to its higher cost (Cai and Hu 2016).

Special types of draw solutions were developed for easy, effective, and economical separation of permeate from the diluted draw solutions. Generally, RO or MD is used for the regeneration of draw solution, and it makes the FO process more expansive in the absence of ideal draw solute than direct RO membrane-based treatment. Non-responsive draw solutes are those with no significant change in their water affinity, temperature, pH, electromagnetic field, or light during the regeneration process,

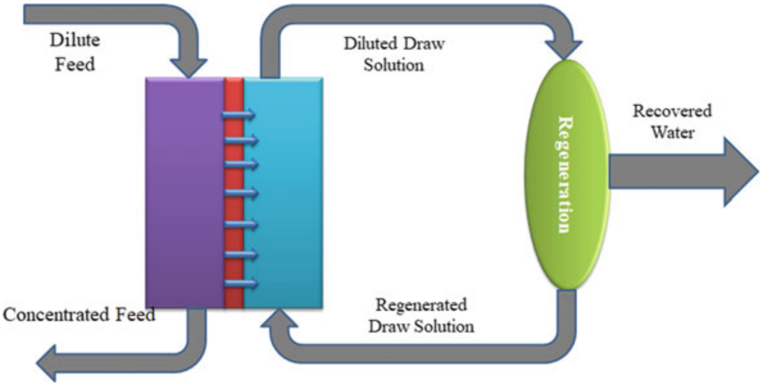


Fig. 18.11 Principle of FO membrane process

such as inorganic salts and polyelectrolytes, surfactants, and zwitterions (Cai and Hu 2016). Non-responsive solutes are very difficult to regenerate. At the same time, responsive draw solutes change their water affinity during phase transitions between two states of different water affinities leading to ease of its regeneration. Magnetic nanoparticles, volatile liquids, NH_3–CO_2 solutions, responsive small molecules, and polymers are examples of responsive draw solutes (Cai and Hu 2016). Fe_3O_4 nanomagnetic particles are used as draw solutions to generate required osmotic pressure and are easily separated by applying a magnetic field during regeneration. Agglomeration, high cost of synthesis, loss with wastewater, and generation of a high magnetic field are problems associated with magnetic nanoparticles. Hydrogels have electrolytes used to extract water in the FO process, and soaked water can be recovered by shrinking them. But higher viscosity of electrolytes increases the concentration polarization problem and reduces the flux, which makes it infeasible for desalination or wastewater treatment (Li et al. 2011).

Soluble gas SO_2, NH_3, and volatiles such as dimethyl ether are used as draw solutes due to their higher solubility and easy regeneration by air stripping or evaporation. But maintaining pressure for their solubility ionization in solution reduces its effectiveness (Cai and Hu 2016). Thermolytic NH_3–CO_2 draw solution is most studied for application in the FO process due to its capability of imposing high osmotic pressure and easy regeneration (McGinnis et al. 2013). Energy consumption with this draw solution was reported as 0.84 kW-h/m^3 at 75% water recovery, which is far less than RO and other thermal processes (McGinnis et al. 2013). Compared to a standalone RO for saltwater desalination at the same water recovery, regeneration by crystallization and RO required 2.15 kW-h/m^3 of energy at 30% water recovery (Yaqub and Lee 2019). But the reverse flux of draw solution toward wastewater causes loss of draw solution and imposes an extra cost of draw solution (Cai and Hu 2016).

18.5.3 *Membrane Electrodialysis (MED)*

MED uses ion-exchange membranes for the separation of ionic and charged impurities from wastewater. Electric potential is applied across the various compartments of ion-exchange membranes, and feed is passed through it. Cations and anions in feed migrate through cation exchange membranes and anion exchange membranes, respectively, in adjacent compartments and result in a dilute product stream and concentrated feed stream, as shown in Fig. 18.12. MED process has the advantages of no phase change, no additional chemical requirement, high selectivity, low electrical resistance, and high mechanical and chemical stability (McGovern et al. 2014). It can produce product water with TDS less than 10 mg/l when a feed has a salinity in the range of 100–1200 mg/l (Akhter et al. 2018). Inorganic–organic ion-exchange membranes have high photoconductivity, efficient luminescence, structural flexibility, and convenient processing due to organic components, whereas inorganic components contribute to high carrier mobilities, band gap tunability, magnetic properties, dielectric properties, and stability. But the formation of the cake layer due to the deposition of salts reduces the ion-exchange capacity and increases energy consumption to maintain desired selectivity (McGovern et al. 2014). Several cleaning agents, such as low-strength acids, alkali, complex agents (EDTA), enzymes, detergents, and disinfectants (NaCl, H_2O_2), are used for cleaning ion-exchange membranes (Wang et al. 2011). The alternating current can also remove impurities from membranes (Akhter et al. 2018).

18.5.4 *Capacitive Deionization (CDI)*

CDI contains porous electrodes that have micropores to adsorb the charged impurities. In the adsorption step of the CDI process, feed flows between oppositely charged porous electrodes, due to which counter ions move in the micropores of electrodes under the influence of electrostatic force, as shown in Fig. 18.13. Immobilized cations are retained within negatively charged electrodes, whereas anions are stored in the positively charged electrode. Immobilized ions are considered to be removed from the solution, and a dilute stream with less salinity is produced. In order to renew porous electrodes once their capacity has been used up, the external voltage must be turned off or reversed. Desorbed ions move back to the bulk solution and undergo additional processing to recover their solids, creating a concentrated stream (Dykstra et al. 2017).

Energy loss and process inefficiency are the major challenges with CDI during the treatment of high-salinity wastewater. Co-ion expulsion in an adsorbed electrode may result from the increase in TDS concentration of the product water stream. At a cell voltage of 1.2 V, good CDI electrodes should have an adsorption capacity of 8 mg NaCl per gram of electrodes (mg/g), while some commercial capacitive electrodes have an adsorption capacity of 14–18 mg/g (Liu et al. 2020). The highest

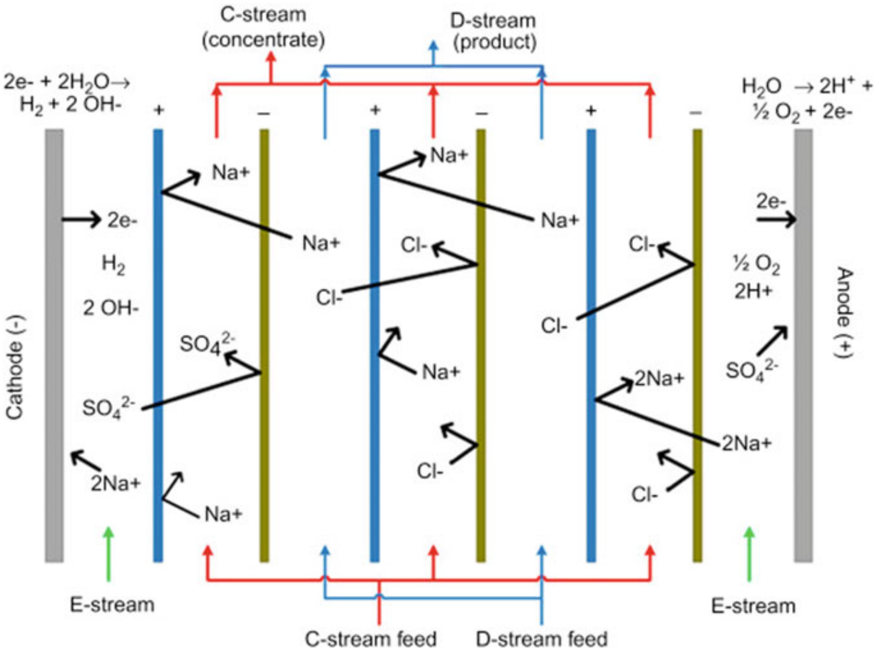


Fig. 18.12 Working of membrane electrodialysis process (Akhter et al. 2018)

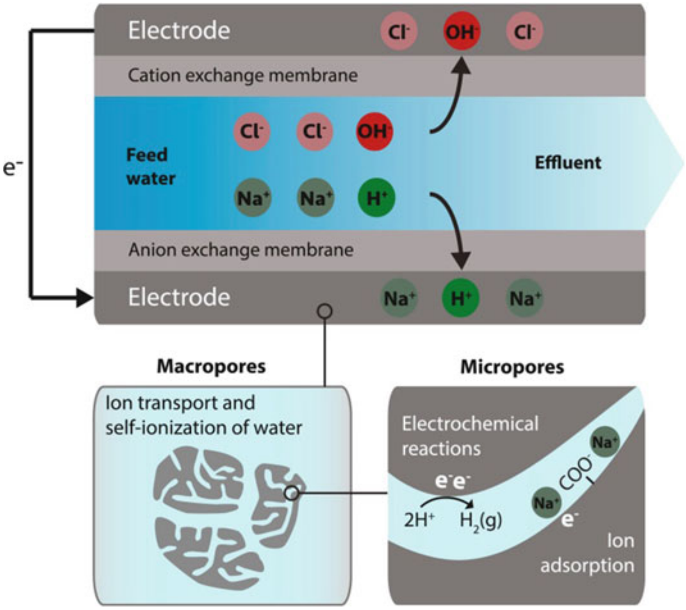


Fig. 18.13 Schematic for membrane capacitive deionization process (Dykstra et al. 2017)

feed concentration with CDI reported to have been used is around 5800 ppm (Liu et al. 2020).

18.5.5 Membrane Distillation (MD)

The thermal gradient between feed and permeate works as a driving force for the MD process. Hydrophobic microporous membranes are used for the isolation of two different temperature solutions. Vapor from the high-temperature feed side passes through pores and condenses on the other side, as shown in Fig. 18.14. Hydrophobicity of MD membranes helps to prevent the permeation of liquid molecules for high selectivity (Lawson and Lloyd 1997). Pores of MD membranes are larger than RO membranes, and it helps to attain a high permeation rate with lower fouling leading to minimal pretreatment requirement. MD processes can be operated at 60 to 80 °C temperature using low-grade waste heat (Lawson and Lloyd 1997). MD membranes have a high contact area per unit of equipment volume and provide the advantage of compact installations to reduce the process's footprint. These processes can be used for feed having high salinity, which is a major limitation of the RO membrane process (Belessiotis et al. 2016).

The four fundamental variations of the MD process are direct contact membrane distillation (DCMD), air gap membrane distillation (AGMD), sweep gas membrane distillation (SGMD), and vacuum membrane distillation (VMD) (Lawson and Lloyd 1997). In DCMD, the hydrophobic membrane is in direct contact with both the hot feed and the cold permeate. The formed vapor moves through membrane pores and condenses at the membrane and cold permeate interface. In AGMD, an air gap is provided between the cold water stream and membrane to reduce heat loss due to

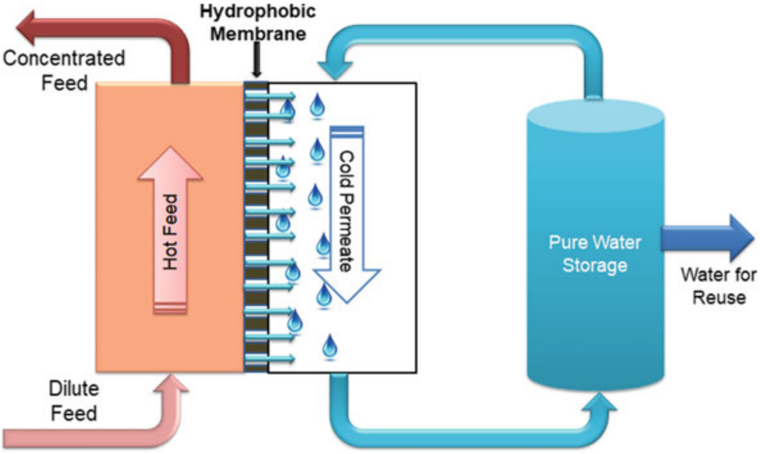


Fig. 18.14 Process of membrane distillation

conduction, but it also increases resistance for mass transfer. SGMD used cold, inert gas (i.e., nitrogen, air) to carry the vapors and pass through a condenser to recover the water. VMD is similar to AGMD, but in this case, a vacuum is created in the air gap to suck the vapors and eliminate heat loss with increased flux. MD becomes an environmentally friendly, energy, and cost-efficient process when thermal energy or waste heat from other processes is utilized to create a temperature gradient. MD was successfully applied in a concentration of ions, colloids, and other nonvolatile aqueous solutions (Lawson and Lloyd 1997). Low flux, higher sensitivity for temperature gradient, high membrane cost, high energy consumption, and chances of membrane wetting are the major limitations of the MD process (Belessiotis et al. 2016). Some recent studies based on the technologies discussed in Sect. 4.1 to 4.5 are given in Table 18.2.

Table 18.2 Studies based on membrane processes

Sr. No.	Technology used	Feed water characteristics	Performance	References
1	Ultrafiltration	500 ppm BSA solution	Flux = 362.2 $\mathrm{Lm^{-2}\ h^{-1}\ bar^{-1}}$; BSA rejection = 97.8%	Dou et al. (2022)
2	Reverse osmosis	2000 ppm NaCl	Flux = 4.28 $\mathrm{Lm^{-2}\ h^{-1}\ bar^{-1}}$; NaCl rejection = 98.5%	Li et al. (2022)
3	Forward osmosis	Pulp and paper industry wastewater; urea used as a draw solution	Flux = 3.9 ± 0.19 $\mathrm{Lm^{-2}\ h^{-1}}$;	Kumar Singh et al. (2021)
4	Membrane electrodialysis	1 mol/L NaOH solution, 1 mol/L NH_4Cl solution, 1–1.1 mol/L $NH_3{\cdot}H_2O$ solution, 1 mol/L NaCl solution, and 0.27 mol/L Na_2SO_4 solution	Feed concentrated up to 1.63 mol/L NaOH and 1.85 mol/L NH_4Cl with purity of 80.71% and 90.40%, respectively	Zhao et al. (2022)
5	Membrane distillation	Sea water (TDS = 65,000 ppm)	Flux = 3.8 $\mathrm{kgm^{-2}\ h^{-1}}$ Water recovery = 78%	Yadav et al. (2022a)
6	Capacitive deionization	Saline water (TDS = 35,000 ppm)	Salt rejection = 95.42%	Liu et al. (2020)

18.6 Current Technologies for the ZLD System

Emerging membrane technologies such as MD, FO, and ED have the potential to make the ZLD system more economical and effective. The expected salinity range for optimal operation of different membrane processes is shown in Fig. 18.15. RO and ED are suitable for preconcentration of wastewater, whereas FO, MD, MDCr, and crystallizer are used for concentration of reject.

18.6.1 RO-Incorporated ZLD System

The evaporation and crystallization cost of dilute wastewater is a major challenge for achieving ZLD by thermal methods. Membrane processes are used in the pretreatment and concentration of wastewater before feeding it to thermal units (Aslam et al. 2022). RO rejects produce very high concentration and lower volume of wastewater which reduces the operational cost and volume requirement of thermal units. When RO membrane technology is used for concentrating feed water before entering thermal systems, then 58–75% of energy and 48–67% of the cost can be reduced (Yaqub and Lee 2019). Athabasca oil company in Canada used RO-incorporated ZLD system to treat the extracted water from the aquifer of a bitumen mining site with an arrangement of units as shown in Fig. 18.16. This basal aquifer water contains an average TDS concentration of 21,300 mg/l, dissolved chlorine 12,458 mg/l, hardness 1430 mg/l as $CaCO_3$, alkalinity 2975 mg/l as $CaCO_3$ sodium 7508 mg/l, TOC 6.9 mg/l, and several other metallic compounds (Loganathan et al. 2016). To achieve near-zero liquid discharge (NZLD), the treatment train consists of chemical oxidation, polymeric UF, single-pass RO, and evaporation crystallization. Potassium permanganate is used for chemical oxidation before membrane processes to avoid scaling due to Fe, Mn, and sulfide. An optimum dose of ferric chloride coagulant was added before feeding to cross-flow UF to destabilize colloids and obtained an effective flux of 53 $L/m^2/h$ at 20 °C in UF (Loganathan et al. 2016). Proper pretreatment

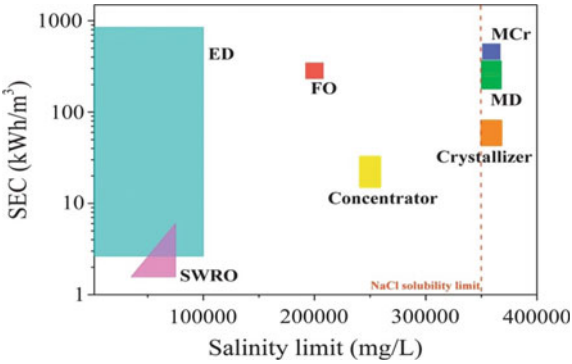


Fig. 18.15 Salinity range for operation of different types of membrane processes (Tsai et al. 2017)

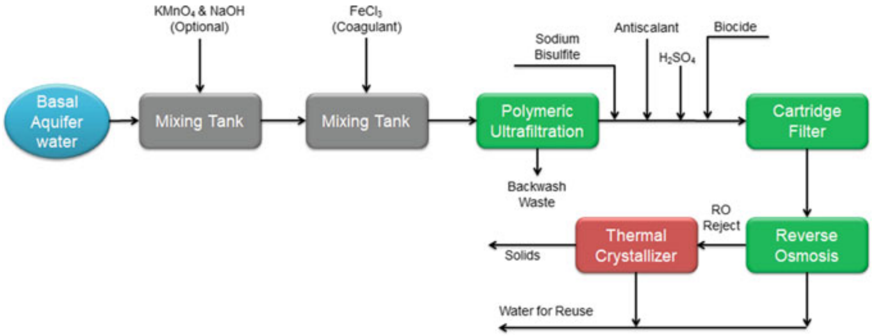


Fig. 18.16 RO-incorporated ZLD system

is required to maintain pH and keep metallic ions in dissolved condition. Pretreated UF permeates passed through a 5-mm cartridge filter to reject particulates before entering the RO system. RO was operated at 50–60% water recovery and 25 °C temperature due to the high concentration of dissolved solids in the feed water, and it resulted in the flux of 23 L/m^2/h, TDS rejection of 98–99%, and Na rejection of 98.4% (Loganathan et al. 2016). In UF, fouling was due to Na and Fe elements mainly, whereas in RO, deposition of Fe and barium was predominant. To reduce fouling of RO, antioxidants, and biocides were added to the RO system. RO reject was treated with evaporation and crystallizer unit to recover most of the sodium salts. PVDF membrane was used in UF, and polyamide membrane was used in RO for this pilot-scale study. Recovered water from the NZLD system was used in the process again (Tong and Elimelech 2016). Salinity limit, fouling tendency, reduced flux, and less life span of RO membranes are major limiting factors when they are used in the ZLD system. Pretreatment such as pH adjustment, ion exchange, chemical softening, and UF can enhance the performance of RO-integrated ZLD (Semblante et al. 2018).

18.6.2 FO-Incorporated ZLD System

FO replaces the secondary RO system in RO-incorporated ZLD system as shown in Fig. 18.17. The retentate from primary RO has a very high brine concentration, creating scaling in the secondary RO system due to exceeding the salinity limit. But FO can be operated under high saline conditions, so RO reject is sent to FO for further concentration of wastewater. Concentrated wastewater obtained from FO is sent to a crystallizer, and draw solute is recovered from diluted draw solution using low-grade heat. Recently developed NH_3/CO_2 thermolytic draw solute can be applied in the FO process to reduce the cost of regeneration by utilizing low-grade heat. As per a report, 803 MGJ of waste heat (temp > 90 °C) is annually produced in the USA from the thermal power plant and can regenerate draw solution by producing 1.9 billion m^3 of water using FO-based ZLD (Juby et al. 2008). Several studies are available for

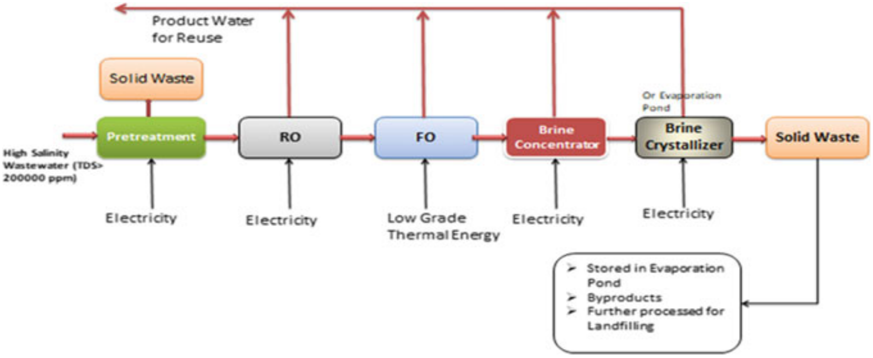


Fig. 18.17 FO-incorporated ZLD system

lab-scale FO-based treatments, but it has not been used at a commercial scale yet. Osmotic applications and systems (OASYS) Water is the only FO provider and has tested its operation at a pilot scale. At the Changxing power plant in China, the FO-incorporated ZLD system had a 650 m^3/day capacity, and wastewater from the cooling tower and flue-gas desulfurization could be concentrated up to 60,000 mg/L using a RO system and up to 220,000 mg/L or more using a FO system with an NH_3/CO_2 draw solution (Juby et al. 2008). FO rejects fed to the crystallizer for further concentration solid (Yaqub and Lee 2019) recovery. Produced water had a solute concentration of < 100 mg/L and was reused in the boiler.

18.6.3 MD-Incorporated ZLD System

Generally, MD is operated at 85 °C and uses low-grade heat of feed water to maintain temperature gradient (Lawson and Lloyd 1997). Hydrophobic microporous membranes made of PTFE, PP, and PVDF are used in this process. These membranes have high chemical and thermal stability, low resistance to mass transfer, and low thermal conductivity to prevent heat loss. MD can concentrate wastewater up to saturation value with the recovery of 60–90% of feed water (Yaqub and Lee 2019). RO reject fed into MD to concentrate it and recover pure water. Concentrated MD reject is sent to the crystallizer or evaporation pond for salt recovery. Membrane distillation crystallization (MDCr) is a hybrid technology that synergizes both MD and crystallization technologies and may be used to achieve ZLD, as shown in Fig. 18.18 (Yadav et al. 2022a).

But MD becomes much more expensive and energy-consuming (40–45 kW-h/m^3) in the absence of low-grade heat (Yaqub and Lee 2019). Also, in the presence of volatile pollutants permeating the water, quality is compromised. Feed concentration, temperature, recirculation rate, and membrane characteristics are the major parameters for MDCr operation. An increase in temperature gradient favors the increase

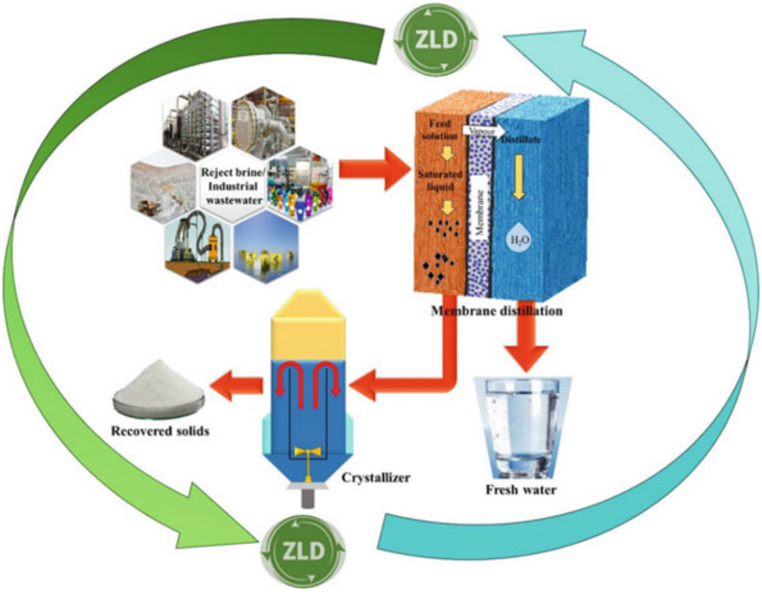


Fig. 18.18 MD-incorporated ZLD system (Yadav et al. 2022b)

in diffusion coefficient and vapor flux. When feed temperature increased from 50 to 70 °C, it resulted in a proportional increase in permeate flow from 4.6 to 9.5 kg/m^2 h (Yadav et al. 2022b). High feed concentration results in high concentration polarization, low heat and mass transfer, high scale deposition, decreased crystal size, and purity of recovered salts. Increasing solid concentration 20 times decreased the flux by 30% (Yadav et al. 2022b). High recirculation results in higher turbulence in the feed channel, which reduces the chances of fouling and polarization. It also enhances heat transfer coefficient and flux by reducing boundary layer resistance. Selectivity of the MD process depends on the hydrophobicity of membranes, and it is compromised due to foulant deposition on the membrane surface (Lawson and Lloyd 1997). Along with hydrophobicity, MDCr membranes should have high mechanical strength at lower thickness, high stability against temperature and chemicals, and low heat and mass transfer resistance. Ceramic-based membranes were also becoming popular due to their ability to provide the above properties. After 6 h of operation, a modified PVDF membrane with TiO_2 nanoparticles and nanocellulose increased permeate flux by 2.5 kg/m^2h at a salt rejection of 97% (Yadav et al. 2022b). Some applications of MDCr are given in Table 18.3 for different sources of wastewater.

Table 18.3 Applications of MDCr for treatment of RO reject and industrial wastewater (Yadav et al. 2022b)

Feed	MDCr configuration	Membrane material and pore size (μm)	Operating temperature (°C)		Flux (Kg/m^{2}h)	Recovery (%)	
			Feed	Permeate		Water	Salt
Seawater (65 g/l)	DCMDCr (HF)	PVDF (0.2)	60	20	3.8	78	68
SWRO reject	DCMDCr (HF)	PP (0.2)	36.1	24.7	0.678	> 90	–
Heavy metal wastewater (214.3 g/l $ZnSO_4$)	–	PTFE (0.083)	65	20	2.61	–	35
Sludge dewatering reject	DCMDCr (HF)	PP (0.2)	45–65	–	0.0013–0.0105	70	60

18.6.4 ED-Incorporated ZLD System

ED can be used for pretreatment and preconcentration of feed water. RO reject is fed into the ED system for its further concentration and water recovery. A highly concentrated stream obtained by ED is sent to the crystallizer for solid recovery. Zhang et al. investigated the potential of RO-ED integrated system, as shown in Fig. 18.19, for achieving near NZLD for wastewater treatment from coal's desulfurization. This lab-scale setup was used to achieve NZLD for wastewater produced from the desulfurization of coal. TDS concentration of the wastewater increased from 78 g/l to 230 g/l using this system at 70% of the water recovery. ED can concentrate feed water up to 100,000 mg/l with 7–15 kW-h/m^3 energy consumption (Zhang et al. 2021).

18.6.5 Capacitive Deionization-Incorporated ZLD System

CDI is a trending desalination technique and has the potential for preconcentration of industrial wastewater before feeding to thermal processes. But CDI is not explored much for ZLD applications. High salinity and fouling problems are the two major challenges in CDI while dealing with industrial wastewater. There are majorly three factors, i.e., cell architecture, operation strategies, and fouling control, that are to be optimized for the application of CDI in the ZLD system (Dykstra et al. 2017). CDI can replace RO in the ZLD system due to its ability for simple operation and cleaning. Classic CDI, membrane CDI (MCDI), and flow electrode CDI (FCDI) are three cell configurations in the cell architecture of CDI, as shown in Table 18.4. Classic CDI

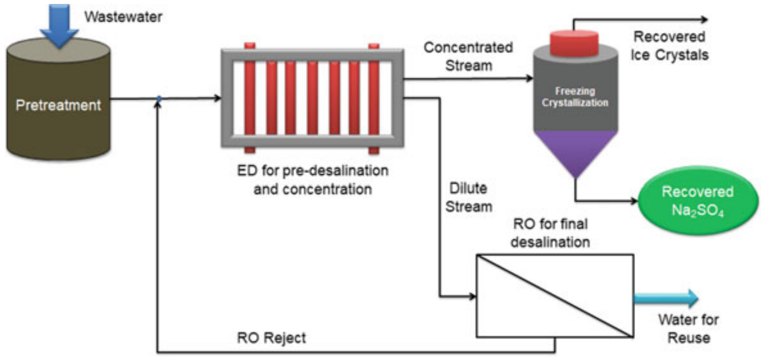
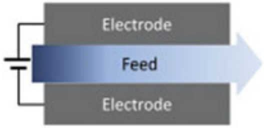
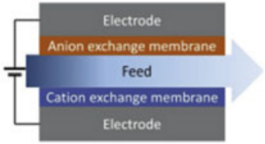
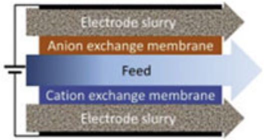


Fig. 18.19 RO-ED integrated ZLD system

is conventional CDI and faces low adsorption capacity and efficiency problems due to co-ion expulsion at high feed concentrations. A study found a decrease in charge efficiency from 0.8 to 0.6 when salinity increased from 1000 ppm to 11,600 ppm. Higher chances of fouling were reported in the presence of organics in the feed (Liu et al. 2020).

In MCDI, the anion exchange membrane (AEM) is positioned before the anode, and the cation exchange membrane (CEM) is positioned before the cathode to reduce the detrimental effects of co-ion expulsion. These ion-exchange membranes force expelled ions to entrap in macropores of the electrode due to bouncing back. To reach charge balance, entrapped co-ions may also draw more counter ions into electrodes, increasing the overall salt removal (Dykstra et al. 2017). MCDI results in greater salt removal, charge efficiency, adaptable working conditions, and better fouling resistance in comparison with classic CDI (Dykstra et al. 2017). It had given 20–30% more salt removal compared to classic CDI and showed the same charge efficiency when feed TDS increased from 1000 to 10,000 mg/l (Liu et al. 2020). Classic CDI and MCDI processes are stopped during the regeneration of electrodes. So, the slurry kind of electrode is used in FCDI in place of a solid electrode, providing the opportunity for its continuous operation. It eliminates the need to recirculate purified water during desorption. Also, more electrode particles can be added in the slurry phase to increase the contact area as compared to a solid phase. A test result showed over 95.42% of salt removal in treating a feed concentration of 35,000 ppm due to a 20 times increase in the contact area between the electrode compartment and the feed channel (Liu et al. 2020). But it needs to be further investigated for application on a commercial scale.

Table 18.4 Configurations and major properties of classic CDI, MCDI, and FCDI (Liu et al. 2020)

Type of CDI	Classic CDI	MCDI	FCDI
Configuration			
Availability	Commercial scale	Commercial scale	Lab scale
Advantages	Simple configuration	High adsorption capacity, high efficiency	Continuous desalination, high feed concentration (TDS > 35,000 mg/l)
Disadvantages	Low adsorption capacity and efficiency discontinuous desalination	Discontinuous desalination	Complicated cell configuration, electrode clogging, lack of test data
Applicability for ZLD	Not recommended	Recommended in the availability of test data	Assessment required

18.6.6 *Challenges with Membrane-Based ZLD Systems and Possible Solution*

The ZLD market in India was estimated to be worth \$39 million in 2012 and is anticipated to expand consistently at a pace of 7% (Yaqub and Lee 2019). There are several constraints while operating ZLD, such as high capital and operational cost, fouling due to recalcitrant organics, mixed recovered salt, leaching from evaporation ponds and landfills, and an increase in greenhouse gas emission for meeting the energy demand of ZLD system. Utilizing renewable energy, advanced pretreatment methods, and the production of various grades of recovered salt can make ZLD feasible (Zhang et al. 2022). In comparison with the capital cost of conventional membrane and thermal-based technologies (i.e., around \$15 m^3), technical and economic assessments of a shale gas facility in the Sichuan Basin revealed that 4000 m^2 of solar-still would be adequate to achieve ZLD with a capital cost lower than \$1 m^3 (Xie et al. 2022). But, this solar-induced evaporation may face problems of scaling, fouling, efficient water production, and availability of high-intensity solar radiation. Vergili et al. analyzed the techno-economic feasibility of membrane-based ZLD for the scenario of treating raw wastewater using membrane filtration, treating membrane filtration concentrates using MD, and incinerating MD concentrate. They found the cost of textile dye bath wastewater treatment using an integrated membrane process with and without RO was 2.01–2.16 and 1.37–1.38 \$/m^3 of influent, respectively, having return periods of 1.51–2.07 year and 0.87–0.91 (Vergili et al. 2012). The second scenario includes UF and NF of raw wastewater, MD for the membrane filtration concentrate, and an incinerator for MD concentrate. This scenario resulted in a cost-to-benefit ratio of 3.58, and the MD process contributed 80–90% of this ratio (Vergili et al. 2012).

Major challenges with membrane-based ZLD systems are shown in Fig. 18.20. Membrane-based processes have challenges of scaling, fouling, and concentration polarization, due to which membrane life is reduced and flux is decreased. Operational conditions such as temperature, pressure, and feed characteristics must be optimized for efficient water recovery and economic performance. A lab-scale study should be explored with real field conditions by proper scaling up of the processes, and energy consumption should be minimized for the desired results. Table 18.5 summarizes the major characteristics of membrane-based ZLD systems with their limitations.

18.7 Conclusion and Future Perspective

Implementing ZLD systems for industrial wastewater management can reduce water resource contamination and allow water reuse across the globe. More strict environmental laws on industrial wastewater discharge are being implemented due to issues with freshwater scarcity and overuse of water resources, pushing the industry

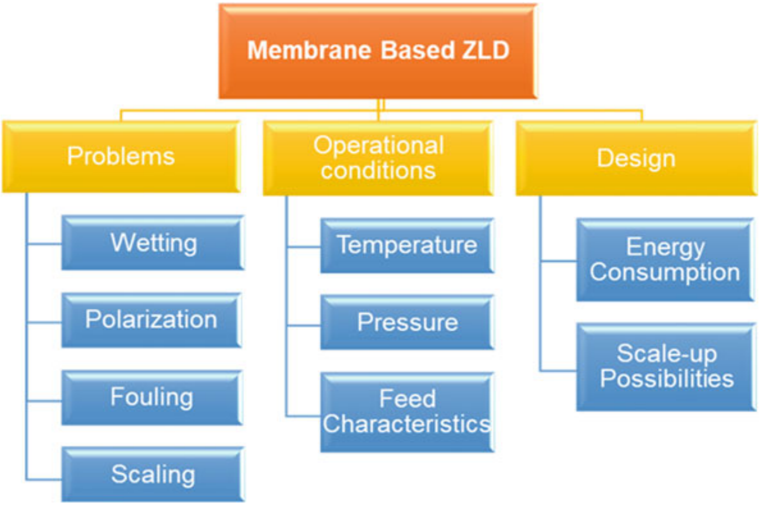


Fig. 18.20 Challenges with membrane-based ZLD systems

toward ZLD applications. In the beginning, thermal ZLD systems, including MVS, evaporator, and crystallizer, were used to recover water and solids from wastewater streams. But high operational and capital costs of conventional ZLD systems limited its wide application. This high energy requirement of ZLD is supplied by electricity which is ultimately produced from fossil fuels and leads to greenhouse gas emissions making the overall ZLD system unsustainable.

The application of membrane-based technologies in the preconcentration of wastewater streams has the potential to make the ZLD process more sustainable, efficient, and economically feasible. RO, FO, MD, EDR, and CDI are emerging membrane-based technologies for the concentration of the first RO reject. RO is the majorly studied and applied membrane process for achieving ZLD. RO reduces the total volume of wastewater by concentrating it and reduces the volume and energy requirement of the crystallizer unit. FO provides good opportunities for recovery of water even at high feed concentration in the availability of ideal draw solute and low-grade heat for its regeneration. NH_3/CO_2 thermolytic draw solute has shown its potential for application in the FO process for achieving ZLD. Still, it requires further study on the pilot and commercial scale for actual field applications. MD processes use hydrophobic membranes in their separation process to restrict the flow of water molecules from the hot feed side. MD had shown high water recovery and high-salinity limit during its operation. But high energy requirement in the absence of low-grade heat and the presence of volatiles in feed water limit their application. Most of the MD techniques are at lab-scale study and need to be tested at the pilot scale to see the full-scale performance and feasibility in the long run of a ZLD system. The MD and FO-incorporated ZLD systems can utilize waste heat energy, decreasing energy needs, operational costs, and greenhouse gas (GHGs) emissions.

Table 18.5 Benefits and limitations of membrane-based ZLD systems (Yaqub and Lee 2019)

Process	RO	MD	FO	EDR	CDI
Salinity limit (TDS in mg/l)	< 70,000	> 200,000	> 200,000	> 200,000	> 100,000 (not explored)
Energy consumption (kW.h/m^3)	2–6, (Feed TDS 1000–35,000 mg/l)	21–66, (Feed TDS up to 35,000 mg/l)	21, (Feed TDS 73,000 mg/l 64% water recovery)	7–25, (Feed TDS 15,000 to 69,000 mg/l)	0.4–2, (TDS < 4000 mg/l)
Technology maturity	Highly commercialized	Lack of field data	Commercialized	Commercialized	Early stage of commercialization
Advantages	Energy efficient	High-salinity limit	High-salinity limit, less fouling, utilization of low-grade heat	Less fouling	Less energy consumption, insensitive for silica fouling
Limitations	Limited salinity, high fouling, and scaling	Low flux, uneconomical in absence of low-grade heat,	Low flux at high salinity, reverse solute flux, cost of draw solution	High energy consumption	Limited salinity, lack of field data
Membrane materials used	Polyamide-based TFC, cellulose acetate	PP, PVDF, PTFE, etc.	Polyamide-based TFC	Polystyrene, polyacrylate, polyethylene, PP, etc.	Activated carbon, CNT, CNT, and graphene composites, etc.
Common morphology	Hydrophilic	Hydrophobic	Hydrophilic	Hydrophobic	Depends on the electrode material

High-salinity feed water, scaling, fouling, and high-pressure requirement are the major limitations with RO-incorporated ZLD system and need to be addressed using new-generation membranes and technologies. Solar-induced crystallization can be the alternate green technique for reducing the cost of the ZLD system. CDI and ED processes are also good options at lower feed concentrations due to their less fouling and easy cleaning tendency. The development of slurry state electrode materials has enhanced the possibility of continuous mode application and applicability for higher feed concentrations of the CDI process. The story of new-generation membranes can address the significant issues with current membrane-based technologies and make ZLD more feasible and sustainable. To address the environmental issues, a lot of studies are required for the life-cycle assessment of energy demand and gas emissions to boost the understanding of the cost–benefit balance of ZLD systems.

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