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Contaminants in Drinking and Wastewater Sources

Challenges and Reigning Technologies

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Dedicated
to
Research Life and Ethics
of
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Foreword

I am glad to announce that a book project entitled *Contaminants in Drinking and Wastewater Sources: Challenges and Reigning Technologies* is going to be published by Springer Nature Singapore Pvt. Ltd. under the dynamic lead editorship of Prof. Manish Kumar. The focal theme of this book is aptly chosen, as the widespread problems of water and environment pollution are jeopardizing our health. In this context, this multidisciplinary book focusing on actual challenges posed by contaminants of emerging concerns (CECs) on various compartments of the water cycle impacted by wastewater discharge and toxic leachates from waste disposal sites is the need of the hour. The main contribution of the present book is to aptly highlight a paradigm shift from conventional "priority" pollutants research to "emerging" or "new generation" unregulated contaminants study of the last 25 years duration. I am fully assured that the reader will get impressive and comprehensive information on structurally diverse groups of chemical compounds that have adverse effects on the aquatic environment, from this excellent meticulous compilation.

Another unique selling point of this book is that it not only defines the impacts of the environmental exposure of trace concentrations of CECs like pharmaceuticals, perchlorate, antibiotics, chlorophenol, microplastics, perfluorooctane-sulphonate and/or their metabolites, but also explores about the technological advancements. The research findings that are included in this book aptly explore the global strength, environmental status, chemical risk assessment and management strategies of CECs with relevant modern techniques, with the principle focus on concurrent "Emerging Water Quality Issues". My personal the most favourite component of this book is the discussion on the global human vulnerability due to the exposure of CECs in the natural environment that provides a unique platform for scientists from branches of science and technology including engineering sciences, agricultural sciences, biogeochemical sciences, hydrogeochemistry, toxicological sciences, social sciences, environmental policy and governance.

I also liked the chronology of the chapters which nicely flows through depicting monitoring and occurrence of CECs (distribution, source and fate in the aquatic environment) in its first part, and moves to advanced removal techniques of CECs (biotic, abiotic, photocatalytic degradation) in the second part for early prediction of risk and management purposes. Simultaneously, the present book also explores the human health perspectives of CECs, health risk assessment study along with case studies on sociological approaches. I hope this book will establish a road map for explaining in details the multifaceted application of biotic (bioreactor, anammox, etc.), abiotic (photocatalysis, ozonization, etc.) and natural removal system (constructed wetland) to be considered as effective treatment techniques for the emerging contaminants in the environment. I congratulate all the editors of the chapters for putting up a great work together.

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Preface

The widespread occurrence of water and environmental pollution is jeopardizing the health and sustainability of the ecosystems upon which all depend. Concerns about pollution have led people around the globe to focus their research on difference forms of contaminants. The changing research focus has resulted in paradigm shift from conventional "priority" pollutants to "emerging" or "new generation" mainly unregulated contaminants research over the last 25 years. Research findings presented in this book explore the global extent, environmental status, chemical risk assessment and management strategies for contaminants of emerging concern (CECs) with relevant modern techniques, with the principle theme of "Emerging Water Quality Issues." This book is a meaningful integration of two major parts covering the subjects related to occurrence, fate and transformation products of emerging pollutants in aquatic environment, overview of water quality and risk study from aquatic toxicity, removal processes and wastewater treatment strategies social-ecological risk perspectives, challenges for regulation and management etc. Each part is comprised of at least seven chapters dealing with diverse topics, such as the life-cycle of emerging contaminants, human and eco toxicological risks posed by CECs, potential recommendations to diminish the effects of emerging contaminants, an update on biological treatment techniques, and sociological aspects. Various research and review papers along with case studies have been included in the present chapters to broaden the critical concept of researchers and engineers about the evaluation of risk assessment methodologies which in turn establish the proper functioning of wastewater treatment methodologies for the effective removal of CECs from various types of wastewater.

Part I of this book consists of seven articles dealing with the occurrence, persistence, metabolic transformations, and adverse human health effects of emerging contaminants in the environment and illustrates the state-of-the-art measurement (affinity-based methods) of detecting contaminants in the aqueous environment through advanced analytical techniques from ppm to ppb level. This part has also highlighted about the CECs of global/national importance such as nanomaterials (carbon nanotubes, graphene based, zeolites, nano composites) pharmaceuticals and personal care products (PPCPs) and artificial sweeteners (ASs), microplastics

(MPs), perchlorate (ClO4-), which are the representatives of different diverse regions across the globe starting from Southeast Asia, East Asia to South Asia. In the first chapter, the authors have critically evaluated and analyzed the anthropogenic biomarkers in Asian groundwater based on 23 studies conducted in six countries (China, India, Japan, Korea, Singapore and Vietnam) to report the community level toxic effects of such biomarkers under different climatic conditions. The second chapter emphasizes the importance of different fundamental/advanced biomolecular techniques (affinity- based chromatography) for the analysis of emerging contaminants in wastewater and the environment. This chapter highlights the importance of different binding agents such as antibodies, molecularly imprinted polymers, and chiral stationary phases with the bioanalytical derivatives like macrocyclic antibiotics, proteins and polysaccharide to have more insight on biological separation events. Chapters in this part provide an overview of various natural attenuation processes for CECs, with specific attention to aqueous photochemistry of pharmaceuticals, evaluated using laboratory-scale and on-site observations. Collectively, this part highlights natural attenuation for specific classes of pharmaceuticals and focused on the governing mechanisms -underlying such attenuation processes based on studies conducted worldwide. This part is also helpful in characterizing the various physico-chemical processes through which MPs enter into the river ecosystems and the fate of the plastic particles in aquatic environments. Moreover, the eco-toxicological effect of MPs towards the aquatic biota, their detection techniques and possible risk management have also been discussed to establish their abundance and to develop possible mitigation strategies to reduce human health hazard. The authors of the fifth chapter have summarized water quality analysis on a total of 1262 groundwater wells distributed all over the country (Sri Lanka) for the determination18 water quality parameters using multivariate statistical analysis techniques. Cluster analysis was used to classify the groundwater wells based on their quality. The purpose of the study is to increase the viability of water recourse management and protection in Sri Lanka by providing statistical analysis result for the entire country. This part also depicts the combined biological/physico-chemical processes such as natural biodegradation, phytoremediation, bioreactor, chemical reduction, adsorption, membrane filtration, ion exchange, electrochemical reduction etc. for the adsorptive removal of ClO_{4-} by iron nanoparticles, catalytic reactors etc. Among physical, chemical and biological ClO_{4-} removal methods, biological treatment is considered as the cheapest and eco-friendly technology. The final chapter of this part elucidates carcinogenic and human health properties of emerging contaminants such as nanoparticle and specific PPCPs. Arsenic, radon, hazardous waste, agricultural chemical, fluoride, etc. are discussed in detail focussing on their role in various types of cancer such as lungs, breast, kidney, bladder, liver etc. These kinds of critical discussions are needed to find economical ways to treat contaminated wastewater in order to reduce risk of cancer.

The eleven chapters in the second part reflect the multifaceted application of biological processes (bioreactor, anammox etc.), abiotic degradation (photo catalysis, ozonation, etc.), natural removal (constructed wetland), and granular sludge reactors as treatment techniques for the emerging contaminants. This diverse part provides an overview of critical concepts needed for evaluation of risk assessment methodologies, which in turn establishes the proper functioning of wastewater treatment methodologies for the effective CEC removal from wastewater. This part emphasizes various removal techniques utilizing photo catalysis, permeable reactive barrier (PRB), bioremediation, metal-organic framework, nanotechnology etc. and assesses the effectiveness of various wastewater treatment strategies. The first article describes case studies evaluating problems that occur during the installation of PRB in pilot-scale before scaling up. The authors have made a comparative study of different case studies, the filler material used, the type of construction used, the date of operational set-up and cost analysis of PRBs. The chapter concludes with an assessment of pros and cons of PRBs. The authors of the second chapter discuss the utility of microbes for chromium (Cr^{6+}) removal to understand the mechanism of Cr-tolerance and remediation through different microbes for an economic, easy and eco-friendly technique that can be used on the pilot and larger scale to ensure Cr6+ free water. Mixed culture bioreactors containing Cr^{6+}-tolerant microbes can be effectively used in treating Cr^{6+} contaminated wastewater as shown by the authors. The third chapter gives an exclusive review of the existing literature on PPCPs removal from water. Pros and cons of the reported PPCPs removal processes are reviewed and evaluated with respect to removal efficiency. The fourth chapter throws light on the advanced applications of nanotechnology in waste water treatment. The various types of nanomaterials such as carbon nanotubes, graphene based, nano composites, metal organic frameworks are discussed focusing on their structures and performances in removal of water contaminants. Bioremediation techniques for water purification and the toxicity of the nanomaterial after treatment are also discussed. This part include a study on the effectiveness and efficiency of bimetallic particles for dechlorination of chlorophenols (CPs) and the effect of degree of chlorination and iron oxide phases on CPs incorporation when using Ni/Fe bimetallic system. This study will surely advance our knowledge on CPs degradation mechanisms and advance removal techniques. An overview of antibiotics removal technologies from water and associated challenges of conventional and advanced treatment (sorption techniques, membrane processes, and ecological processes like constructed wetlands, integrated constructed wetland) are critically analyzed in this part. There is very little information available about the eco-toxicological effects of antibiotics on aquatic and terrestrial organisms. Therefore, the seventh chapter mainly deals with the health impact of antibiotics and antibiotic resistance (AR) and their removal techniques to estimate potential risks associated with the water treatment plants and effluent discharges to the environment. A critical assessment on the state-of-the art removal techniques, major pollutant detoxification pathways and their impact on groundwater flow regime are presented. This part highlights the basic science of the water quality treatment, occurrence/fate, and contaminant biodegradation along with the mobility and biological detoxification of pollutants. Chapter eight includes recent studies on beneficial chemicals/products and biogas generated from water hyacinth as well as its probabilities of success in commercialization. Chapter nine reviews literature on the uses of water hyacinth for phytoremediation as well as composting of water hyacinth and its application. Effective treatment of wastewater is essential for public health and sanitation, water reclamation, preventing environmental pollution and protecting water resources from contaminants getting introduced into surface water systems. The final chapter of this part has critically reviewed and summarized the currently available literature regarding the worldwide occurrence, fate and transport of perfluorooctane sulphonate (PFOS) in the environment. This study also discusses the various advanced removal processes like physical adsorption, membrane filtration and redox processes and other conventional removal technologies available for the sustainable remediation of PFOS. Literature gaps are identified and future directions are suggested accordingly. The future challenges of such different state-of-the-art techniques are discussed and provides readers with an overview of cost-benefits of the available technologies for effective in-situ treatment of CECs.

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Dr. Manish Kumar
Prof. Ryo Honda
Prof. Daniel D. Snow
Dr. Santanu Mukherjee

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About the Editors

Dr. Manish Kumar is a Fellow of the Royal Society of Chemistry (FRSC) and faculty at Discipline of Earth Sciences at Indian Institute of Technology Gandhinagar, Gujarat, India. He earned his Ph.D. in Environmental Engineering from the University of Tokyo, Japan, and has been the recipient of prestigious fellowships like Water Advanced Research and Innovation (WARI) Fellowship, Japan Society for the Promotion of Science (JSPS) foreign research fellowship, Brain Korea (BK)-21 post-doctoral fellowship, Monbukagakusho scholarship, Linnaeus-Palme stipend from SIDA, Sweden, and Research Fellowship from CSIR, India, etc. Dr. Kumar is active in the fields of hydro(bio)geochemistry, contaminant transport and modeling, metal speciation, isotope fingerprinting, emerging contaminants and removal. He supervised 6 Ph.D. thesis and more than 20 Master's dissertations. He has published over 80 papers in international peer-reviewed journals and has 17 years' research/teaching experience. He is the member of global collaboration on wastewater based epidemiology of COVID-19.

Dr. Daniel D. Snow is a Research Professor in Natural Resources at the University of Nebraska, and the Director of the Water Sciences Laboratory, a part of the Nebraska Water Centre and Daugherty Water for Food Institute. His research is focused on the use of analytical chemistry and mass spectrometry to understand how water becomes contaminated and what we can do to prevent it. A good part of his work in the Water Sciences Laboratory involves creating analytical methods for new or "emerging" environmental contaminants like steroids, pharmaceuticals, algal toxins, explosives, and pesticides. In 2015, his team was awarded with Excellence in Environmental Engineering and Science Grand Prize by American Academy of Environmental Engineers and Scientists.

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Dr. Santanu Mukherjee obtained his Ph.D. from the University of Bonn and worked as a guest scientist in FZJ, Juelich. He was a visiting researcher in Savannah River Ecological Laboratory, USA. He is the recipient of multiple accolades such as EGU-Young Scientist Travel Award, ICAR international fellowship, GRIFA (Italian Pesticide Agency) grant, EU-COST action biochar grant, etc. His research interest includes the fate of emerging contaminants, the role of dissolved and particulate organic matter in deciding contaminants fate in the environment.

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Part I

Monitoring of Contaminants of Emerging Concern (CECs) in the Aquatic Environment

Chapter 1
Pharmaceuticals, Personal Care Products, and Artificial Sweeteners in Asian Groundwater: A Review

Keisuke Kuroda and Jun Kobayashi

1.1 Introduction

Pharmaceuticals and personal care products (PPCPs) are a group of contaminants of emerging concern (CECs) in the aquatic environment, which have gained global attention in the last 20 years because of their frequent occurrence and potentially adverse effects on human health and aquatic ecosystems (aus der Beek et al. 2016; Oaks et al. 2004; Schwarzenbach et al. 2006). The typical class of PPCPs found in the aquatic environment includes antibiotics, anti-inflammatories, analgesics, anticonvulsants, β-blockers, stimulants, contrast media, cosmetics, fragrances, insect repellents, and other diverse chemicals used for human and veterinary uses (Daughton and Ternes1999). Artificial sweeteners (ASs), which are sugar substitutes, have also been ubiquitously found in the water environment, owing to high human consumption and the ASs' high environmental persistence (Buerge et al. 2009; Kokotou et al. 2012). After consumption, both PPCPs and ASs are typically disposed of in wastewater via toilets, sinks, or bathrooms, and transported to wastewater treatment plants (WWTPs). There, because conventional WWTPs can only partly remove these compounds, their residues are discharged into receiving waters (Heberer 2002; Lange et al. 2012; Tambosi et al. 2010; Tran et al. 2018). There are also direct pathways of PPCPs and ASs into the water environment, such as sewage disposal, septic tank leakage, leakage from sewerage systems, livestock breeding, and fertilization (Sui et al. 2015).

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Asia, with a population of 4.6 billion as of 2020 (60% of the world population; https://population.un.org/wpp/), is a major consumer and producer of pharmaceuticals. For example, India and China were the two largest consumers of antibiotics in 2010 (Van Boeckel et al. 2014). In Asia, groundwater is an essential source of domestic water. In China, more than 400 of the country's 657 cities (61%) use groundwater as the major source of water supply (Liu and Zheng 2016). In India, around 80% of the rural population and 50% of the urban population use groundwater for domestic purposes (Chakraborti et al. 2011). Therefore, there is an urgent need to identify possible PPCP contamination in the groundwaters of various Asian regions.

The occurrence and fate of PPCPs and ASs in the world's groundwater have been summarized in a number of reviews (Lapworth et al. 2012; Postigo and Barceló 2015; Sui et al. 2015). These papers, however, rarely include studies on groundwater in Asia. This limited inclusion of Asian groundwater studies is partly because only a few Asian studies existed when the reviews were published. Since then, however, an increasing number of studies have been conducted on PPCPs and ASs in the groundwater of multiple Asian countries. Recently, a few country-specific review papers have been published on CECs, including PPCPs and ASs, in the groundwater of China (Dong et al. 2018) and India (Sackaria and Elango 2019). To date, however, there have been no reviews summarizing the results of studies investigating the occurrence of PPCPs and ASs in the groundwater of multiple Asian countries.

Hence, the objective of this chapter is to review the occurrence, sources, pathways, and fates of various pharmaceuticals, personal care products, and artificial sweeteners in groundwater across Asia. An overview of field studies from six Asian countries (China, India, Japan, Korea, Singapore, and Vietnam), as well as country-by-country analysis, is provided. The detection frequencies and concentrations of 13 representative PPCPs and ASs are compared among the studies. In addition, the main sources, pathways, and fates of the contaminants; the utility of PPCPs and ASs as anthropogenic markers or indicators of groundwater pollution; and the potential risk to humans and aquatic organisms; are summarized. Finally, future challenges are discussed from an Asian perspective.

1.2 Overview of PPCP and AS Studies on Asian Groundwater

Based on a database search using Scopus and Google Scholar, 22 scholarly publications were identified as suitable for analysis. The criteria for selection were: (i) the study involves detection of at least one PPCP or AS in Asian groundwater, (ii) the number of surveyed sites (wells) and samples are clearly specified, and (iii) the full text and its supplementary information are available in English. In addition, the results of the authors' recent investigation of groundwater in Tokyo were included. In total, 23 studies from six countries were summarized for review (Table 1.1). Most of the studies were conducted in China (10), followed by India (4), Japan (3), Vietnam (3), Singapore (2), and Korea (1).

The number of investigated groundwater sites per study ranged widely (from 3 to 50), as did the number of samples per study (3–148). We regarded spring water samples as groundwater samples because the properties of spring waters usually reflect those of nearby groundwaters. In 12 of the 23 studies (52%), information on the depth of groundwater wells or aquifers was obtained, with the latter ranging from very shallow (up to 2 m below ground level; hereafter, mbgl) to deep (up to 500 mbgl). In the other studies, where depth information was not provided, it appeared that most of the surveyed groundwater was shallow (<50 mbgl), based on the qualitative information in the papers.

The number of analyzed PPCPs and ASs also varied greatly, from 3 to 79 PPCPs and up to 7 ASs. Most of the studies employed targeted analysis with liquid chromatography-tandem mass spectrometry (LC-MS/MS) or gas chromatography-mass spectrometry (GC-MS). In the three studies, however, screening analysis of up to more than 1300 compounds (including 79 PPCPs) was employed, using GC-MS with automated identification and quantification database system (AIQS), and liquid chromatography time-of-flight mass spectrometry (LC-TOF-MS) (Duong et al. 2015; Kong et al. 2016; Li et al. 2016). As a general tendency, the number of detected PPCPs and ASs in the groundwater (up to 29 pharmaceuticals and 4 ASs) was less than the number of measured PPCPs and ASs in the respective studies. This would suggest that the groundwater was less contaminated, compared to surface waters, for example, because of the more direct pathways for the transport of contaminants in the case of the latter (e.g., direct discharge of wastewater effluent), as well as other factors such as differences in environmental fate and transport processes (e.g., sorption, volatilization, degradation, etc.), as evidenced by European (Loos et al. 2010) and US studies (Barnes et al. 2008; Focazio et al. 2008).

1.3 Country-by-Country Analysis

1.3.1 China

The occurrence of PPCPs and ASs in Chinese groundwater has been reported in 10 studies, the most among Asian countries. The geological scale of the groundwater studies in China varied widely, from the national (Li et al. 2015) and regional scale (Kong et al. 2016; Li et al. 2016) to watershed (Gan et al. 2013; Jiang et al. 2019; Xiang et al. 2018; Yang et al. 2018) and local scale (Peng et al. 2014; Tong et al. 2014; Yao et al. 2018). Dong et al. (2018) summarized the occurrence of a wide range of CECs, including PPCPs and ASs, in groundwater in China. This chapter summarizes seven further papers that were not discussed in Dong et al. (2018).

Table 1.1 Summary of studies on PPCPs and ASs in Asian groundwater

Country	Location	Number of site/sample	Depth[a] (mbgl)	Compounds analyzed	Compounds detected	LOD[b]/LOQ[c] (ng/L)	Maximum conc. (ng/L)	References
China	Tianjin	5/15	n.a. [d]	7 ASs	4 ASs (acesulfame, cyclamate, saccharin, sucralose)	0.1–2.3 (LOD), 0.4–7.5 (LOQ)	Cyclamate (100)	Gan et al. (2013)
	Guangzhou	33/132	<10	13 antibiotics, 15 other pharmaceuticals, 8 personal care products (PCPs), 1 industrial chemical	4 antibiotics, 11 other pharmaceuticals, 7 PCPs, 1 industrial chemical	0.1–6 (LOQ)	Salicylic acid (2014.7)	Peng et al. (2014)
	Shahu County, central China	27/44	15–100	19 antibiotics	19 antibiotics	0.05–5.3 (LOQ)	Erythromycin dehydrate (377.8)	Tong et al. (2014)
	12 cities from northern China	12/12	5–70	11 other pharmaceuticals, 5 endocrine-disrupting chemicals (EDCs)	4 other pharmaceuticals, 5 EDCs	0.01–1 (LOD), 0.004–5.5 (LOQ)	Sulpiride (60.1)	Li et al. (2015)

(continued)

Table 1.1 (continued)

Country	Location	Number of site/sample	Depth[a] (mbgl)	Compounds analyzed	Compounds detected	LOD[b]/LOQ[c] (ng/L)	Maximum conc. (ng/L)	References
	Dalian rural areas	13/13	2.5–100	21 antibiotics, 58 other pharmaceuticals as well as more than 1221 organic chemicals	1 antibiotic (sulfamethoxazole), 3 other pharmaceuticals, 1 PCP (L-menthol)	4–20 (LOD)	Nicotine (689)	Li et al. (2016)
	Beijing and Tianjin	27/27	n.a.	21 antibiotics, 58 other pharmaceuticals as well as more than 1221 organic chemicals	1 antibiotic (oleandomycin), 3 other pharmaceuticals, 3 PCPs	4–200 (LOQ)	2-phenoxy-ethanol (1328)	Kong et al. (2016)
	Shahu County, central China	39/99	10, 25 or 50	14 antibiotics	14 antibiotics	0.01–2.16 (LOD)	Clorotetracycline (59.6)	Yao et al. (2017)
	Dongjiang River Basin	11/33	2–13	48 antibiotics, 6 X-ray contrast media, 24 other pharmaceuticals, 8 PCPs, 5 ASs, 7 other organic chemicals	6 antibiotics, 2 X-ray contrast media, 10 other pharmaceuticals, 6 PCPs, 4 ASs, 5 other organic chemicals	0.03–153 (LOD), 0.01–45.8 (LOQ)	Acesulfame (4580)	Yang et al. (2018)

(continued)

Table 1.1 (continued)

Country	Location	Number of site/sample	Depth[a] (mbgl)	Compounds analyzed	Compounds detected	LOD[b]/LOQ[c] (ng/L)	Maximum conc. (ng/L)	References
China	Shanghai	3/3	n.a.	13 psychiatric pharmaceuticals, 2 metabolites	9 psychiatric pharmaceuticals	0.05–1.06 (LOD), 0.17–3.54 (LOQ)	Lorazepam (46.83)	Xiang et al. (2018)
	Changzhou, Yangtze River Delta	5/5	n.a.	27 antibiotics, 16 other pharmaceuticals, 1 PCP	16 antibiotics, 13 other pharmaceuticals, 1 PCP	0.02–14.75 (LOD), 0.09–58.99 (LOQ)	Caffeine (503.76)	Jiang et al. (2019)
India	Patancheru, Telangana	5/5	n.a.	7 antibiotics, 5 other pharmaceuticals	5 antibiotics, 5 other pharmaceuticals	10–50 (LOQ)	Cetirizine (28,000)	Fick et al. (2009)
	Patancheru, Telangana	15/26	n.a.	3 fluoroquinolone antibiotics	3 fluoroquinolone antibiotics	10 (LOQ)	Ciprofloxacin (770)	Rutgersson et al. (2014)
	Varanasi, Uttar Pradesh	26/26	10–200	3 antibiotics, 11 other pharmaceuticals, 1 AS, 1 industrial chemical, 21 pesticides and metabolites, 3 per- and polyfluoroalkyl substances (PFASs)	3 antibiotics, 10 other pharmaceuticals, 1 AS, 11 pesticides and metabolites, 3 PFASs	0.1–100 (LOD)	Sulfamethoxazole (120)	Lapworth et al. (2018)

(continued)

Table 1.1 (continued)

Country	Location	Number of site/sample	Depth^a (mbgl)	Compounds analyzed	Compounds detected	LOD^b/LOQ^c (ng/L)	Maximum conc. (ng/L)	References
	Ganges River Basin	14/14	n.a.[4]	2 antibiotics, 10 other pharmaceuticals, 3 PCPs, 5 ASs	2 antibiotics, 8 pharmaceuticals, 3 PCP, 3 ASs	0.06–15 (LOD)	Caffeine (262)	Sharma et al. (2019)
Japan	Central Tokyo	15/15	10–33	11 other pharmaceuticals, 2 PCPs	7 other pharmaceuticals, 2 PCPs	0.1–12 (LOQ)	Crotamiton (592)	Nakada et al. (2008)
	Central Tokyo	50/50	10–500	5 other pharmaceuticals, 1 PCP	5 other pharmaceuticals, 1 PCP	0.10–21 (LOQ)	Crotamiton (1400)	Kuroda et al. (2012)
	Central Tokyo	14/14	10–30	5 antibiotics, 10 other pharmaceuticals, 2 PCPs	5 antibiotics, 10 other pharmaceuticals	0.28–3.47 (LOQ)	Ibuprofen (1006)	This study
Korea	Buyeo-gun	30/30	10–15	17 antibiotics, 15 other pharmaceuticals, 1 PCP, 5 ASs, 6 pesticides	14 antibiotics, 11 other pharmaceuticals, 1 PCP, 1 pesticide, 4 ASs	0.03–4 (LOD)	Acesulfame (1330)	Lee et al. (2019)

(continued)

Table 1.1 (continued)

Country	Location	Number of site/sample	Depth[a] (mbgl)	Compounds analyzed	Compounds detected	LOD[b]/LOQ[c] (ng/L)	Maximum conc. (ng/L)	References
Singapore	An urban catchment	11/138	4.7–11	6 ASs	3 ASs (acesulfame, cyclamate, saccharin)	3–30 (LOQ)	Cyclamate (790)	Tran et al. (2014a)
	An urban catchment	11/148	4.7–11	1 antibiotic, 14 other pharmaceuticals, 1 PCP, 1 X-ray contrast medium	1 antibiotic, 14 other pharmaceuticals, 1 PCP, 1 X-ray contrast medium	0.3–6.0 (LOQ)	Caffeine (16,249)	Tran et al. (2014b)
Vietnam	Hanoi	10/10	8–50	22 antibiotics, 36 other pharmaceuticals, 2 PCPs	1 antibiotic (lincomycin), 2 others (caffeine and carbamazepine)	0.03–6.38 (LOQ)	Caffeine (78)	Kuroda et al. (2015)
	Hanoi and Ho Chi Minh City	26/44	n.a.	14 pharmaceuticals, 4 PCPs as well as 922 organic chemicals	1 pharmaceutical (caffeine), 3 PCPs	10 (LOD)	Caffeine (2700)	Duong et al. (2015)
	Hanoi and Halong	12/12	n.a.	5 ASs, 5 X-ray contrast media	4 ASs (acesulfame, cyclamate, saccharin, sucralose)	0.015–23 (LOD), 0.039–57 (LOQ)	Acesulfame (130)	Watanabe et al. (2016)

[a] Depth of wells. Mbgl: meters below the ground level

[b] *LOD* limit of detection. The numbers include method detection limit (MDL) and instrumental detection limit (IDL)

[c] *LOQ* limit of quantification. The numbers include method quantification limit (MQL) and instrumental quantification limit (IQL)

[d] *n.a.* not available

Li et al. (2015) provided a national-scale overview of the occurrence of 11 pharmaceuticals and 5 endocrine-disrupting chemicals (EDCs) in groundwater (5–70 mbgl) in 12 representative cities in northern China and found that pharmaceuticals (ketoprofen, mefenamic acid, nalidixic acid, and sulpiride) were found in groundwater in only 4 cities out of 12 (Li et al. 2015). In those cities, the groundwater was predominantly recharged by reclaimed water (treated wastewater). The general level of the pharmaceuticals was low (maximum: 60.1 ng/L for sulpiride) compared to other Asian studies, probably reflecting high dilution and/or attenuation in the groundwater.

Groundwater was analyzed at the regional scale for more than 1300 organic pollutants, including 79 PPCPs, in the rural areas of Dalian (Li et al. 2016), as well as Beijing and Tianjin (Kong et al. 2016). Four pharmaceuticals (nicotine, cotinine, sulfamethoxazole, and antipyrine) and a personal care product (PCP; L-menthol) were found at Dalian, and three pharmaceuticals (metformin, oleandomycin, and 1,1,1-trichloro-2-methyl-2-propanol) and four PCPs (acetophenone, 2-phenoxy-ethanol, L-menthol, and squalane) were detected in Beijing and Tianjin. The number of detected PPCPs was small compared to the number of analyzed PPCPs, partly because the limit of detection was marginally high (e.g., 20 ng/L for sulfamethoxazole; Li et al. 2016).

At the watershed scale, Gan et al. (2013) examined seven ASs (acesulfame, aspartame, cyclamate, neohesperidin dihydrochalcone (NHDC), neotame, saccharin, and sucralose) in the water environment of Tianjin, including five groundwaters. Four ASs (acesulfame, cyclamate, saccharin, and sucralose) were detected in the groundwater, with cyclamate the most abundant species (up to 99 ng/L), followed by saccharin (up to 63 ng/L) and acesulfame (up to 22 ng/L). The sources of the ASs in the groundwater were considered to be irrigation by wastewater, sludge application, animal feces, etc.

Yang et al. (2018) investigated the occurrence of 78 CECs in the surface water and groundwater in the Dongjiang River Basin in southern China. In the groundwater, 18 pharmaceuticals, six PCPs, four ASs, and five other organic chemicals were found. In terms of ASs, acesulfame, cyclamate, and sucralose were found in all the groundwater locations, with a maximum concentration of 4580 ng/L for acesulfame. Regarding PPCPs, methylparaben, salicylic acid, and diethyltoluamide (DEET) showed the highest detection frequency (72.7%). In contrast, compounds commonly detected in groundwater in other studies, such as caffeine, sulfamethoxazole, and carbamazepine, showed low detection frequencies (27.3%, 18.2%, and 9.1%, respectively), similar to those in Li et al. (2015).

The occurrence of psychiatric pharmaceuticals in river water and groundwater was studied in Shanghai, to investigate the effect of three psychiatric hospitals from which the treated effluents were discharged into the nearby rivers (Xiang et al. 2018). In the groundwater, nine pharmaceuticals (carbamazepine, mianserin, amitriptyline, diazepam, oxazepam, estazolam, temazepam, fluoxetine, and lorazepam) were detected, with the maximum concentration being 46.83 ng/L for lorazepam.

In Changzhou, in the Yangtze River Delta, Jiang et al. (2019) found 29 out of 42 pharmaceuticals, and a PCP (DEET), in rural groundwater from private wells. The concentration in the groundwater was the highest for caffeine (maximum concentration: 503.76 ng/L; detection frequency: 100%), followed by DEET (114.92 ng/L; 80%), sulfamethoxypyridazine (107.14 ng/L, 40%), ketoprofen (85.10 ng/L; 60%), and roxithromycin (63.72 ng/L; 80%). These groundwater PPCP levels were higher than in other Chinese groundwater, presumably because of a lack of effective treatment of waste from human and/or breeding animals (Jiang et al. 2019).

At the local scale, the groundwater near two landfill sites in Guangzhou was investigated (Peng et al. 2014), and 22 PPCPs were detected, with salicylic acid (detection frequency: 98%; maximum concentration: 2014.7 ng/L), methylparaben (97.2%; 83.2 ng/L), and triclocarban (79.6%; 36.2 ng/L) being the most prevalent. The source of PPCPs in the groundwater was inferred to be septic tank effluents rather than landfill leachates, as the PPCP concentrations in the groundwater did not correlate with the distance from the closest landfill sites.

The occurrence of 19 and 14 antibiotics in groundwater was investigated by Tong et al. (2014) and Yao et al. (2017), respectively, both in Shahu County, central China, within the Yangtze River system. Both studies found at least one antibiotic in all the groundwater samples. In Tong et al. (2014), clarithromycin, azithromycin, and roxithromycin showed 100% detection frequency, while erythromycin dehydrate (377.8 ng/L), tetracycline (115.2 ng/L), and chlortetracycline (86.6 ng/L) showed the highest concentrations. Yao et al. (2017) found that the antibiotic levels in the groundwater were highest in spring (131 ng/L, as an average of the total antibiotics in the groundwater samples), as compared to summer (20.3 ng/L) and winter (33.7 ng/L) (there was no fall survey). Fluoroquinolones and tetracyclines were the dominant antibiotics, in contrast to the area's surface waters, where macrolides, especially erythromycin, were dominant. The authors conjectured that this difference may have been due to the more hydrophilic nature of fluoroquinolones and tetracyclines. Agricultural and municipal wastewaters were likely the primary sources of the antibiotics in the groundwater, with fish ponds being a further source of some antibiotics, such as tetracyclines.

1.3.2 India

India is among the top five global pharmaceutical producers (Balakrishna et al. 2017). Major pharmaceutical industries are located in Hyderabad, Bangalore, Ahmedabad, Dehradun, and Mumbai (Sackaria and Elango 2019). In particular, Hyderabad City accounts for nearly 80% of India's domestic pharmaceutical production (Mathew and Unnikrishnan 2012). A broad range of PPCPs have been investigated in the water environment of India (Balakrishna et al. 2017; Philip et al. 2018). In the case of groundwater, Sackaria and Elango (2019) reviewed the occurrence of diverse CECs, including PPCPs, in the country. Therefore, in this chapter, four studies, three of which were also reviewed in Sackaria and Elango (2019), are introduced in more detail.

Early studies on PPCPs in Indian groundwater focused on antibiotics (Fick et al. 2009; Rutgersson et al. 2014). Fick et al. (2009) reported very high levels of antibiotics in the groundwater and river water in the Patancheru region, along the Isakavagu stream and Nakkavagu River, in 2008. A local WWTP, Patancheru Enviro Tech Limited (PETL), received wastewater from pharmaceutical manufacturers (Larsson et al. 2007) and discharged effluents with extremely high levels of pharmaceuticals (mg/L level) into the Isakavagu stream. As a result, cetirizine and ciprofloxacin showed extremely high concentrations in both the river water (up to 530 μg/L and 2500 μg/L, respectively) and groundwater (up to 28 μg/L and 14 μg/L, respectively). In the same study, the concentrations in the undiluted effluent from PETL were 2.1 mg/L (cetirizine) and 14 mg/L (ciprofloxacin). Although the well with the highest levels of the two antibiotics is no longer used for human consumption, other wells that had a lower but still very high concentration of antibiotics were used for drinking water supply.

In the same area of the Patancheru region, the groundwater was sampled in 2011 and analyzed for fluoroquinolone antibiotics (Rutgersson et al. 2014). The maximum concentration was 770 ng/L for ciprofloxacin, more than 10 times lower than in the 2008 study (Fick et al. 2009), probably because the discharge from PETL into the Isakavagu stream had gradually decreased. Nevertheless, the authors stated that the discharge from isolated industries or illegal dumping would also contribute to groundwater contamination in areas upstream from PETL.

In Varanasi, beside the Ganges River in northern India, Lapworth et al. (2018) reported the prevalent occurrence of several pharmaceuticals, such as sulfamethoxazole (detection frequency: 77%), sulfanilamide (62%), carbamazepine (27%), and sucralose (15%), in both shallow (<100 mbgl) and deep (>100 mbgl) groundwater. High detection frequencies and concentrations of contaminants were found not only in shallow wells but also in some large municipal deep wells, which have a long history (>30 years) of intense pumping.

Sharma et al. (2019) studied the occurrence of 31 CECs in 14 groundwater samples along the Ganges River and found that the most frequently detected compounds were caffeine (100%), DEET (100%), and sucralose (100%), followed by ketoprofen (93%), carbamazepine (79%), hydrochlorothiazide (71%), and cyclamate (50%). The sum of detected PPCPs in the groundwater ranged from 34 to 293 ng/L, and the geometric mean was approximately half that of the PPCPs found in the river waters. In the groundwater, caffeine showed the highest concentration (15–262 ng), followed by ibuprofen (<15–49.4 ng/L), sucralose (0.53–24.6 ng/L), and ketoprofen (<15–23.4 ng/L). Elevated groundwater concentrations were generally observed in the urbanized and industrialized middle and lower reaches of the Ganges River, but specific elevated concentrations (e.g., sucralose) were also observed in the semirural and rural upper Himalayan reach.

1.3.3 Japan

In Japan, the occurrence of PPCPs in groundwater has been investigated in central Tokyo (Kuroda et al. 2012; Nakada et al. 2008). In these studies, crotamiton and carbamazepine were the most frequently detected PPCPs, followed by propyphenazone, DEET, and caffeine. In the city-wide survey of 50 wells, the PPCP detection frequency was high in unconfined aquifers (<30 mbgl, 66% detection frequency) and spring waters (100%), but even confined aquifers (30–500 mbgl) showed a 44% PPCP detection frequency (Kuroda et al. 2012). The source of PPCPs in Tokyo's groundwater was inferred to be leakage of sewage from sewer pipes. This groundwater pollution by sewage was also considered to be the source of other contaminants in Tokyo's groundwater, including chlorate, perchlorate (Kosaka et al. 2013), perfluoroalkyl acids (PFAAs; Kuroda et al. 2014; Murakami et al. 2009), *N*-nitrosodimethylamine (NDMA; Van Huy et al. 2011), nitrate (Kuroda and Fukushi 2008; Kuroda et al. 2007), and bacteria (Kuroda et al. 2008; Kuroda et al. 2012). PPCPs have also been detected in river waters in Japan (Kobahashi and Horiuchi 2007; Nakada et al. 2008). Although not the case in Tokyo, the infiltration of river waters was considered to be the source of groundwater PPCPs in areas such as basins with highly permeable grounds (Kobahashi and Horiuchi 2007).

Ten years after a comprehensive survey of PPCPs in Tokyo's groundwater in 2007 (Kuroda et al. 2012), the authors conducted a sampling campaign of 12 groundwaters and springs in Tokyo and analyzed 17 PPCPs, in 2017 and 2018. The results (Table 1.2) showed that all 12 samples were positive for more than four PPCPs. All 17 PPCPs except for triclosan were detected, and crotamiton (12/12, 100%) and carbamazepine (10/12, 83%) were again the most frequently detected, followed by sulfamethoxazole, sulfamonomethoxine, ampicillin, ibuprofen (7/12, 58%), caffeine, and bezafibrate (6/12, 50%). Large concentrations of ibuprofen (1006 ng/L), caffeine (86.7 ng/L), and bezafibrate (78.7 ng/L) were detected. The maximum concentration of ibuprofen was comparable to sewage influents in the region (Nakada et al. 2006).

In this 2017–2018 survey, we revisited seven groundwater sites and two springs that had been examined in the 2007 survey (Kuroda et al. 2012) and compared the concentrations of crotamiton and carbamazepine (Fig. 1.1). The occurrence of PPCPs in the two surveys was somewhat similar in the case of crotamiton and carbamazepine, but the 2017–2018 survey tended to show more frequent detection of PPCPs, partly because the limit of detection was lower in the 2017–2018 survey (0.38–1.61 ng/L) than in the 2007 survey (0.82–21 ng/L). In contrast, there was a clear difference in the occurrence of caffeine, which was detected in four locations in the 2017–2018 survey (with concentrations up to 86.7 ng/L) and in none of the nine locations in the 2007 survey. As caffeine is somewhat labile to biodegradation, the detection of caffeine is considered to indicate recent (or 'fresh') contamination by sewage (Buerge et al. 2003; Nakada et al. 2008). In the 2017–2018 survey, the groundwater samples were mostly taken from unconfined aquifers (<30 mbgl), and the widespread detection of PPCPs, including caffeine, suggests that the shallow groundwater and springs in

Table 1.2 Summary of PPCP concentrations in the 2017–2018 survey of groundwater and spring waters in Tokyo

	Detection frequency (%)	Min. (ng/L)	Max. (ng/L)	Median (ng/L)
Ampicillin	58	<0.77	4.21	0.98
Bezafibrate	50	<0.03	78.7	0.19
Caffeine	50	<1.61	86.7	3.74
Carbamazepine	83	<0.38	13.3	1.66
Clarithromycin	17	<0.45	0.94	<0.45
Crotamiton	100	0.3	44.4	2.09
Cyclophosphamide	8	<0.28	0.51	<0.28
Gliclazide	8	<0.32	1.03	<0.32
Ibuprofen	58	<2.15	1006	12.6
Indometacin	17	<0.66	3.19	<0.66
Oseltamivir	8	<0.55	0.60	<0.55
Sulfadimethoxine	42	<0.52	0.99	<0.52
Sulfamethoxazole	58	<0.59	21.7	1.01
Sulfamonomethoxine	58	<0.50	2.30	0.90
Triclocarban	0	<0.35	<0.35	<0.35
Triclosan	0	<3.47	<3.47	<3.47
Trimethoprim	17	<0.45	1.00	<0.45

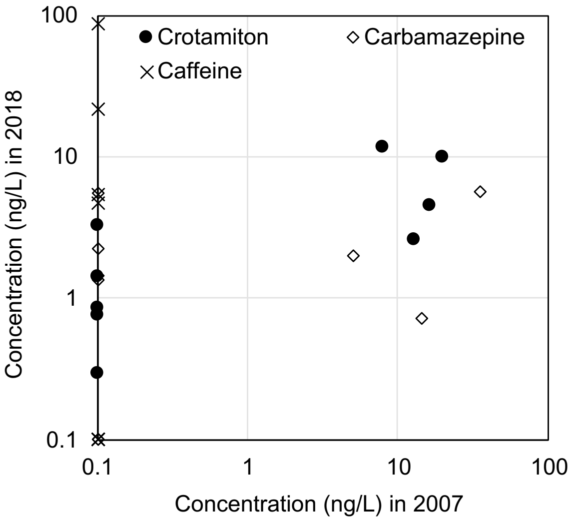

Fig. 1.1 Comparison of the crotamiton, carbamazepine, and caffeine concentrations in Tokyo groundwater between the 2007 survey (Kuroda et al. 2012) and the 2017–2018 survey (the present study)

Tokyo were still vulnerable to pollution by sewage and that the pollution was still ongoing.

1.3.4 Korea

Lee et al. (2019) investigated the occurrence of 44 CECs in groundwater in the rural areas of Chungcheong Province, where agriculture such as rice, apple, and pear cropping and cattle raising were actively practiced (Lee et al. 2019). A total of 31 CECs were detected in the surveyed wells, which were shallow (10–15 mbgl). The detected concentrations of PPCPs (e.g., caffeine, up to 15 ng/L; crotamiton, up to 3.9 ng/L; carbamazepine, up to 0.26 ng/L) were lower than in the other Asian countries, presumably because the survey was conducted in rural areas with less PPCP usage and more background groundwater. Nevertheless, the occurrence of the compounds showed an interesting contrast between agricultural and non-agricultural areas; antibiotics, anthelmintics, β-blockers, and pesticides were detected only in agricultural groundwater. In comparison, the concentrations of artificial sweeteners were significantly higher in non-agricultural groundwater than in agricultural groundwater. These results clearly reflect the different human activities in these areas.

1.3.5 Singapore

Tran et al. investigated the occurrence of 17 PPCPs (Tran et al. 2014b) and six artificial sweeteners (Tran et al. 2014a) in surface water and groundwater in an urban area of Singapore. In both studies, groundwater samples from ten wells in catchments with sewerage systems, and those from a well in a catchment without known wastewater sources (background groundwater), were surveyed in multiple sampling campaigns. The surveyed catchments were served by relatively old and shallow sewer systems, with the age of the sewer pipes being greater than 15–20 years. The surveyed wells were shallow (4.7–11 mbgl).

Nine PPCPs (acetaminophen, clofibric acid, carbamazepine, caffeine, crotamiton, diclofenac, DEET, gemfibrozil, and salicylic acid) and three artificial sweeteners (acesulfame, cyclamate, and saccharin) were detected in groundwater samples. In the groundwater from sewered catchments, DEET (detection frequency: 100%), caffeine (83%), carbamazepine (67%), acetaminophen (58%), and salicylic acid (58%) were the most frequently detected PPCPs, with maximum concentrations of 16,249 ng/L (caffeine), 4689 ng/L (acetaminophen), 3481 ng/L (DEET), and 1994 ng/L (salicylic acid). The median concentrations in the groundwater samples (68.5 ng/L for caffeine, 49.5 ng/L for DEET, 23 ng/L for acetaminophen, 17 ng/L for salicylic acid, and 0.7 ng/L for carbamazepine) were two to three orders of magnitude lower than those in raw wastewater samples measured in the same study. Artificial sweeteners showed lesser detection frequency (cyclamate, 48%; acesulfame, 44%; saccharin, 36%) with lower groundwater concentrations (e.g., maximum concentration of cyclamate: 730 ng/L) than the PPCPs.

In the background groundwater samples, DEET and caffeine showed high detection frequency (100% and 80%, respectively) and median concentrations (67.5 ng/L and 34.6 ng/L, respectively), similarly to the groundwater in sewered catchments. The other PPCPs and artificial sweeteners were not detected. Therefore, the authors suggested that acetaminophen, carbamazepine, salicylic acid, acesulfame, cyclamate, and saccharin were suitable markers of raw wastewater in the groundwater.

1.3.6 Vietnam

In Hanoi, ten groundwater samples were surveyed for 58 PPCPs (Kuroda et al. 2015). Among the samples, only three groundwaters were positive for pharmaceuticals: specifically, caffeine, lincomycin, and carbamazepine. Caffeine was the most frequently detected (3/10, 30%), with concentrations of 57–78 ng/L. Lincomycin and carbamazepine were detected in two and one samples, respectively, with concentrations of 0.13–2.1 ng/L. On the basis of hydrogeological and hydrochemical studies conducted at the same study sites, the source of PPCPs in the groundwaters was inferred to be the neighborhood pond water (Kuroda et al. 2017a, b; Kuroda et al. 2015).

Duong et al. (2015) analyzed 940 organic pollutants in groundwater in Hanoi and Ho Chi Minh City, using the same screening analysis as Li et al. (2016) and Kong et al. (2016). Among the 19 PPCPs analyzed, a pharmaceutical (caffeine) and three PCPs (L-menthol, squalane, and DEET) were detected. L-menthol was the most frequently detected (22 samples out of 44), followed by squalane (14), DEET (7), and caffeine (2). The two PPCPs were abundantly detected in the surface waters of Hanoi and Ho Chi Minh City (Duong et al. 2014). In one Hanoi well, the maximum caffeine concentration was very high for groundwater, at 2.7 μg/L, one-tenth that of the raw wastewater in Hanoi (Kuroda et al. 2015). Therefore, the observed presence of caffeine in two wells likely reflects the direct entry of leachate from surface water, sewage canals, or underground septic tanks (Duong et al. 2015).

Watanabe et al. (2016) investigated the occurrence of five artificial sweeteners (acesulfame, aspartame, cyclamate, saccharin, and sucralose) and five X-ray contrast media (iopamidol, iohexol, diatrizoic acid, iopromide, and metrizoic acid) in the groundwaters of Hanoi, Haiphong, and the Halong Bay area. In those groundwater samples, artificial sweeteners were detected at a maximum of 130 ng/L for acesulfame, which was comparable to the levels in WWTP effluents in Hanoi (150–210 ng/L, median 190 ng/L) and several times lower than in the pond and river waters in the urban area (240–890 ng/L). Interestingly, elevated groundwater concentrations of artificial sweeteners were found only in suburban and rural areas, while in the urban area only acesulfame was detected, and at very low levels (max. 0.49 ng/L). The X-ray contrast media were not detected in the groundwater, despite their abundance in the surface waters and wastewater (maximum 4000 ng/L iohexol in WWTP effluents).

1.4 Comparison of Selected Compounds Among Studies

This section compares the detection frequencies and concentrations of three antibiotics (ciprofloxacin, sulfamethoxazole, and trimethoprim; Table 1.3), six other pharmaceuticals (acetaminophen, caffeine, carbamazepine, crotamiton, diclofenac, and ibuprofen; Table 1.4), three ACs (acesulfame, cyclamate, and sucralose), and a personal care product, DEET (Table 1.5), in Asian groundwater. The compounds were selected based on their frequent and abundant occurrence across the studies, in more than two Asian countries. It should be noted that the study objectives, site selection criteria, and sample numbers were not consistent across the studies, which would affect the detection frequencies and concentrations, as Lapworth et al. (2012) pointed out. Each study had specific characteristics; for example, a reconnaissance study in a large region or across multiple cities (e.g., Kuroda et al. 2012; Sharma et al. 2019), a catchment-scale investigation (e.g., Tran et al. 2014b; Yang et al. 2018), or a local survey in specific sites such as landfill sites (Peng et al. 2014). The site selection criteria also varied; and generally, in studies where the sampling sites are selected without strict criteria, the detection frequencies of the compounds are significantly lower than in studies where the sampling sites are selected as potentially contaminated (Lapworth et al. 2012).

1.4.1 Antibiotics

Antibiotics are used as human and animal medicine to treat diseases caused by microorganisms such as bacteria, fungi, or protozoa (Kümmerer 2009a) and are heavily used in Asia (Van Boeckel et al. 2014). In China, for example, 162,000 tons of antibiotics were administered in 2013, with human use accounting for 48%, and the remainder being veterinary antibiotics (Dong et al. 2018). The environmental release of antibiotic residues leads to resistant bacteria (Kümmerer 2009b), and the spread of antibiotic-resistant bacteria in the environment has become a worldwide concern (Michael et al. 2013). It is a particularly significant challenge in Asia since wastewater containing antibiotics is often directly discharged into the environment without sufficient treatment (Kumar et al. 2019; Lundborg and Tamhankar 2017; Mutiyar and Mittal 2014). The occurrence of antibiotics and their resistant genes in the environmental matrices have been actively examined in Asia (e.g., in China (Qiao et al. 2018) and India (Philip et al. 2018))

Table 1.3 Detection frequency (%) and concentration range (ng/L) of antibiotics in Asian groundwater

Detection freq. (%)	Sample number	Concentration range (ng/L)	Country/region	References
Ciprofloxacin (fluoroquinolones)				
100	5	44–14,000	India (Patancheru)	Fick et al. (2009)
39	44	<2.05–5.4	China (Shahu County)	Tong et al. (2014)
35	26	<10–770	India (Patancheru)	Rutgersson et al. (2014)
Sulfamethoxazole (sulfonamides)				
77	26	<0.1–34	India (Varanasi)	Lapworth et al. (2018)
58	14	<0.59–21.7	Japan (Tokyo)	This study
40	5	<0.97–2.18	China (Changzhou)	Jiang et al. (2019)
36	14	<2.0–4.13	India (Ganges River Basin)	Sharma et al. (2019)
33	99	<1.11–7.29	China (Shahu County)	Yao et al. (2017)
27	30	<0.246–4.23	Korea (Buyeo-gun)	Lee et al. (2019)
24	132	ND[a]–124.5	China (Guanzhou)	Peng et al. (2014)
23	44	<0.11–0.8	China (Shahu County)	Tong et al. (2014)
23	13	<20–70	China (Dalian rural areas)	Li et al. (2016)
18	33	ND–25.7	China (Dongjiang River Basin)	Yang et al. (2018)
Trimethoprim (other antibiotics)				
83	5	<10–55	India (Patancheru)	Fick et al. (2009)
40	5	<0.49–3.96	China (Changzhou)	Jiang et al. (2019)
32	44	<0.05–5.2	China (Shahu County)	Tong et al. (2014)
17	14	<0.45–1.0	Japan (Tokyo)	This study
4	132	ND–10.5	China (Guanzhou)	Peng et al. (2014)

[a] *ND* not detected

Table 1.4 Detection frequency (%) and concentration range (ng/L) of other selected pharmaceuticals in Asian groundwater

Detection freq. (%)	Sample number	Concentration range (ng/L)	Country/region	References
Acetaminophen (anti-inflammatory and analgesic)				
60	5	<0.46–14.63	China (Changzhou)	Jiang et al. (2019)
5	148	<5.0–4689	Singapore	Tran et al. (2014b)
43	14	<0.8–1.92	India (Ganges River Basin)	Sharma et al. (2019)
3	30	<0.082–0.647	Korea (Buyeo-gun)	Lee et al. (2019)
Caffeine (stimulant)				
100	14	15.5–262	India (Ganges River Basin)	Sharma et al. (2019)
100	5	n.a.[a]–503.76	China (Changzhou)	Jiang et al. (2019)
90	30	<0.205–15	Korea (Buyeo-gun)	Lee et al. (2019)
87	148	<6.0–16,249	Singapore	Tran et al. (2014b)
58	12	<1.7–109.5	China (12 cities from northern China)	Li et al. (2015)
50	14	<1.61–86.7	Japan (Tokyo)	This study
3	10	<0.16–78	Vietnam (Hanoi)	Kuroda et al. (2015)
27	33	ND[b]–50.9	China (Dongjiang River Basin)	Yang et al. (2018)
27	15	<4.6–56.8	Japan (Tokyo)	Nakada et al. (2008)
25	4	<10–170	Vietnam (Ho Chi Minh City)	Duong et al. (2015)
16	50	<0.82–19	Japan (Tokyo)	Kuroda et al. (2012)
3	40	<10–2700	Vietnam (Hanoi)	Duong et al. (2015)
Carbamazepine (anticonvulsant)				
100	3	0.27–7.05	China (Shanghai)	Xiang et al. (2018)
83	14	<0.38–13.3	Japan (Tokyo)	This study

(continued)

Table 1.4 (continued)

Detection freq. (%)	Sample number	Concentration range (ng/L)	Country/region	References
79	14	<0.1–27.2	India (Ganges River Basin)	Sharma et al. (2019)
62	148	<0.3–9.3	Singapore	Tran et al. (2014b)
60	5	<1.13–0.81	China (Changzhou)	Jiang et al. (2019)
58	12	<1–103.2	China (12 cities from northern China)	Li et al. (2015)
40	15	<0.4–117	Japan (Tokyo)	Nakada et al. (2008)
38	50	<0.10–97	Japan (Tokyo)	Kuroda et al. (2012)
27	26	<1–86	India (Varanasi)	Lapworth et al. (2018)
10	30	<0.098–0.255	Korea (Buyeo-gun)	Lee et al. (2019)
10	10	<0.09–0.25	Vietnam (Hanoi)	Kuroda et al. (2012)
9	33	ND–18.1	China (Dongjiang River Basin)	Yang et al. (2018)
Crotamiton (antipruritic)				
100	14	0.29–44.4	Japan (Tokyo)	This study
87	15	<1.3–592	Japan (Tokyo)	Nakada et al. (2008)
67	30	<0.081–1.14	Korea (Buyeo-gun)	Lee et al. (2019)
36	50	<0.51–1400	Japan (Tokyo)	Kuroda et al. (2012)
4	148	<0.3–12.4	Singapore	Tran et al. (2014b)
Diclofenac (anti-inflammatory and analgesic)				
60	5	<1.05–7.66	China (Changzhou)	Jiang et al. (2019)
18	33	ND–6.03	China (Dongjiang River Basin)	Yang et al. (2018)
14	14	<0.9–1.56	India (Ganges River Basin)	Sharma et al. (2019)

(continued)

Table 1.4 (continued)

Detection freq. (%)	Sample number	Concentration range (ng/L)	Country/region	References
8	26	<1–9.2	India (Varanasi)	Lapworth et al. (2018)
3	148	<1.5–7	Singapore	Tran et al. (2014b)
Ibuprofen (anti-inflammatory and analgesic)				
100	5	<8.89–55.81	China (Changzhou)	Jiang et al. (2019)
58	14	<2.15–1006	Japan (Tokyo)	This study
36	14	<15–49.4	India (Ganges River Basin)	Sharma et al. (2019)
33	15	<0.1–0.6	Japan (Tokyo)	Nakada et al. (2008)
27	33	ND–48.7	China (Dongjiang River Basin)	Yang et al. (2018)
11	132	ND–57.9	China (Guanzhou)	Peng et al. (2014)

[a] *n.a.* not available
[b] *ND* not detected

In Asia, the antibiotics most found in groundwater are ciprofloxacin, sulfamethoxazole, and trimethoprim (Table 1.3). In Patancheru, India, the groundwaters at all the wells showed fluoroquinolone ciprofloxacin, with concentrations up to 14 μg/L (Fick et al. 2009). In the same study, the concentration of cetirizine, an antihistamine pharmaceutical, was even higher, at 28 μg/L. The extremely high concentrations of pharmaceuticals in some of the groundwater samples were considered to be due to contamination by wastewater from local pharmaceutical production facilities (see Sect. 1.3.2 for details). In the other locations, the antibiotics were less frequently detected and in lesser concentrations (up to 10 ng/L in most studies), lower than in non-Asian studies (Lapworth et al. 2012). Sulfamethoxazole and trimethoprim have been found in environmental waters worldwide (Thiebault 2020). The two are typically consumed in combination, with a ratio of 5:1 in human consumption (Salter 1982), and the concentration ratio of sulfamethoxazole to trimethoprim has recently been suggested to be useful for identifying wastewater origins (i.e., human or livestock; Thiebault 2020).

Table 1.5 Detection frequency (%) and concentration range (ng/L) of artificial sweeteners and personal care products in Asian groundwater

Detection freq. (%)	Sample number	Concentration range (ng/L)	Country/region	References
Acesulfame (artificial sweetener)				
100	33	12.9–4580	China (Dongjiang River Basin)	Yang et al. (2018)
100	15	12–22	China (Tianjin)	Gan et al. (2013)
78	9	0.30–110	Vietnam (Hanoi)	Watanabe et al. (2016)
73	30	<0.500–1330	Korea (Buyeo-gun)	Lee et al. (2019)
67	3	4.5–130	Vietnam (Halong)	Watanabe et al. (2016)
41	138	<3.0–730	Singapore	Tran et al. (2014a)
7	14	<1.6–2.31	India (Ganges River Basin)	Sharma et al. (2019)
Cyclamate (artificial sweetener)				
100	33	2.75–110	China (Dongjiang River Basin)	Yang et al. (2018)
100	15	92–100	China (Tianjin)	Gan et al. (2013)
100	3	2.4–65	Vietnam (Halong)	Watanabe et al. (2016)
50	14	<0.5–0.339	India (Ganges River Basin)	Sharma et al. (2019)
44	138	<3.0–790	Singapore	Tran et al. (2014a)
33	30	<0.170–155	Korea (Buyeo-gun)	Lee et al. (2019)
33	9	ND[a]–4.9	Vietnam (Hanoi)	Watanabe et al. (2016)
Sucralose (artificial sweetener)				
100	33	46.8–2440	China (Dongjiang River Basin)	Yang et al. (2018)
100	14	0.532–24.64	India (Ganges River Basin)	Sharma et al. (2019)
60	15	ND–9.6	China (Tianjin)	Gan et al. (2013)
33	3	ND–47	Vietnam (Halong)	Watanabe et al. (2016)

(continued)

Table 1.5 (continued)

Detection freq. (%)	Sample number	Concentration range (ng/L)	Country/region	References
22	9	ND–18	Vietnam (Hanoi)	Watanabe et al. (2016)
15	26	<10–23	India (Varanasi)	Lapworth et al. (2018)
DEET (insect repellent)				
100	148	1.8–3481	Singapore	Tran et al. (2014b)
100	14	2.76–14.8	India (Ganges River Basin)	Sharma et al. (2019)
80	5	<1.00–114.92	China (Changzhou)	Jiang et al. (2019)
73	33	ND–53.8	China (Dongjiang River Basin)	Yang et al. (2018)
25	4	<10–20	Vietnam (Ho Chi Minh City)	Duong et al. (2015)
20	15	<3.6–69.7	Japan (Tokyo)	Nakada et al. (2008)
16	50	<3.0–62	Japan (Tokyo)	Kuroda et al. (2012)
15	40	<10–400	Vietnam (Hanoi)	Duong et al. (2015)

[a] *ND* not detected

1.4.2 Other Pharmaceuticals

Acetaminophen, caffeine, carbamazepine, crotamiton, diclofenac, and ibuprofen are the most studied PPCPs in Asian groundwater (Table 1.4). Acetaminophen, diclofenac, and ibuprofen are anti-inflammatory and analgesic pharmaceuticals (AIAPs), a pharmaceutical class with very wide usage. They typically occur in wastewater at high concentrations (e.g., in Asia, 4500–86,800 ng/L for acetaminophen in influents in India; Balakrishna et al. 2017). In groundwater, their concentrations are mostly below 100 ng/L or even below 10 ng/L, except in a few studies (e.g., 4689 ng/L for acetaminophen in Singapore; Tran et al. 2014b). The relatively low concentrations of AIAPs in groundwater compared to wastewater, despite their low sorptive nature, would be partly due to their relatively high biodegradability (Aydin et al. 2019).

Caffeine is a stimulant, but also categorized as a ‘lifestyle product’ and used as an ingredient in various beverages and food products. Carbamazepine is an anticonvulsant or anti-epileptic, for controlling seizures. The two are among the most investigated pharmaceuticals in aquatic environments. In 2013, the global consumption of caffeine was almost 1 million tons, and this number has been increasing at a rate greater than that of population growth (Quadra et al. 2020). Consequently, the caffeine levels in raw wastewater reach tens of a microgram per liter in many parts of the world (Quadra et al. 2020). In contrast, the detection frequency of caffeine in groundwater varies considerably (3–100%), with varying maximum concentrations (15–16,249 ng/L). This variable occurrence of caffeine in groundwater would be partly due to its lability to biodegradation (Buerge et al. 2003). In comparison, carbamazepine is known to be highly resistant to biodegradation (Clara et al. 2004; Tran et al. 2019). Therefore, despite being far less consumed (e.g., estimated at 1014 tons per year; Zhang et al. 2008) and far less abundant in Asian wastewater (e.g., tens to hundreds of ng/L; Tran et al. 2014b) than caffeine, carbamazepine has been detected as ubiquitously as caffeine, with a maximum concentration of 117 ng/L (Tokyo, Japan; Nakada et al. 2008).

Among the Asian countries, crotamiton, an antipruritic (anti-itching) pharmaceutical for treating scabies, has been detected at high concentrations (up to 1400 ng/L) only in Japanese groundwater. This would likely be due to its high consumption in Japan, as it is abundant in Japanese raw wastewater (median 921 ng/L; Nakada et al. 2006) compared to the raw wastewater in other countries (e.g., median 34.6 ng/L in Singapore; Tran et al. 2014b and 60 ng/L in Switzerland; Kahle et al. 2009). Crotamiton shows high persistence during biological wastewater treatment processes (Nakada et al. 2006), but appears to be less persistent than carbamazepine over a long residence time in groundwater (Kuroda et al. 2012).

The concentrations of these PPCPs in Asian groundwater are comparable to or lower than in North America and Europe (Jurado et al. 2012; Kahle et al. 2009; Lapworth et al. 2012; Postigo and Barceló 2015; Sui et al. 2015).

1.4.3 Artificial Sweeteners and DEET

ASs are ubiquitous in Asian groundwater. In many studies, the detection frequencies of acesulfame, cyclamate, and sucralose were more than 50%, and the maximum concentrations more than 100 ng/L (Table 1.5). In comparison, the abundance of individual ASs varied widely among the studies and countries. For example, in China, acesulfame and sucralose had a greater concentration range than cyclamate and saccharin, in groundwater from the Dongjiang River Basin (Yang et al. 2018), but in Tianjin, cyclamate and saccharin were more abundant than sucralose and acesulfame (Gan et al. 2013). In Singapore, acesulfame, cyclamate, and saccharin showed similar detection frequency (35.9–43.8%) and concentration range (mean: 39–65 ng/L), but sucralose was not detected. The maximum concentrations of ASs in Asian groundwater ranged from 790 ng/L for cyclamate (Singapore; Tran et al. 2014a) to 4580 ng/L for acesulfame (China; Yang et al. 2018). These AS concentrations were comparable or slightly less than in groundwater in North America (Buerge et al. 2009; Engelhardt et al. 2011) or Europe (Van Stempvoort et al. 2011; Van Stempvoort et al. 2013).

The above-mentioned differences in ASs concentrations among the studies would reflect the difference in sources, usage, consumption rate, and environmental attenuation of the respective ASs. Many studies have suggested that wastewater is a major source of ASs in surface water and groundwater (e.g., Lange et al. 2012; Oppenheimer et al. 2011; Tran et al. 2014a). In Singapore, wastewater from residential and commercial areas showed significantly higher AS concentrations than hospital and industrial wastewaters (Tran et al. 2014a). Some ASs are added to livestock feed (e.g., NHDC, sucralose, and saccharin in China; Gan et al. 2013), and sulfonylurea herbicides are known to generate saccharin upon degradation in soil (Buerge et al. 2011). Therefore, pig manure and sulfonylurea herbicides used in upstream farmlands may be a source of saccharin in the Tianjin groundwater (Gan et al. 2013). ASs can also be present at fairly high concentrations in precipitation (e.g., up to 0.16 μg/L for acesulfame and up to 0.91 μg/L for cyclamate; Gan et al. 2013), and precipitation is inferred to be an important source of saccharin and cyclamate in the surface waters in Tianjin (Gan et al. 2013). In terms of biodegradation, it has been reported that acesulfame is the most persistent AS, followed by sucralose, saccharin, and cyclamate, in biological treatment and soil–water systems (Buerge et al. 2009, 2011).

Diethyltoluamide (DEET) is the most commonly used active ingredient in insect repellents. Nearly all insect repellents sold to consumers are applied as lotions, solids, or sprays (Aronson et al. 2012; Merel and Snyder 2016; Weeks et al. 2012), and DEET that has been applied to skin or clothing may volatilize to a small degree, be absorbed dermally, or be washed off into wastewater. Meanwhile, some fraction of DEET will enter the air, and some overspray may enter the soil and groundwater.

As shown in Table 1.5, the occurrence and concentrations of DEET in Asian groundwater varied among the studies. Singapore had the highest detection rate (100%) and maximum concentration (3481 ng/L; Tran et al. 2014b). This may be because of the high consumption of DEET in this tropical country; DEET concentrations in surface waters and wastewater tend to be highest during the summer months (Dumouchelle 2005; Hinkle et al. 2005). In Singapore, DEET was abundant not only in groundwater from sewered catchments, but also in background groundwater taken from a catchment with no known wastewater sources, possibly because of outside use of DEET (Tran et al. 2014b). The concentration ranges of DEET in Asian groundwater are similar to those in groundwater from North America and Europe (Merel and Snyder 2016).

1.5 Sources, Pathways, and Fates of PPCPs and ASs in Asian Groundwater

The sources of groundwater pollution can be categorized into point sources and non-point (diffuse) sources. Pollution by point sources refers to contamination by spatially discrete sources, such as effluents from industrial plants and hospitals, or discharge from WWTPs, landfills, and septic tanks. In comparison, non-point sources tend to stretch over a broad geological region, making it difficult even to define, let alone identify, hotspots, but instead demanding a focus on areas. Examples include agricultural activities involving fertilizer use, manure, sludge, leakage from sewerage systems, and stormwater runoff. Groundwater recharge sources, such as irrigation or artificial groundwater recharge practices, can also be sources of contaminants. In areas without sewage collection or treatment systems, discharge of domestic wastewater to nearby waterways (rivers, streams, canals, ponds, and lakes) is often a major pathway of wastewater-derived contaminants into groundwater.

The main potential sources and pathways of PPCPs and ASs in Asian groundwater in the reviewed papers are summarized in Table 1.6.

Table 1.6 Main potential sources and pathways of PPCPs and ASs in Asian groundwater

Sources and pathways	Country/region	References
Infiltration of contaminated surface waters (e.g., rivers, lakes, and canals)	China (Shahu County)	Tong et al. (2014)
	China (Shahu County)	Yao et al. (2017)
	India (Patancheru)	Fick et al. (2009)
	India (Varanasi)	Lapworth et al. (2018)
	India (Ganges River Basin)	Sharma et al. (2019)
	Vietnam (Hanoi)	Kuroda et al. (2015)
	Vietnam (Hanoi and Ho Chi Minh City)	Duong et al. (2015)
Leakage from sewerage system	Japan (Tokyo)	Nakada et al. (2006)
	Japan (Tokyo)	Kuroda et al. (2012)
	Japan (Tokyo)	This study
	Korea (Buyeo-gun)	Lee et al. (2019)
	Singapore	Tran et al. (2014a)
	Singapore	Tran et al. (2014b)
Leakage from septic tank	China (Guanzhou)	Peng et al. (2014)
	Vietnam (Hanoi and Halong)	Watanabe et al. (2016)
Direct discharge of untreated wastewater	China (Beijing and Tianjin)	Kong et al. (2016)
	China (Changzhou)	Jiang et al. (2019)
Irrigation by sewage/sludge application	China (Tianjin)	Gan et al. (2013)
Infiltration of reclaimed water	China (12 cities from northern China)	Li et al. (2015)

In the case of studies where more than two potential sources and pathways were suggested, those that were most representative, based on the study information, were selected

Infiltration of contaminated surface waters was found to be a major source and pathway of PPCPs and ASs in groundwater in Asia, as reported in China, India, and Vietnam (Table 1.6). Rivers and lakes are typical sources of nearby groundwater, and the recharge issuing from them brings the contaminants from the surface water to the groundwater (Díaz-Cruz and Barceló 2008). In Shahu County, central China, the mean concentrations of multiple antibiotics showed a high correlation between surface water and groundwater, indicating possible surface water–groundwater interaction (Tong et al. 2014). In Vietnam, untreated wastewater is often disposed into nearby ponds and streams in suburban and rural areas; while, in urban areas, untreated wastewater and effluents from septic tanks are transported by canals. These ponds and canals have been suggested to be a source of PPCPs in the groundwater in Hanoi and Ho Chi Minh City (Duong et al. 2015; Kuroda et al. 2015).

Another major source and pathway of PPCPs and ASs is leakage from sewerage systems, as reported in the urban and residential areas of Japan, Korea, and Singapore (Table 1.6). In Tokyo, based on calculations using carbamazepine as a marker of sewage, 0.8–1.7% of the dry weather flow of sewage was estimated to exfiltrate into the unconfined aquifers (Kuroda et al. 2012).

There are multiple other sources and pathways of PPCPs and ASs in Asian groundwater, such as leakage from septic tanks and direct discharge of untreated wastewater (Table 1.6). Identifying the sources and pathways of groundwater pollution is often difficult because of insufficient available information; thus, multiple sources and pathways are often considered. For example, in the Ganges River Basin, where infiltration of the river water through bank infiltration or irrigation is considered as the main source of PPCPs and ASs in groundwater, other possible sources might include leakage from septic tanks (or unpaved septic tanks) and leaching from landfills, flaws in sewage disposal practices, and stormwater runoff filtration via unpaved drainage systems (Sharma et al. 2019).

Once PPCPs and ASs enter into the subsurface, they undergo various processes that affect their fate, such as volatilization, adsorption to soil organics, and biodegradation. Groundwater residence time, redox conditions, and total loading are also important factors in determining the presence and persistence of PPCPs and ASs in the subsurface and groundwater (Lapworth et al. 2012). It is widely known that the biological activity which degrades organic pollutants is higher in the soil zone than in the groundwater, where the bacterial population is less abundant and diverse (Alvarez and Illman 2005). Moreover, microbial degradation of organic pollutants generally prefers aerobic to anaerobic conditions (Watanabe et al. 2010). Several persistent PPCPs and ASs, such as carbamazepine, sulfamethoxazole, and sucralose, can remain in groundwater for long periods and reach into deep confined aquifers (Kuroda et al. 2012; Lapworth et al. 2018; Tong et al. 2014). Intense exploitation of groundwater may play a role in this deep migration of anthropogenic contaminants; excessive pumping, for example, has been common in many Asian cities, and in some cases has even changed the groundwater flow and recharge regimes (Haque et al. 2013). In Hanoi, Vietnam, excessive pumping has reportedly led to elevated levels of arsenic in deep aquifers (Kuroda et al. 2017b; Winkel et al. 2011), suggesting vulnerability in the deep aquifers of Asian cities.

1.6 Utility of PPCPs and ASs as Anthropogenic Markers/Tracers

PPCPs and ASs have been utilized as markers and tracers of specific sources, to characterize local hydrogeology and groundwater pollution in detail (Kuroda et al. 2012; Lapworth et al. 2012; McCance et al. 2018; Stuart et al. 2014; Van Stempvoort et al. 2011). Many Asian studies have suggested various PPCPs and ASs as suitable markers/tracers in groundwater (Kuroda et al. 2012; Lapworth et al. 2018; Lee et al. 2019; Nakada et al. 2008; Sharma et al. 2019; Tran et al. 2014a, b; Watanabe et al. 2016; Yang et al. 2018). However, the appropriate markers appear to differ with the specific country and study site, likely reflecting varying usage and environmental fate. Carbamazepine, crotamiton, and caffeine, for example, have been suggested as sewage markers in the groundwater in Japan (Kuroda et al. 2012; Nakada et al. 2008); whereas, in Singapore, crotamiton was rarely detected, and caffeine was frequently detected in background groundwater with no known wastewater sources in the catchment. Alternatively, acetaminophen, carbamazepine, and salicylic acid were suggested as suitable PPCP markers of raw wastewater in the groundwater in Singapore (Tran et al. 2014b). In Korea, carbofuran, sulfathiazole, sulfamethoxazole, and oxfendazole were proposed as indicators of potential groundwater contamination from agricultural activities (Lee et al. 2019). In the Ganges River Basin, India, ketoprofen, DEET, and caffeine have been suggested as markers of wastewater in surface and groundwater (Sharma et al. 2019). With regard to ASs, acesulfame is commonly suggested as a persistent marker of wastewater, as it occurs ubiquitously in China (Yang et al. 2018), Korea (Lee et al. 2019), Singapore (Tran et al. 2014a), and Vietnam (Watanabe et al. 2016). Likewise, sucralose is suggested as a similar marker in India (Sharma et al. 2019) and China (Yang et al. 2018) and was utilized to detect trace river water infiltration into deep aquifers in the Ganges River Basin (Lapworth et al. 2018). Cyclamate and saccharin have also been ubiquitously detected in Singapore (Tran et al. 2014a) and China (Yang et al. 2018). The identification of different markers for the respective sources in different regions would require further investigation.

1.7 Risk Assessment for Human Health and Aquatic Organisms

Assessments of the risk from PPCPs and ASs in groundwater, to human health and aquatic organisms, have been performed in China (Jiang et al. 2019; Li et al. 2015; Peng et al. 2014; Xiang et al. 2018; Yao et al. 2017) and India (Fick et al. 2009; Sharma et al. 2019). In many studies, the risk is evaluated by calculating the risk quotient (RQ), which is the ratio of environmental concentration to PNEC (predicted no effect concentration). The risk is classified into three levels: RQ 0.01–0.1, low risk; RQ 0.1–1, medium risk; and RQ > 1, high risk (Hernando et al. 2006). The study results showed that there was no considerable risk to human health, as the RQs of the selected individual compounds were generally below 0.01 (Jiang et al. 2019; Sharma et al. 2019). An exceptional case was groundwater in Patancheru, India, where very high concentrations of antibiotics (e.g., up to 14 μg/L for ciprofloxacin), presumably resulting from insufficiently treated industrial effluents, may induce the development of antibiotic-resistant bacteria (Fick et al. 2009). A subsequent study of quinolone resistance (*qnr*) genes in the region (Rutgersson et al. 2014) showed no apparent correlation between the *qnr* genes in villager fecal samples and the fluoroquinolone antibiotic concentration in the groundwater. Nevertheless, *qnr* genes were prevalent in the fecal samples of residents from all investigated Indian villages, apparently reflecting the broad usage of fluoroquinolone antibiotics in that country. With regard to the ecological risk, on the other hand, compounds such as caffeine, triclocarban, triclosan, and several antibiotics (e.g., sulfamethoxazole) can pose a medium to high risk to sensitive species such as algae (Fick et al. 2009; Peng et al. 2014; Sharma et al. 2019; Yao et al. 2017).

1.8 Concluding Remarks and Future Challenges

This chapter provided a comprehensive review of the occurrence, sources, and fate of PPCPs and ASs in Asian groundwater. The review consisted of 23 studies from six countries (China, India, Japan, Korea, Singapore, and Vietnam). The concluding remarks and future challenges may be summarized as follows.

1. The number of studies on PPCPs and ASs in Asian groundwater has been rapidly increasing over the last few years. Nevertheless, the number and diversity of the studied countries remain low and have not significantly increased. For example, the publications since 2017 are on China (4), India (2), Korea (1), and Japan (this chapter), with Korea being the only new country represented. Moreover, there have been no studies on Southeast Asia (except for Vietnam) or Middle Eastern Asia. Asia consists of more than 50 countries, with great diversity in its geographic, socio-economic, and environmental conditions. As groundwater is a major source of drinking water in many Asian regions, more studies are needed on the occurrence and sources of PPCPs and ASs, and on their potential risks, in many different countries and regions.
2. The surveyed groundwater was mostly taken from shallow wells (typically < 30 mbgl). While, in many studies, shallow groundwater was most vulnerable to pollution by PPCPs and ASs, deep groundwater was also contaminated to some extent in a few countries, partly due to excessive pumping of deep wells (Kuroda et al. 2012; Lapworth et al. 2012). Since hydrogeological heterogeneity is often prominent in young Asian sedimentary aquifers, future studies could focus more on the occurrence of PPCPs and ASs in deep aquifers in various hydrogeological settings, which will facilitate better understanding of local hydrology and aquifer vulnerability. Determination of suitable groundwater markers and tracers in each

region is also important, and future studies should provide more detailed information on the local aquifers (e.g., geology, recharge, flow direction, residence time) and sampling wells (e.g., depth, usage). This latter information was not available in almost half the studies reviewed here.

3. While a diverse variety of PPCPs and ASs in Asian groundwater have been studied, their transformation products have received little attention, though transformation products and human metabolites have been generally gaining increasing attention in recent years. In biological processes such as wastewater treatment, the removal of a compound often simply involves transformation of the compound, and the transformation products can be more recalcitrant or toxic than the parent compounds (Postigo and Barceló 2015). The occurrence and fate of transformation products of various CECs in groundwater have been studied in North America and Europe (Postigo and Barceló 2015), but rarely in Asia (Xiang et al. 2018), suggesting future opportunities for research.
4. In many studies, the groundwater survey is a one-time event; however, temporal change in PPCPs and ASs in groundwater is an important factor, as in the case of the Tokyo groundwater discussed in this chapter. As groundwater has a long residence time, groundwater contaminants often reflect past pollution conditions. For example, while groundwater is generally less contaminated by CECs than nearby river waters, several CECs can be present in groundwater at higher concentrations than in river waters, as in the case of some persistent industrial compounds which have been banned but remain in the groundwater as a legacy (Jurado et al. 2012). Therefore, continuous efforts should be made to monitor groundwater quality, for the sake of the human and environmental future.

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Chapter 2
Affinity-Based Methods for the Analysis of Emerging Contaminants in Wastewater and Related Samples

Sazia Iftekhar, Susan T. Ovbude, and David S. Hage

Symbols and Abbreviations

Ab	Antibody
Ag	Antigen
AGP	α_1-Acid glycoprotein
BSA	Bovine serum albumin
CBH I	Cellobiohydrolase I
CSP	Chiral stationary phase
DLLME	Dispersive liquid–liquid micro extraction
ELISA	Enzyme-linked immunosorbent assay
GC	Gas chromatography
GC-MS	Gas chromatography coupled to mass spectrometry
HPLC	High-performance liquid chromatography
IAC	Immunoaffinity chromatography
IgG	Immunoglobulin G
K_a	Association equilibrium constant
k_a	Second-order association rate constant
k_d	First-order dissociation rate constant
LC	Liquid chromatography
LC-MS	Liquid chromatography coupled to mass spectrometry
LC-MS/MS	Liquid chromatography coupled to tandem mass spectrometry
LLE	Liquid–liquid extraction
MIP	Molecularly imprinted polymer
MMIP	Magnetic molecularly imprinted polymer
MRM	Multiple reaction monitoring
RPLC	Reversed-phase liquid chromatography

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SELEX	Systemic evolution of ligands by exponential enrichment
SPE	Solid-phase extraction
SPME	Solid-phase microextraction

2.1 Introduction

Wastewater and water pollution has emerged as a global problem as a result of the increased contamination of environmental water and its sources (Kolpin et al. 2002; Matamoros et al. 2012; García-Córcoles et al. 2019; Kumar et al. 2019a, b). Emerging man-made contaminants that may be present in wastewater and water in the environment range from pharmaceuticals and personal care products to steroids and pesticides or herbicides (Kolpin et al. 2002; Nelson and Hage 2006; Matamoros et al. 2012; García-Córcoles et al. 2019). In some cases, these contaminants occur at trace or ultra-trace levels in water samples and may be present along with interfering compounds. Such factors can make it challenging to analyze these contaminants by current analytical techniques (Nelson and Hage 2006; Huang et al. 2015; García-Córcoles et al. 2019; Singh et al. 2019).

A variety of approaches for sample pretreatment have been employed to analyze emerging contaminants in wastewater and environmental water samples (García-Córcoles et al. 2019). In liquid–liquid extraction (LLE), the target analyte is transferred from an aqueous sample to an organic liquid phase based on the different solubilities exhibited by these two liquid phases for the target. This method is well-established but is laborious and often requires a large volume of organic solvent (Wu et al. 2010; García-Córcoles et al. 2019, Deka et al. 2015). Solid-phase extraction (SPE) is the most widely used pretreatment method for environmental testing (Batt et al. 2008; Wu et al. 2010; García-Córcoles et al. 2019). In this approach, the sample is introduced into an SPE cartridge containing a solid sorbent, which is then washed with solvents to remove interfering compounds and elute the desired target agent for analysis. However, SPE is still susceptible to interferences and requires moderate amounts of organic solvents (García-Córcoles et al. 2019). Solid-phase microextraction (SPME) is a variation of SPE that uses a fiber that contains an extracting phase for compound isolation and introduction into a system for analysis by methods such as gas chromatography (GC) or liquid chromatography (LC) (Lord and Pawliszyn 2000; Piri-Moghadam et al. 2016). SPME requires less solvent than SPE but is more expensive and its extraction devices can be fragile (Lord and Pawliszyn 2000; Wu et al. 2010). Dispersive liquid–liquid microextraction (DLLME) is a method based on the dispersion of droplets of a liquid extractant within an aqueous sample (García-Córcoles et al. 2019). This can result in rapid extraction; however, DLLME does require a dispersive solvent and can be difficult to automate (García-Córcoles et al. 2019).

Many analytical methods have also been used to examine emerging contaminants in environmental water samples (García-Córcoles et al. 2019; Kumari et al.

2017). Common examples are GC or GC coupled with mass spectrometry (GC-MS), high-performance liquid chromatography (HPLC or LC), which is often used in combination with MS (LC-MS) or tandem MS (LC-MS/MS), and enzyme-linked immunosorbent assays (ELISAs) (Nelson and Hage 2006; García-Córcoles et al. 2019). GC and GC-MS are most readily applied for the analysis of volatile compounds and can provide low detection limits for such analytes, but derivatization or other pretreatment steps may be required to extend these methods to more polar targets (Fatta et al. 2007; Comerton et al. 2009; García-Córcoles et al. 2019). LC, LC-MS, and LC-MS/MS are often employed for the separation and analysis of polar or thermally labile compounds in water (García-Córcoles et al. 2019). LC-

LC-MS/MS has been of particular interest for this work and can lead to the analysis of trace organic contaminants in water at low levels (Comerton et al. 2009; García-Córcoles et al. 2019; Kumar 2016). However, sample pretreatment is still often needed in LC-MS/MS to minimize matrix effects and to provide suitable selectivity and detection limits (Comerton et al. 2009). ELISAs employ antibodies and enzyme labels and can be used as a cost-effective means for the rapid detection of specific emerging contaminants, such as antibiotics or pesticides (Aga and Thurman 1997). Some limitations of ELISAs are that they do require antibodies that can bind to the given target and they are mainly used in a manual format, which is most commonly employed in screening assays (Aga and Thurman 1997; Nelson and Hage 2006; Nicolardi et al. 2012).

Affinity chromatography is an alternative approach that has been used with emerging contaminants for both sample pretreatment and analysis in environmental testing (Nelson and Hage 2006). Affinity chromatography and high-performance affinity chromatography (HPAC) are liquid chromatographic methods that employ a biological-related binding agent, known as the affinity ligand, that is immobilized onto a solid support and used as a stationary phase (Hage 2006). Figure 2.1 shows a typical separation scheme that is used in affinity chromatography. The target analyte and sample are first introduced onto the affinity column in the presence of an application buffer. The analyte is often strongly retained under these conditions, which have been selected to mimic the natural binding conditions of the analyte and immobilized agent. Other sample components, which are non-complementary to the immobilized binding agent, tend to elute under the same conditions as a non-retained peak. After elution of these non-retained components, the retained analyte is then released by passing through the column and support an elution buffer that causes release of the retained analyte, such as by changing the pH of the mobile phase or by adding a competing agent. The analyte is then measured as it elutes from the column or is collected for use in a separate analysis method. The original application buffer is then reapplied to the system. The column and support are allowed at that time to regenerate prior to the next sample injection (Hage 2006; Hage et al. 2012; Zheng et al. 2014; Zhang et al. 2018).

There are many types of binding agents and formats that can be used in affinity chromatography. For instance, the binding agent that is used in affinity chromatography may consist of an immobilized antibody, enzyme, transport protein, or DNA/RNA sequence, among many other possibilities (Hage 2006). The immobilized

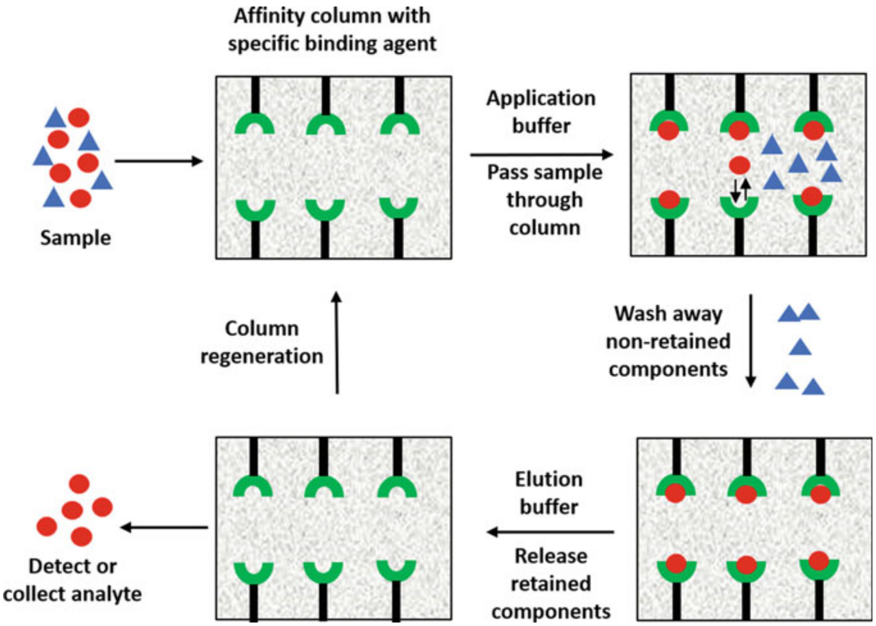

Fig. 2.1 Typical separation scheme for affinity chromatography

agent provides for strong and selective binding to the desired target and can often be reused for many samples, which results in good precision and reproducibility for an extraction or analysis. When used in an analytical method, affinity columns can be coupled to common chromatographic detectors, such as those used for absorbance and fluorescence measurements or mass spectrometry (Hage 2006). Affinity chromatography has been utilized for sample analysis and purification for many types of targets, including those of environmental interest (Nelson and Hage 2006). This method can be used as the basis for chiral separations, flow-based immunoassays, and multidimensional methods. In addition, this technique has been utilized for characterizing the interaction rates and affinities of targets with their binding agents, including some systems of environmental interest (Hage et al. 2012; Zheng et al. 2014; Zhang et al. 2018; Shim et al. 2019).

This chapter will examine how affinity chromatography and related methods such as affinity extraction have been employed in the pretreatment and analysis of emerging contaminants in wastewater and related samples. Applications that will be considered will include those in which the affinity ligand is an antibody, molecularly imprinted polymer, or chiral stationary phase (Nelson and Hage 2006; Huang et al. 2015; Teixeira et al. 2019). Various formats in which these affinity ligands have been employed will also be discussed. These formats will include off-line and online extraction methods, chromatographic immunoassays, chiral separations, and multidimensional methods based on techniques such as GC, LC or LC-MS, and LC-MS/MS.

2.2 Affinity Methods Using Antibodies

2.2.1 *General Principles of Antibody-Based Affinity Separations*

Immunoaffinity chromatography (IAC) refers to an affinity chromatographic technique that employs antibodies as binding agents for the selective extraction or detection of target analytes (Hage and Phillips 2006; Nelson and Hage 2006; Zhang et al. 2018). Antibodies are glycoproteins that are generated by the body in response to a foreign agent, or antigen, such as a virus or bacterial cell. A typical antibody, as represented by immunoglobulin G (IgG) in Fig. 2.2, has a Y-shaped structure. The portion of this structure known as the F_c region is located in the lower stem of the Y and is highly conserved from one type of antibody to the next one. The structure of IgG also contains two F_{ab} regions that have identical antigen-binding sites and that are located in the upper arms of an antibody (Hage and Phillips 2006; Nelson and Hage 2006; Zhang et al. 2018).

The interaction of antibody (Ab) with its binding target or antigen (Ag) can be described by the following reaction and equations (Hage and Phillips 2006).

$$\mathrm{Ab} + \mathrm{Ag} \leftrightarrow \mathrm{Ab} - \mathrm{Ag} \tag{2.1}$$

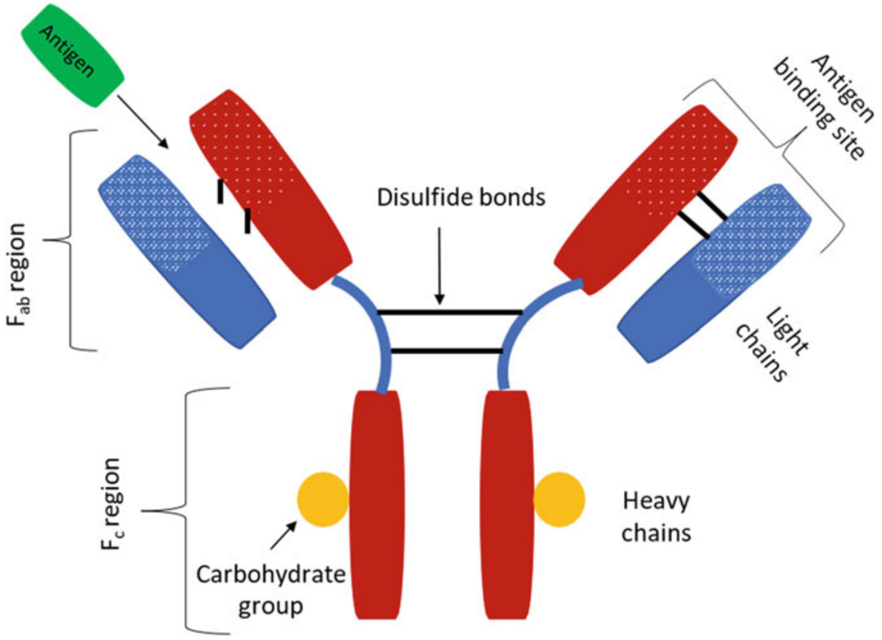

Fig. 2.2 General structure of an antibody using immunoglobulin G (IgG) as an example

$$K_a = \frac{k_a}{k_d} \tag{2.2}$$

$$K_a = \frac{[\mathrm{Ab} - \mathrm{Ag}]}{[\mathrm{Ab}][\mathrm{Ag}]} \tag{2.3}$$

In these equations, K_a is the association equilibrium constant for the reversible binding of Ab with Ag. The antibody–antigen complex that is formed by this process is represented by Ab–Ag, and the square brackets "[ ]" in Eq. (2.2) represent the molar concentrations of the reactants and product of this interaction. The term k_a is the second-order association rate constant for the binding of Ab with Ag, and k_d is the first-order dissociation rate constant for the resulting complex (Hage 1998; Hage and Phillips 2006). The interactions that occur in Eq. (2.1) between the antibody and antigen involve ionic interactions, hydrogen bonding, hydrophobic interactions, and/or van der Waals forces. The combination and arrangement of these interactions can result in strong and selective binding between an antibody and its target (Hage and Phillips 2006).

The two most common types of antibodies used for IAC and environmental analysis are monoclonal antibodies and polyclonal antibodies (Hage and Phillips 2006). Polyclonal antibodies are produced by immunizing animals such as mice and rabbits with purified antigens. This results in many types of antibodies being produced by various cells of the animal's immune system (i.e., a polyclonal preparation). Monoclonal antibodies are produced through the fusion of antibody-producing cells from the immunized animals with myeloma cells to create hybrid cells (known as hybridomas) that can each produce a single type of antibody with a well-defined binding strength and specificity. These antibodies can then be immobilized, labeled, or used in various formats as binding agents for the capture or analysis of their given targets (Hage and Phillips 2006).

2.2.2 *Off-Line Immunoextraction*

Affinity extraction makes use of a binding agent such as an antibody for the concentration or isolation of an analyte prior to detection of this target by another method. The employment of immobilized antibodies in this format is known as immunoextraction (Hage 1998). Immunoextraction can be coupled to various methods that include both GC and LC, with the later often making use of reversed-phase LC (RPLC) analytical columns (Hage 1998; Nelson and Hage 2006). Immunoextraction can be coupled to these methods in either online or off-line modes. Advantages of immunoextraction compared to traditional SPE include the higher selectivity and reduced interferences that can be obtained by antibody-based extraction when working with trace analytes and complex matrices (Hage 1998; Nelson and Hage 2006). In off-line immunoextraction, antibodies against the target analyte are typically immobilized onto a low-performance support such as activated agarose. This support is contained within an SPE cartridge or disposable syringe (Hage 1998). This support is then used in a sample application and elution scheme like the one shown in Fig. 2.1 to capture and concentrate the desired target and to wash away non-bound sample components. The target analyte is then collected by passing an elution buffer through the support (Ferguson et al. 2001; Nelson and Hage 2006; Qiao et al. 2009; Ryu et al. 2015; Laranjeiro et al. 2018). This target can be used directly or placed into an alternative solvent for analysis by LC, GC, MS, or capillary electrophoresis (Hage 1998; Hage and Nelson 2001). This technique avoids the laborious extraction and derivatization steps that are often needed in trace analysis with more traditional sample pretreatment methods. Off-line immunoextraction does typically require manual steps for sample handling and solution transfer, which can limit the precision and accuracy of this method. In addition, some off-line immunoextraction techniques, such as those used with GC, may require solvent evaporation and target resuspension in an organic solvent, thereby increasing the cost and overall analysis time (Ferguson et al. 2001; Nelson and Hage 2006; Qiao et al. 2009; Ryu et al. 2015; Laranjeiro et al. 2018).

A number of reports have described the use of off-line immunoextraction with RPLC for environmental analysis (Hage and Nelson 2001). For example, this combination has been used to determine 17β-estradiol, estrone, and 17α-ethynylestradiol in wastewater (Ferguson et al. 2001). In this approach, monoclonal antibodies that could specifically bind 17β-estradiol or estrone were immobilized to controlled-pore glass beads. Samples of wastewater effluent were filtered and spiked with deuterium-labeled estrogens. The estrogens in these samples were extracted by using commercial supports in a layered-bed SPE system that contained both an ethylvinylbenzene-divinylbenzene polymer and a C18 adsorbent. The extracts were collected, evaporated to dryness, and resuspended in a solution of 5% methanol in water. The resuspended extracts were then passed through the immunosorbent and eluted with 70% methanol in water. The recovery was greater than 90% for both 17β-estradiol and estrone. Separation of estrogens in the eluted fraction was carried out on an analytical RPLC column, and these compounds were detected by MS using selected ion monitoring and electrospray ionization (ESI). Figure 2.3 shows some chromatograms that were obtained with and without the use of immunoextraction for wastewater effluents from sewage plants. The chromatograms generated when using off-line immunoextraction resulted in well-defined peaks for each of the target steroids, with detection limits for these analytes in the low ng L^{-1} range (Ferguson et al. 2001).

Several other reports have utilized off-line immunoextraction for the analysis of trace contaminants in wastewater and related samples. One study used this method to measure levonorgestrel (Qiao et al. 2009) by employing polyclonal antibodies for this analyte that were immobilized to activated Sepharose. Levonorgestrel was measured at levels in the ng L^{-1} range in wastewater (Qiao et al. 2009). Immunoextraction followed by LC-MS/MS has been used to measure zearalenone in surface waters that were collected upstream from a water treatment plant (Laranjeiro et al. 2018). This work used a commercial wide bore immunoaffinity column that contained monoclonal antibodies specific for this mycotoxin. This immunosorbent was combined with a C18 RPLC column and LC-MS/MS to detect zearalenone in the low-to-mid ng L^{-1} range (Laranjeiro et al. 2018).

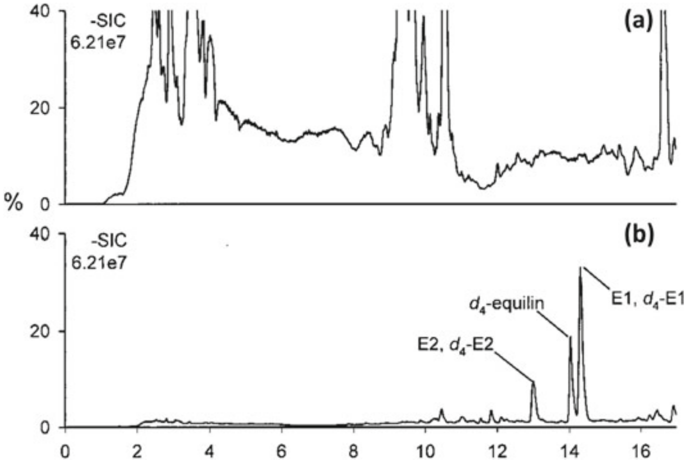

Fig. 2.3 Summed-ion chromatograms for the analysis of wastewater effluents from sewage plants by RPLC and electrospray-ionization mass spectrometry both without (**a**) and with (**b**) sample pretreatment based on immunoextraction. The peaks labeled E1 and E2 represent estrone and 17β-estradiol, respectively, which were passed into the immunoextraction support along with their deuterated forms, d_4-E1 and d_4-E2. Equilin was used as an internal standard along with its deuterated form, d_4-equilin. Adapted with permission from Ferguson et al. (2001). Copyright 2001 American Chemical Society

Off-line immunoextraction was combined with LC and high resolution MS for the detection and analysis of 8-isoprostaglandin F2α, an oxidative stress biomarker (Ryu et al. 2015). In this work, sewage samples were spiked with an internal standard and treated to deconjugate 8-isoprostaglandin F2α glucuronide. The samples were then passed through a column containing monoclonal antibodies for 8-isoprostane that were immobilized onto Sepharose. The analytes were eluted from the immunoaffinity column and placed into a solution of 20% acetonitrile in water. This was followed by analysis using a C18 RPLC column with high-resolution ESI-MS. The detection limit for 8-isoprostaglandin F2α was 0.3 ng L^{-1}, and immunoextraction allowed for the effective removal of interfering components from the sample matrix (Ryu et al. 2015).

2.2.3 Online Immunoextraction

In online immunoextraction, a support and column containing immobilized antibodies are used to specifically extract one or more analytes and to directly transfer these retained components to a second technique for analysis (Hage 1998). The use of an online approach for immunoextraction helps to produce shorter analysis times and higher reproducibility than off-line extraction (Nelson and Hage 2006). Immunoextraction has frequently been combined online with RPLC (Thomas et al.

1994; Rollag et al. 1996; Nelson et al. 2004, 2007). A typical system for immunoextraction/RPLC, as shown in Fig. 2.4, makes use of at least three mobile phases: an application buffer and elution buffer for immunoextraction, and one or more solutions for analyte separation on a RPLC column. The sample containing the desired analyte is first introduced into the immunoextraction column in the presence of this column's application buffer. As the antibodies in this column capture and retain the desired analyte, the non-binding sample components are washed away. The immunoextraction column is then switched online with a small RPLC precolumn and an aqueous elution buffer, which often involves a decrease in pH. This elution buffer causes the analyte to dissociate from antibodies and to pass onto the RPLC precolumn, where the aqueous buffer acts as a weak mobile phase and allows the analyte band to be refocused. This small column is then switched online with a second and longer analytical RPLC column while a mobile phase that contains an organic modifier is passed through both these columns and results in a separation of the analytes based on their polarity (Thomas et al. 1994; Nelson and Hage 2006).

This type of system has been used to couple immunoextraction online with RPLC-MS/MS for the trace analysis of diuron in effluents from a wastewater treatment plant

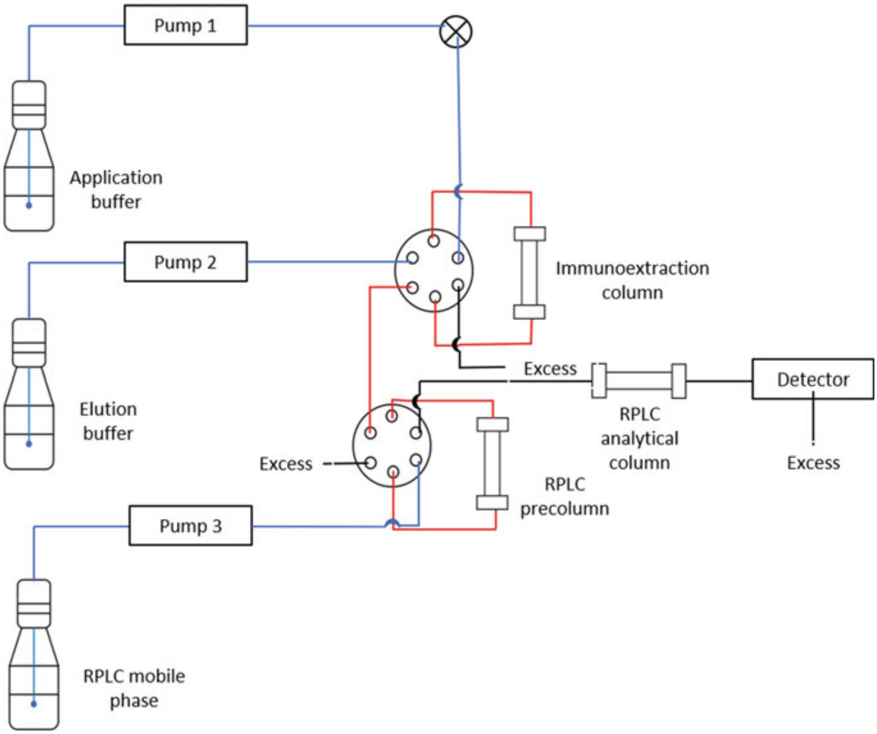

Fig. 2.4 General scheme for the online coupling of immunoextraction with RPLC. This format is based on a system described by Thomas et al. (1994)

(Zhang et al. 2006). This method was based on an immunoextraction column that utilized monoclonal antibodies against diuron that were contained in a sol-gel support. This immunoextraction support was coupled online with a reversed-phase silica monolith analytical column. This method gave a detection limit of 0.9 ng L^{-1} for diuron and a recovery for this analyte of 93% (Zhang et al. 2006). Immunoextraction can also be coupled online with GC (Hage 1998). This approach has been used for the quantification of atrazine in wastewater (Dalluge et al. 1999). Monoclonal antibodies against atrazine were immobilized onto beaded cellulose for this application. After the sample had been injected onto the antibody-containing support, the retained analytes were desorbed and passed onto a cartridge that contained a nonpolar styrene-divinylbenzene copolymer for collection of the eluting compounds. The retained compounds were later desorbed from the copolymer cartridge by using ethyl acetate and introduced onto a GC system for separation and analysis. The elution of atrazine and retained compounds was monitored by using a flame ionization detector and nitrogen phosphorous detector, which gave mass detection limits for atrazine of 120–170 pg and 15 pg, respectively (Dalluge et al. 1999).

2.2.4 Chromatographic Immunoassays

Antibodies have also been used in chromatographic systems for the binding and indirect detection of emerging contaminants in the environment. This is accomplished by using a technique which is known as a chromatographic immunoassay (Hage 1998; Nelson and Hage 2006). This type of technique is advantageous for the detection of trace analytes that are not present in sufficient quantities to be detected directly (Hage and Nelson 2001; Nelson and Hage 2006).

In a competitive binding immunoassay, the analyte and a fixed amount of a labeled analog of the analyte are allowed to compete for a limiting number of antibodies. The amount of labeled analog that is bound to the antibodies, or that remains free in solution, is then measured and used to determine the amount of analyte that was present in the sample (Hage 1998). There are a variety of formats that have been reported for conducting this type of method by chromatography (Hage et al. 1993, 1999; Hage and Nelson 2001; Nelson et al. 2003). One approach is to mix the antibodies with the sample and labeled analog and then capture the antibodies and their complexes with the analog or analyte by a column, thus separating the free and bound fractions of the labeled analog, as illustrated in Fig. 2.5. This approach has been used in a method for the analysis of β-lactam antibiotics in the effluents of sewage treatment plants (Benito-Pena et al. 2005). This approach used polyclonal antibodies prepared against 6-aminopencillanic acid (i.e., a common structural component of β-lactam antibiotics); a labeled analog that contained a fluorescent tag; and a column-containing protein A/G (i.e., an antibody-binding agent) to capture the antibodies and their immunocomplexes. Upon desorption of the antibody-bound labeled analog and analyte from the protein A/G column, the fluorescence generated

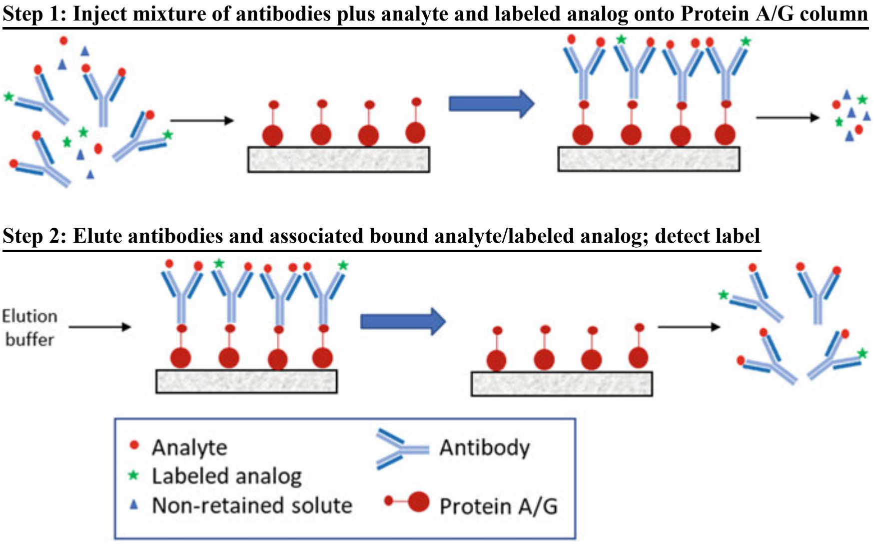

Fig. 2.5 Scheme for a competitive binding immunoassay based on the use of protein A/G column to capture the antibodies and complexes of the antibodies with the analyte and a labeled analog of the analyte. This method is based on an assay described by Benito-Pena et al. (2005)

by the labeled analog was measured and used to determine the concentration of β-lactam antibiotics in the sample. The total analysis time was 23 min per sample, and good agreement was seen for this system with a reference method (Benito-Pena et al. 2005). A similar format has been used with protein G columns, polyclonal antibodies, and labeled analogs containing long-wavelength fluorophores to measure linear alkylbenzenesulfonates in groundwater, wastewater, and sludge (Sanchez-Martinez et al. 2005, 2006).

Another type of competitive immunoassay that has been used with LC for the detection of environmental contaminants is one that has employed restricted-access media to capture and separate the unbound forms of the labeled analog and analyte from antibodies and immune complexes (see Fig. 2.6). This method has been used to screen wastewater and other types of samples for atrazine (Onnerfjord et al. 1998). In this approach, a fluorescein-labeled analog of atrazine was incubated with the sample and a small amount of anti-atrazine antibodies. This mixture was then introduced onto a restricted-access column with a support that contained a non-polar reversed-phase stationary phase within its pores but not on its exterior surface. This type of support was able to retain the labeled analog and analyte in their free forms but did not bind to the antibodies or immune complexes. The amount of atrazine in the samples was then indirectly measured by monitoring the fluorescence due to the antibody-bound labeled analog in the non-retained peak. A detection limit of 20 pg mL^{-1} was obtained for atrazine, and a throughput of 80 samples per hour was possible with this method (Onnerfjord et al. 1998).

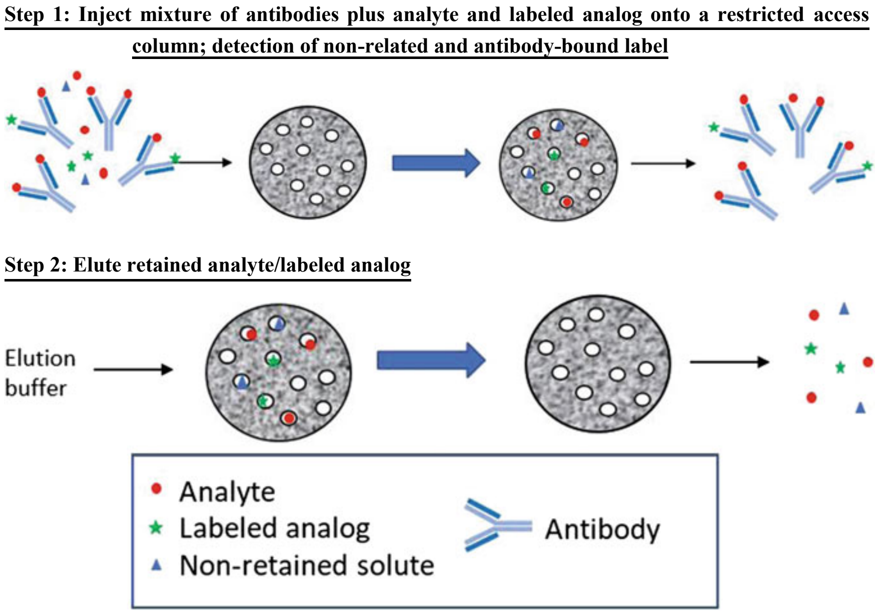

Fig. 2.6 Scheme for a competitive binding immunoassay based on the use of restricted-access media column to capture the non-bound forms of an analyte and a labeled analog in the presence of antibodies for these agents. This method is based on an assay described by Onnerfjord et al. (1998)

2.3 Affinity Methods Using Molecularly Imprinted Polymers (MIPs)

2.3.1 General Principles of MIPs

Molecularly imprinted polymers (MIPs) have also been used as affinity matrices in separations for environmental analysis. Figure 2.7 illustrates a common approach for preparing this type of support (Shen et al. 2012). MIPs are formed through the polymerization of one or more functional monomers in the presence of a template (e.g., the target analyte) and a cross-linking agent (Nelson and Hage 2006; Huang et al. 2015). The functional monomers are responsible for creating sites that bind to specific groups on the template. An initiator is present in the mixture to start the polymerization process, and a solvent is used that can create pores for later access of the analyte to the imprinted sites. After polymerization, the template and any remaining reagents are washed away, leaving behind a binding pocket that is complementary in shape to the template. This material can then be used to bind or isolate the analyte/template from samples (Nelson and Hage 2006; Huang et al. 2015).

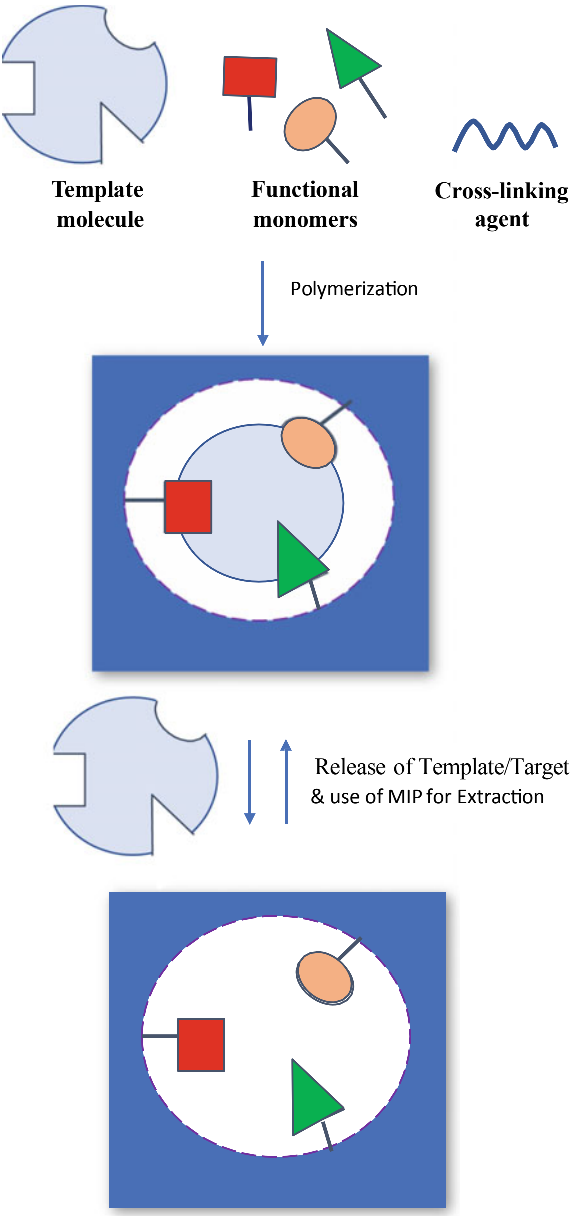

Fig. 2.7 General process for the preparation of a molecularly imprinted polymer (MIP)

There are several approaches for making a MIP based on the types of interactions that are present between the functional monomers and template (Huang et al. 2015). In the first approach, covalent bonds are formed between the template and functional monomers prior to polymerization. This results in stable interactions between the template and monomers and helps to provide homogenous binding sites in the final polymer (Martın-Esterban 2013). A limitation of this technique is that the strong interactions between the template and monomers can sometimes make removal of the template difficult (Huang et al. 2015). An alternative is to use an approach in which the functional monomers are instead allowed to bind to the template through non-covalent interactions (e.g., electrostatic forces, van der Waals forces, or hydrogen bonding) (Tamayo et al. 2007; Bergmann and Peppas 2008; Malitesta et al. 2012). This is the most common way for preparing MIPs because it is simple and can result in many interactions between the functional monomers and template. However, this method can also result in heterogeneous binding pockets and a decrease in selectivity (Huang et al. 2015). It is also possible to use a method for MIP preparation that combines covalent and non-covalent interactions (Fuchs et al. 2012; Zhan et al. 2013).

Many techniques have been employed for synthesizing MIPs with controlled physical properties and sizes. Examples of these techniques are bulk polymerization, suspension polymerization, and precipitation polymerization (Huang et al. 2015). In bulk polymerization, MIPs are prepared as monoliths by mixing the functional monomers, template, cross-linking agent, and initiator in a suitable solvent. Suspension polymerization involves polymerization of these components when they are dispersed in water and in the presence of a surfactant and stabilizer. Precipitation polymerization is used to synthesize MIP microspheres by dissolving the functional monomers, template, cross-linking agent, and initiator in a large amount of a pore-forming solvent (Huang et al. 2015).

Most MIPs are used with organic solvents because water tends to disrupt the interactions that occur between the analyte and support. However, a few reports have employed aqueous solvents with MIPs (Nelson and Hage 2006; Huang et al. 2015). MIPs possess excellent stability and good selectivity for their targets, which has made them of interest as supports for SPE, sensors, and chromatography (Nelson and Hage 2006). For instance, MIPs can serve as an alternative to immunoaffinity supports for the detection of analytes against which antibodies may be difficult to obtain (Nelson and Hage 2006; Huang et al. 2015).

2.3.2 Use of MIPs in Solid-Phase Extraction

Traditional MIPs have been used in many studies for SPE and the selective extraction of analytes from complex water matrices. For instance, MIPs have been used with wastewater to extract and detect amphetamines, antidepressants, benzimidazoles, bisphenol A, β-blockers, carbamazepine, carbaryl, catechols, cyanide, 17β-estradiol, herbicides, ketoprofen, mercury, sulfonamides, and water-soluble acidic dyes (Say et al. 2004; Tarley and Kubota 2005; Watabe et al. 2006; Liu et al. 2006; Ou et al. 2006; Beltran et al. 2007; Sambe et al. 2007; Sanchez-Barragan et al. 2007; Gros et al. 2008; Cacho et al. 2009; Gonzalez-Marino et al. 2009; Luo et al. 2011; Qin et al. 2012; Madikizela et al. 2018; Hudson et al. 2019). As noted previously, the extraction of analytes by combining MIPs with SPE makes use of forces such as electrostatic interactions, hydrophobic interactions, and hydrogen bonding between the analyte and binding pockets within the MIP (Sun and Qiao 2008; Huang et al.2015). The use of these forces for retention can be challenging in the direct presence of an aqueous sample, as water will tend to compete for many of these interactions and weaken binding between the polymer and target (Ou et al. 2006).

Another possible issue with MIPs is the presence of any remaining template in the polymer may result in leakage of this template during an extraction and loss of sensitivity for detecting the same compound in samples (Anderson et al. 1997). To overcome this problem, MIPs can instead be prepared by using a dummy template that is related to but different from the analyte (Huang et al. 2015).

This type of MIP has been prepared with silica microparticles for the extraction of bisphenol A from water samples (Zhao et al. 2010). These MIPs were made by using templates that were analogs of bisphenol A, such as 4,4-dihydroxybiphenyl and 3,3,5,5-tetrabromobisphenol A. These MIPs avoided contamination of samples by the MIP while also providing a high binding capacity and good recognition for bisphenol A (Zhao et al. 2010). A similar strategy has been employed for the analysis of bisphenol A when using SMPE (Liu et al. 2019).

Magnetic MIPs, or MMIPs have also been utilized for the extraction and analysis of emerging contaminants in aqueous samples (Ansell and Mosbach 1998; Lu et al. 2005, 2006). An advantage of using MMIPs for SPE is they can easily be collected from a solution by applying an external magnetic field. This type of material has been employed as an adsorbent for the selective extraction and detection of bisphenol A in a variety of water samples, including tap water, drinking water, and river water (Lin et al. 2012). In this approach, bisphenol F was employed as a dummy template and used in surface molecular imprinting on supramagnetic core-shell nanoparticles. The use of this material for SPE resulted in a detection limit of 2.50 pg mL^{-1} for bisphenol A in spiked water samples examined by HPLC and a recovery for bisphenol A of 84.7–93.8% (Lin et al. 2012). Other emerging contaminants that have been analyzed by using MMIPs are 4-nitrophenol and sulfonamides (Kong et al. 2012; Li-Li et al. 2013; Mehdinia et al. 2013).

2.3.3 Online Use of MIPs

Most applications of MIPs for extraction have used these materials in off-line protocols for sample pretreatment. MIPs in packed cartridges have recently been coupled online with LC for the separation and measurement of sulfathiazole in wastewater (Zazouli et al. 2017). The MIP in this example was synthesized by employing methacrylic acid as a functional monomer, sulfathiazole as the template, and ethylene glycol dimethacrylate as the cross-linking agent (Zazouli et al. 2017). A sequential injection technique was then employed. A sample-containing sulfathiazole was first loaded onto the MIP column for extraction. The isolated analyte was then passed onto a C18 RPLC column by gradient elution and monitored by absorbance detection. A recovery of 90% for sulfathiazole and a detection limit of 0.05 ng mL^{-1} was obtained (Zazouli et al. 2017). MIPs have also been coupled online with LC and absorbance detection to measure trace levels of estrones and bisphenol A in river water, lake water, and well water (Ou et al. 2006; Xu et al. 2009).

2.4 Affinity Methods Using Chiral Stationary Phases

Several other affinity ligands have been used for the separation and analysis of emerging contaminants in water samples (Nelson and Hage 2006). Many of these ligands are chiral stationary phases (CSPs) that possess the ability to interact differently with some enantiomeric compounds. Examples of chiral binding agents that have been used as stationary phases for emerging contaminants include polysaccharides, serum transport proteins, enzymes, and macrocyclic antibiotics (Teixeira et al. 2019).

2.4.1 Polysaccharide-Based Methods

Polysaccharide derivatives of amylose and cellulose can be utilized to obtain CSPs because of their chiral structures and good enantioselectivity (Ali et al. 2009). The properties of these agents that result in chiral recognition include the types of sugars and linkages that are present between the sugars, as well as the three-dimensional arrangement and structures of the sugar chains (Chen et al. 2007; Lämmerhofer 2010). Phenylcarbamates and benzoate derivatives are the most common types of polysaccharide CSPs (Chen et al. 2007; Chankvetadze 2012). For instance, 3,5-dimethylphenyl *tris*-phenylcarbamate derivatives of cellulose and amylose are often used as CSPs (Franco et al. 2001; Teixeira et al. 2019). These polysaccharide derivates can be coated by adsorption onto silica supports (Okamoto et al. 1984; Park et al. 2003) and used for separations in either normal-phase or reversed-phase modes (Lämmerhofer 2010). Alternatively, polysaccharide CSPs can be produced by covalently immobilizing a polysaccharide derivative directly onto a support (Ali and Aboul-Enein 2006, 2007).

Several types of emerging contaminants in water have been analyzed by using polysaccharide CSPs. In one study, lansoprazole, omeprazole, pantoprazole, and rabeprazole were examined in wastewater and river water by using such a phase (Zhao et al. 2016). These samples were first extracted by SPE and liquid–liquid microextraction. The contents of the extracts were then separated and analyzed by LC-MS/MS using a column that contained a 3,5-dimethylphenyl *tris*-phenylcarbamate derivate of cellulose. A recovery of 89–107% was observed for all sets of enantiomers, and detection limits of 0.67–2.29 ng L^{-1} were obtained (Zhao et al. 2016). Chiral peptides were extracted from wastewater and river water by magnetic SPE, followed by their separation and analysis using ultra-performance LC-MS/MS and a 3,5-dimethylphenyl *tris*-phenylcarbamate derivative of amylose as the stationary phase (Zhao et al. 2018). This method resulted in detection down to the low ng L^{-1} range (Zhao et al. 2018). Dummy MIPs were coated onto magnetic multi-walled carbon nanotubes and used with DLLME to extract and concentrate non-steroidal anti-inflammatory drugs such as ketoprofen, ibuprofen, and flurbiprofen from river water, wastewater, and lake water samples (Yuan et al. 2018). This was followed by the chiral separation and analysis of these drugs by using LC-MS/MS and a CSP based on an amylose derivative (Yuan et al. 2018).

2.4.2 Macrocyclic Antibiotic-Based Methods

Macrocyclic antibiotics are another class of compounds that can be used as CSPs (Ilisz et al. 2012). Glycopeptide-based macrocyclic antibiotics such as teicoplanin and vancomycin have been used in several reports for the analysis of chiral compounds and environmental samples (Ward and Farris 2001; Nikolai et al. 2006; Camacho-Muñoz and Kasprzyk-Hordern 2017). The structure of these glycopeptides is based on a central framework that is composed of a heptapeptide in which five of the seven amino acid residues are common to all members of this family (Ilisz et al. 2012). Many types of interactions are possible between an analyte and this CSP, such as π-π interactions, hydrophobic interactions, hydrogen bonding, dipole–dipole interactions, ionic interactions, and van der Waals forces (Ilisz et al. 2009). These binding agents also possess many regions that enable them to take part in chiral recognition (Teixeira et al. 2019). These CSPs are usually immobilized to silica and can be used in many common elution modes (Ilisz et al. 2012; Min et al. 2015; Ismail et al. 2016; Teixeira et al. 2019).

Vancomycin has been employed as a CSP with LC-MS/MS for analyzing the enantiomers of β-blockers such as atenolol, metoprolol, and propranolol in wastewater samples (Nikolai et al. 2006). Some typical chromatograms that were acquired by this method are shown in Fig. 2.8. Detection limits of 2–17 ng L^{-1} were observed in wastewater, and mean recoveries of 67–106% were obtained for these enantiomers (Nikolai et al. 2006). Teicoplanin has been used as a CSP in the reversed-phase mode for the separation of several drugs by ultra-performance LC-MS/MS for wastewater and surface water samples (Camacho-Muñoz and Kasprzyk-Hordern 2017). Drugs that have been examined by this approach have included chloramphenicol, ibuprofen, ifosamide, indoprofen, and some metabolites of ibuprofen (Camacho-Muñoz and Kasprzyk-Hordern 2017).

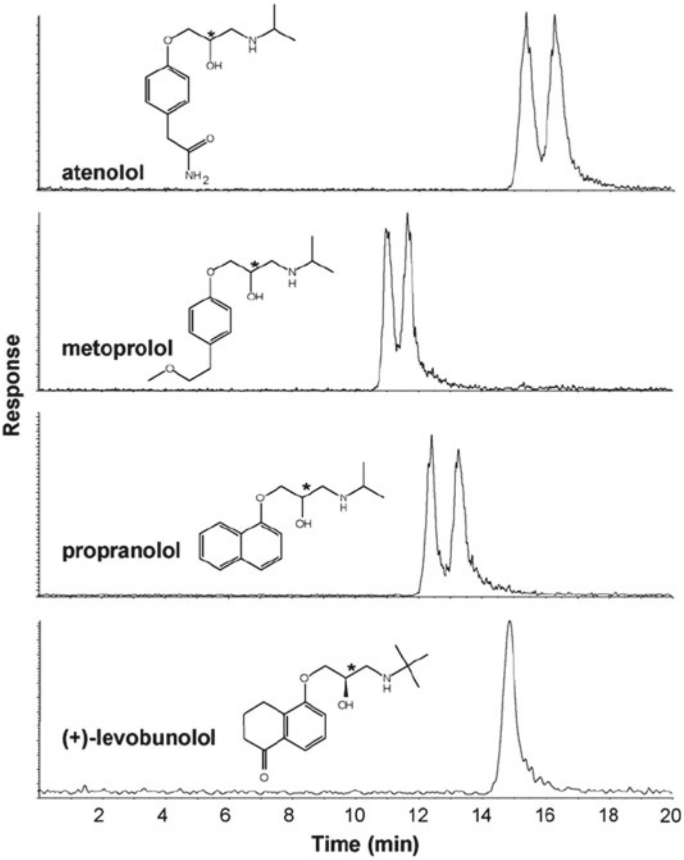

Fig. 2.8 Chromatograms obtained by multiple reaction monitoring for the separation of racemic atenolol, metoprolol, and propranolol, with (+)-levobunolol being included as an internal standard. The asterisks shown in the chemical structures represent the chiral centers. Reproduced with permission from Nikolai et al. (2006). Copyright 2006 Elsevier

2.4.3 Protein-Based Methods

Serum transport proteins such as α_1-acid glycoprotein (AGP) are known to bind many classes of drugs (Hage and Austin 2000) and can be used as CSPs (Patel et al. 2006; Barclay et al. 2012). AGP has a molecular weight of 41–43 kDa and a carbohydrate content of 45% (w/w) (Kremer et al. 1988; Fournier et al. 2000). AGP can be immobilized covalently or through adsorption and cross-linking to a support such as silica (Patel et al. 2006; Teixeira et al. 2019). AGP can then be employed for the chiral separation of many acidic, basic, and neutral drugs (Patel et al. 2006). One study examined the use of four different CSPs in work with wastewater samples. The analytes were metopropol and two of its metabolites: deaminated metoprolol and α-hydroxy metoprolol (Barclay et al. 2012). These compounds were first extracted by SPE. The chiral separation of these compounds was then investigated by LC-MS/MS using CSPs based on AGP, a cellulose derivative, vancomycin, and cellobiohydrolase I (CBH I) (Barclay et al. 2012). Complete separation of the enantiomers for metopropol and its metabolites was seen with the AGP and CBH I columns, allowing analysis in the pM to nM range for several of the analytes (Barclay et al. 2012)

CBH I, as used in the previous example (Barclay et al. 2012), is an enzyme that can also act as a CSP. CBH I has a molecular weight of 52.2 kDa and takes part in fungal cellulose degradation (Patel et al. 2006). This enzyme is composed of loops and a concave β-sandwich that forms a 40 Å-long tunnel in which the active site is located (Henriksson et al. 1996). CBH I can be covalently coupled to silica for use as a CSP (Patel et al. 2006). A CBH I column has been used with MS to separate and measure 56 drugs in wastewater after extraction by SPE (Camacho-Muñoz and Kasprzyk-Hordern 2017). These drugs included amphetamine, cocaine, heroin, opioid analgesics, anesthetics, stimulants, sedatives, and some designer drugs. A good separation was obtained for each pair of 18 enantiomers, and detection limits were acquired in the parts-per-trillion range (Camacho-Muñoz and Kasprzyk-Hordern 2017). Multi-residue analysis of chiral β-blockers, antidepressants, and amphetamines in wastewater has also been conducted by utilizing CBH I and vancomycin as CSPs with LC-MS/MS detection (Evans et al. 2015).

2.5 Potential Areas for Future Work

Besides the tools and applications that have already been mentioned, there are many other binding agents and formats for affinity chromatography and extraction that might be used in the future for the analysis of emerging contaminants in wastewater and related samples. One class of such binding agents is the aptamers. Aptamers are typically made up of single-stranded oligonucleotides with 20–100 base pairs and that can undergo relatively strong and specific interactions with target molecules (Musheev and Krylov 2006; Li et al. 2019). It is possible to generate aptamers against a given target by using a method known as the systematic evolution of ligands by exponential enrichment (or SELEX) (Musheev and Krylov 2006; Li et al. 2019). The specificity exhibited by aptamers toward their targets is due to the complex three-dimensional shapes that form in these binding agents, which may be composed of loops, stems, bulges, triplexes, hairpins, quadraplexes, and pseudoknots (Pichon et al. 2015). Aptamers have been harnessed in a number of applications, and especially in biosensors (Li et al. 2019). In aptamer-based extractions, these binding agents are usually immobilized to a solid support and packed in a column (Pichon et al. 2015). Aptamers have been used as absorbents for the extraction of arsenites from groundwater as well as to bind cocaine and diclofenac in drinking water (Kim et al. 2009; Hu et al. 2011). Optical aptamer-based sensors have been employed for the detection of 17β-estradiol and bisphenol A in wastewater (Yildirim et al. 2012, 2014).

An aptamer sensor based on electrochemical detection has been employed for the detection of cocaine (Yang et al. 2016), and an aptamer sensor with colorimetric detection has been utilized for the analysis of methamphetamine and cocaine in wastewater (Mao et al. 2019).

Two other examples of binding agents that may be useful in future work with emerging contaminants are boronic acids and serum albumin. Boronic acids can undergo selective and reversible interactions with 1,2- or 1,3-diols and can be used to bind saccharides and glycosylated biomolecules (Liu et al. 2005; Mader and Wolfbeis 2008). For instance, 3-aminophenylboronic acid has been employed as a binding agent in an electrochemical biosensor for the detection of bacteria in water samples (Wannapob et al. 2010). Bovine serum albumin (BSA) is a serum transport protein that is known to bind many drugs and that can act as a CSP (Patel et al. 2006). In recent work, an affinity sorbent containing BSA has been used to bind to various drugs, hormones, and pesticides in water samples (see Fig. 2.9) and coupled online with LC-MS/MS for the analysis of such compounds (Papastavros et al. 2018). The same binding agents should be valuable in future work for examining similar targets in samples that include wastewater and drinking water.

2.6 Summary and Conclusions

This review has discussed various techniques that can be employed in affinity chromatography for the analysis of environmental contaminants in wastewater and related samples. Advantages of using affinity chromatography and associated methods for such work include their selectivity and strong binding for a target analyte, which often allows their direct use with complex matrices (Hage 2006; Zhang et al. 2018). These methods can also be simple and fast to use and can be used either off-line or online with other analytic methods for capturing and measuring emerging contaminants in environmental samples (Nelson and Hage 2006).

Several examples were provided of binding agents that have been used in affinity-based separations for environmental analysis. The first group of binding agents that was considered were the antibodies. It was shown how antibodies have been utilized in various formats for the analysis of wastewater and environmental samples, with these formats including both off-line and online immunoextraction and various forms of chromatographic immunoassays. Emerging contaminants that have been examined by these methods have ranged from herbicides to drugs and hormones. MIPs are another class of binding agents that have been used in environmental analysis. This group of synthetic agents has been used in both off-line and online modes for the specific extraction of emerging contaminants such as hormones, pharmaceuticals, dyes, and herbicides. A third set of binding agents that have been used in affinity chromatography for the analysis of wastewater and associated samples are CSPs. Various forms of CSPs have been employed in this work, including polysaccharide derivatives, macrocyclic antibodies, and protein-based binding agents.

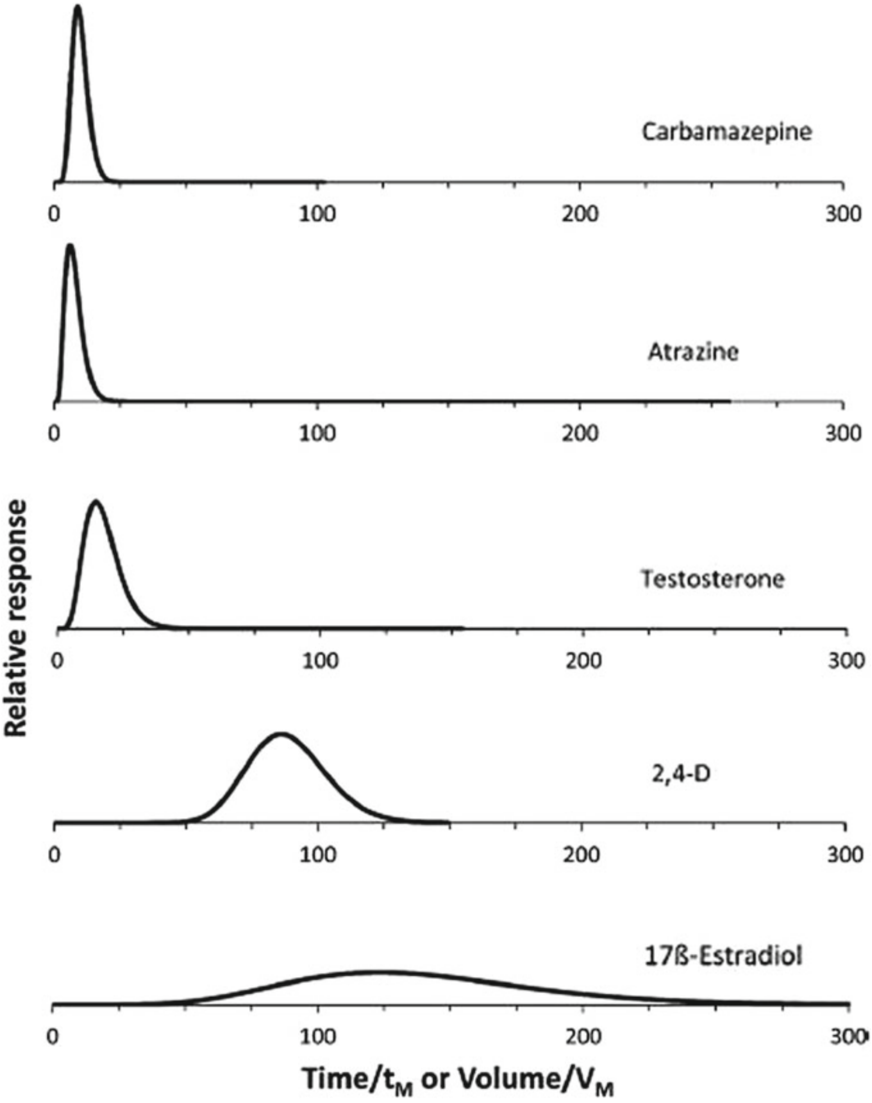

Fig. 2.9 Simulated chromatograms for the elution on a column containing bovine serum albumin (BSA) for representative drugs, hormones, and herbicides that are found as emerging contaminants in environmental water samples. Reproduced with permission from Papastavros et al. (2018). Copyright 2017 Wiley-VCH

Examples were also provided of alternative binding agents that have been used in environmental analysis and that may be used in future work with emerging contaminants in water. These alternative agents included aptamers, serum albumin, and boronates. Based on the variety of binding agents and formats that have already been used in environmental testing, it is expected that affinity chromatography and related methods will continue to grow in use and play an even larger role in the future for the detection of contaminants in wastewater and related samples.

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Chapter 3
Natural Attenuation of Pharmaceuticals in the Aquatic Environment and Role of Phototransformation

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3.1 Introduction

Degradation of water quality due to the discharge of pollutants of emerging concern, such as pharmaceuticals, hormones, and personal care products (PCPs), has raised concern regarding their fate and impact on the ecosystem. Thus, in the past decade, an increasing number of studies have focused on the occurrence, fate, and transport of these micropollutants in the ecosystem. Major causal factors for pharmaceutical contamination of aquatic systems are increased usage and improper disposal of pharmaceuticals across all classes. Owing to economic feasibility, India is also host to a large number of pharmaceutical industries, which may also serve as point sources of water contamination. Presence of extremely low concentration of pharmaceuticals, even in the ng/L range, can cause chronic effects in aquatic and human life (Mompelat et al. 2009; Kumar et al. 2019a, b, c). The most pronounced and widely reported chronic effect of pharmaceutical moieties on aquatic life is endocrine disruption, i.e., disruption in the normal functioning of sex hormones, thyroid hormones, and the neuroendocrine systems (Kim et al. 2007; Pal et al. 2010). Additionally, the occurrence

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of antibiotics in water can cause antibiotic resistance in the natural microbial community and can make containment and combating of infectious diseases difficult (Kumarasamy et al. 2010; Laxminarayan and Chaudhury 2016; Raghunath 2008; Shim et al. 2019).

In spite of the analytical challenges many pharmaceuticals from various prescription classes, such as, analgesics, antibiotics, anti-epileptics, non-steroidal anti-inflammatory drugs (NSAIDs), β-blockers, lipid regulators, chemotherapeutics, and steroid hormones have been detected in the aquatic environment (Heberer et al. 2002; Mohapatra et al. 2018). Most pharmaceuticals of human and veterinary origin are not entirely removed in wastewater treatment plants (WWTPs) and thus end up in the receiving surface waters (Singh et al. 2019). Surface water is one of the major sources of potable water (Lin et al. 2006a). However, incomplete removal of pharmaceuticals in WWTPs makes surface waters, the major sink for pharmaceutical discharges. Jiang et al. (2013) reported the presence of 80 types of pharmaceuticals, personal care products, and endocrine disruptors in rivers, lakes, and sediments in 14 countries. Antibiotics and NSAIDs were predominantly found in the aquatic environment. The reported highest concentrations were in the order of μg/L in treated sewage in three developed countries, i.e., UK, Canada, and Japan. However, their concentration was only a few ng/L in surface water due to the substantial dilution effect. Hormones, such as estrogens, plasticizers, such as nonylphenols (NPs), bisphenol A (BPA), and octylphenols (OPs) are all endocrine-disrupting chemicals (EDCs) that are commonly present in surface water in many countries. The reported concentration of such EDCs was in the range of several hundreds of ng/L. Compared to estrogens, BPA, NPs, and OPs were more common in the water environment. These EDCs were also detected in drinking water sources in the USA (Padhye et al. 2014) and Germany.

Depending on the physicochemical properties of pharmaceuticals, such as polarity, aromaticity, and distribution coefficient (K_d), they can persist and be transported over long distances downstream and can cause chronic effects on aquatic life. Although the released pharmaceuticals undergo substantial dilution in surface waters (Heberer 2002), they may conserve their parent structures or may get transformed into more active metabolites in the course of mobilization. In contrast, negligible dilution effects were observed for certain pharmaceuticals, such as, gemfibrozil (17 μg/L), ibuprofen (37 μg/L), doxycycline (74 μg/L), ketoprofen (10 μg/L), and acetaminophen (13 μg/L) in surface waters receiving treated and untreated sewage in Costa Rica (Spongberg et al. 2011). Similarly, caffeine has been reported to be present at a maximum concentration of 1.1 mg/L in surface water. Such a high concentration of caffeine was possibly caused by discharges from coffee bean production facilities located upstream (Spongberg et al. 2011). In addition to dilution/dispersion, there are various other biotic and abiotic attenuation processes taking place simultaneously in surface water. The combined action of these attenuation processes determines the fate of pharmaceuticals in receiving water bodies. Natural attenuation processes include sorption onto colloids, dissolved organic matter (DOM), and sediments (Osenbrück et al. 2007; Kumari et al. 2017; Patel et al. 2019), biodegradation, chemical and physicochemical transformation (Sammartino et al. 2008) and direct and indirect phototransformation (Chianese et al. 2017; Zhang et al. 2008a, b; Kumar et al. 2019b, c).

The nature of surface water and sediments can determine the extent and type of natural attenuation processes that can occur. For instance, some pharmaceutical contaminants were reported to have a higher affinity for the cationic organic matter of a clay soil compared to the anionic organic matter from a sandy soil (Dordio et al. 2007). Chemical reactions, including the formation of complexes with various cations (e.g., Ca^{2+}) from aquatic organic matter and tetracycline, has also been reported (Kemper 2008). Many pharmaceuticals, such as carbamazepine, are reported to be fairly persistent in the environment owing to their complex chemistry. Hence, the concentration of pharmaceuticals, such as carbamazepine, is expected to be similar in the influent and effluent of WWTPs and downstream of the receiving water body (Ashton et al. 2004; Hernando et al. 2006). On the other hand, diclofenac, which is a very popular over-the-counter NSAID, undergoes rapid phototransformation, although it is resistant to biodegradation. Additionally, some pharmaceuticals may undergo incomplete or partial biotransformation, leading to the formation of more toxic and harmful by-products.

Natural action in rivers incidentally can attenuate pharmaceuticals to a great extent and may thus improve the water quality. However, it may be noted that such attenuation systems work best when non-point source discharges into the river are minimal, and the river has an ample influx of clean and unpolluted run-off (Gurr and Reinhard 2006). A better understanding of the natural attenuation processes can indicate the time frame for the natural improvement of surface water quantity. Surface water bodies, of improved water quality, may serve as a useful source for indirect potable reuse (Gurr and Reinhard 2006). Lin et al. (2006b) established that over a distance of 10 km, alkylphenol (AP) ethoxylate metabolites and pharmaceuticals underwent significant attenuation via natural processes such as phototransformation (67–100%). The river water quality and climatic conditions may influence the time required and extent of removal of pharmaceuticals for surface water through natural attenuation processes. Natural attenuation processes include hydrolysis, volatilization, sorption, biotransformation, and phototransformation (Gurr and Reinhard 2006; Lin et al. 2006a). The contribution of each of these processes may vary from river to river and from one pharmaceutical to another. The current review aims to understand the mechanisms governing these attenuation processes and to evaluate the physicochemical properties of various pharmaceuticals vis-à-vis their susceptibility to natural attenuation in surface waters. Finally, the review tries to evaluate the potential of natural attenuation processes for removal of pharmaceuticals from surface water.

3.2 Various Types of Natural Attenuation Processes

3.2.1 Physical Parameters and Hydrogeological Conditions

Three major factors responsible for attenuating pharmaceuticals in a river are hydrogeological conditions, dissolved organic matter, and physical conditions prevailing in an aquatic environment (Yang et al. 2017; Das et al. 2016; Kumar et al. 2019b, c). The physical parameters include the flow rate of water in the river, penetration depth of sunlight, depth of water column, ambient temperature, turbulence, mixing, and rate of exfiltration and infiltration. Immediately, after discharge of wastewater into the river bodies, pharmaceuticals undergo rapid dilution depending on the flow conditions of the river. The aqueous concentrations were inversely proportional to flow in the river. In an Indian river receiving sewage and industrial effluents, the concentration of pharmaceuticals encountered in monsoon was substantially lower due to the higher flow rates encountered in the monsoon season (Mutiyar et al. 2018).

DOM can enhance the mobility of hydrophobic pharmaceuticals, such as diclofenac, bezafibrate, and gemfibrozil (Yang et al. 2017). Various researchers have studied the correlation between the concentration of pharmaceuticals and various physicochemical and water quality parameters, including pH, temperature, oxidation–reduction potential (ORP), chemical oxygen demand (COD), turbidity, and electrical conductivity (Yang et al. 2017). A negative correlation was obtained between the total concentration of pharmaceuticals and temperature and ORP, while a positive correlation was observed with COD and turbidity (Yang et al. 2017). Both temperature and redox potential were identified as important parameters affecting the attenuation of pharmaceuticals (Massmann et al. 2006, 2008).

Regionally, the concentration of pharmaceuticals in a river is highly variable. Medicine consumption patterns, hydrology, sewage water management practices, and the extent of urbanization may all affect the concentration of pharmaceuticals in a river. A significant difference in the spatial distribution of 33 pharmaceuticals was seen other than for carbamazepine, which has been reported to be resistant to biodegradation (Burns et al. 2018). A host of environmental processes, including in-stream degradation and dilution, may be prevalent in rivers flowing in geographically distinct domains. These factors may vary to differing extents in neighboring rivers leading to varying spatial concentration patterns of pharmaceuticals. For example, Burns et al. (2018) studied the attenuation processes in two adjacent rivers. In one river, the reduction in concentration moving downstream was symptomatic of in-stream removal processes, such as photolysis and microbial degradation, while a fluctuating concentration of various pharmaceuticals was observed in the neighboring river due to a complex dynamics between dilution and merging of other polluting sources (i.e., tributaries and urban drainage) with the river.

Variation in flow rate is one of the major factors that cause temporal variation in the concentration of pharmaceuticals. Low flow rate elevates the concentration and vice versa. Additionally, higher usage of pharmaceuticals during winter or decreased biodegradation in winter contributes to the increased concentration of pharmaceuticals in winter (Camacho-Munoz et al. 2010). The lack of significant seasonal differences in concentration of pharmaceuticals found in River Ouse was attributed to its lower annual variability in flow rate compared to that in River Foss (i.e., two orders of magnitude vs. three orders of magnitude flow variation). Gago-Ferrero et al. (2017) reported a persistent occurrence of antidepressants and benzodiazepines over the year due to their continuous consumption throughout the year. In contrast, antihypertensive and β-blockers experienced the highest occurrence in the summer compared to the winter season.

3.2.2 Sorption

Of the various phenomena taking place simultaneously in a water-sediment system, sorption/desorption processes significantly affect the fate and transport of hydrophobic pharmaceuticals. Generally, the sorption behavior of any compound is estimated with the help of the sorption coefficient (K_D), also defined as the solid–water distribution coefficient. It is affected by several factors, such as, fraction of organic carbon, type of sediment, surface sorption on mineral constituents, percentage distribution of clay, sand and silt, ion exchange capacity, pH of the system, and ability to form complexes with metal ions, such as, Ca, Mg, Fe or Al, and H–bonding. Neither the organic fraction nor any of the other parameters are homogeneously distributed across a river segment, thus sorption capacity may vary widely. Differences in fraction organic carbon in sediments and the nature of organic matter give rise to differences in sorption capacity. The soft amorphous rubbery organic matter shows lower sorption of hydrophobic pharmaceuticals than the hard condensed glassy organic matter. The rubbery organic matter mainly consists of partially degraded or reconstituted biopolymers (e.g., polysaccharides, lignin, lipoproteins, amino acids, lipids, and humic substances), while condensed organic matter is present in kerogen, black carbon, and coal. Pharmaceuticals with high octanol/water partition coefficient (log K_{ow}) show higher sorption on sediments rich in organic matter. Such compounds can strongly adsorb via hydrophobic interactions onto fats and lipids of bacterial origin present in sediments (e.g., aliphatic and aromatic groups). Additionally, they can also undergo electrostatic sorption onto negatively charged extracellular polysaccharide moieties. Finally, chemical interactions with several bacterial proteins and nucleic acids have also been reported. Since K_D shows large variability due to difference in organic matter fraction (f_{OC}), an organic carbon normalized partition coefficient (K_{OC}) is commonly used (Eq. 3.1) (Radović et al. 2016).

$$K_D = f_{OC} \times K_{OC} \tag{3.1}$$

This organic carbon normalized sorption coefficient, K_{OC}, for any compound shows lower variability compared to K_D. Equation (3.1) can be used when the fraction of organic carbon in soil/sediment is predetermined. Often the K_{OC} values are predicted based on a correlation between K_{OC} and the octanol/water partition coefficient (K_{ow}). For hormones, such as 17β-estradiol (estradiol), estrone, and 17α-ethinyl estradiol (EE2), the log K_{OC} values are in the range of 3.40–3.81, 3.45–3.85, and 3.71–4.12, respectively. Hence, these compounds are expected to sorb significantly onto the sediments (Lee et al. 2003a, b). For sediment and soil samples having organic matter with low to intermediate polarity, Karickhoff (1981) suggested a correlation (Eq. 3.2) for predicting the organic carbon normalized sorption coefficient, K_{OC} (ml g^{-1}):

$$\log K_{OC} = 0.989 \times \log K_{OW} - 0.346 \tag{3.2}$$

The K_{ow} values correspond to the partitioning of an organic compound between the octanol phase and the aqueous phase at equilibrium. High K_{ow} is a characteristic of hydrophobic compounds having poor solubility. Such compounds also show a higher tendency to sorb onto organic matter (Stangroom et al. 2000). Compounds with log $K_{ow} < 2.5$ are characterized by low sorption and higher bioavailability. A moderate degree of sorption is expected for organics depicting log K_{ow} values between 2.5 and 4, while a high degree of sorption is expected for compounds with log K_{ow} values greater than 4.0 (Rogers 1996).

The log K_D values for sorption of anti-influenza drugs (favipiravir, peramivir, laninamivir, laninamivir octanoate, oseltamivir, oseltamivir carboxylate, amantadine, zanamivir) on river sediments were in the range of 0.1–1.4. The values are 3–4 orders of magnitude lower than for other pharmaceuticals, as reported by Azuma et al. (2017). Such low values indicate a higher concentration of anti-influenza drugs in the liquid phase compared to their loading on river sediments. The K_{OW} values for these drugs were in the range −7.1 to 2.7, i.e., below the threshold for sorption (Rogers 1996). Similarly, Radović et al. (2016) studied the sorption behavior of 17 pharmaceutical compounds onto four different river sediments. Sorption equilibrium could be described by the Freundlich isotherm, and sorption capacity followed the order erythromycin » doxycycline » simvastatin » clopidogrel » bisoprolol » lorazepam » azithromycin » diclofenac » atorvastatin » metoprolol » carbamazepine » diazepam » trimethoprim » enalapril.

Radović et al. (2016) studied the sorption behavior of a variety of pharmaceuticals on sediments with varying sand, silt and clay content, as shown in Table 3.1. The K_D of any pharmaceutical was affected by the percentage distribution of clay, silt, sand. Sediment-1, which was mainly composed of 93.50% fine-grained silt with an average particle size of 0.003 mm, showed the greatest sorption capacity for the pharmaceuticals studied. In contrast, sediment-4, which was mainly composed of sandy gravel (94.74%) with granule size range 0.032–0.063 mm, showed the lowest sorption capacity. The sorption capacity of various sediments for the studied pharmaceuticals followed the order: Sediment-1 (OC=1.28%) > Sediment-2 (OC=0.229%) > Sediment-3 (OC= 0.06%)> Sediment-4 (OC=0%), such that sorption decreased with decrease in the organic carbon (OC) content. A comparison of log K_D values for sorption of anti-influenza drugs on sandy and clayey sediments revealed higher

Table 3.1 Physicochemical characteristics of river sediments and the corresponding water samples (Adapted with permission from Radović et al., copyright Springer Nature, 2016)

Sediment	Organic carbon (%)	Clay (%)	Silt (%)	Sand (%)	Gravel (%)	Dominant fraction	Texture	Water pH
1	1.28	0.00	93.50	5.22	0.00	0.003	Fine-grained sand	8.05
2	0.229	0.00	0.42	38.83	60.52	0.20–1.60	Sandy gravel, medium grained	7.1
3	0.06	0.00	0.11	27.60	72.23	0.80–3.15	Sandy gravel, medium grained	6.95
4	0.00	0.00	0.00	94.74	5.26	0.032–0.063	Sandy gravel	7.3

log K_D values for sandy soil compared to clayey soil. In contrast, a reverse trend was seen for favipiravir and laninamivir drugs (Azuma et al. 2017).

Pharmaceuticals with relatively low log K_{OW} are difficult to sorb easily onto sediments and vice versa. However, there exist some exceptions to this rule as observed for metoprolol (log $K_{OW} = 1.88$), bisprolol (log $K_{OW} = 2.12$), and erythromycin (log $K_{OW} = 3.06$). Metoprolol has higher water solubility and low log K_{OW}. It is reported to sorb significantly onto silty sediments (Radović et al. 2016), possibly due to its high pK_a value (9.6). In the neutral pH range, metoprolol remains in the undissociated form which causes a higher tendency for it to sorb onto the organic matter compared to its more polar dissociated form. This phenomenon may also explain the high sorption of bisoprolol and erythromycin. However, erythromycin has a relatively higher value of log K_{OW} and lower water solubility. In contrast, pharmaceuticals with low pK_a values are reported to sorb strongly onto sediments having relatively larger particles even when the organic carbon fraction in the sediments is low (0.06%). This behavior was observed for sorption on sediment with low silt content (0.11%) (Radović et al. 2016). Although several studies have highlighted a strong correlation between sorption coefficient and the organic carbon content, in pesticide sorption studies Radović et al. (2016) obtained the largest values of K_D for sediments with a low percentage of silt and a high percentage of medium-grained sandy gravel. Thus, the organic carbon fraction is not the only factor influencing the sorption capacity of pharmaceuticals estimated by the K_D or K_F values.

In general, low solubility, high log $K_{ow,}$ and positive charge favor sorption of pharmaceuticals on sediment. However, for some pharmaceuticals, such as, highly hydrophobic compounds (log $K_d > 4$), including several anticancer drugs, tamoxifen or different neutral forms of the antidepressant fluoxetine, and gemfibrozil (an acidic lipid regulator), analgesics and anti-inflammatories (e.g., ketoprofen, mefenamic acid, diclofenac, indomethacin,), and lipid regulator, fenofibrate, the sorption behavior is more complex. Such pharmaceuticals can be either in neutral or ionic form depending upon pH of the water-sediment system. In such cases, the sorption capacity may be evaluated based on the pH-dependent octanol–water partition coefficient (Corada-Fernández et al. 2015). Hydrophilic interactions and ion exchange between ionic pharmaceuticals and sediments may also result in differences in sorption. Pharmaceuticals with at least one amine group (e.g., metoprolol, fluoxetine, and tamoxifen) are positively charged ($pK_a > 8$) under neural pH commonly encountered in water-sediment systems. In spite of low log K_{ow} values (1.88–3.16), positively charged metoprolol and clarithromycin were positively correlated with the clay content in soil indicating the importance of cation-exchange processes between negatively charged surfaces of clays and/or organic matter present in the sediment with the ionic pharmaceuticals (Lara-Martín et al. 2015). Similar ion exchange phenomenon is also reported for several psychoactive drugs and antibiotics (Lara-Martín et al. 2015; Schaffer et al. 2012). A strong interaction is expected between aromatic moieties of the compounds and aromatic fractions of natural organic matter. Thus, the sorption of pharmaceuticals on sediments cannot be determined solely based on log K_{ow}. Even comparatively more polar compounds (log $K_d < 1$), such as propranolol, hydrochlorothiazide, and trimethoprim have been found to remain associated with sediments. Compounds that tend to sorb strongly usually accumulate on the top layers of sediments, while leaching into groundwater is more prevalent for compounds that do not sorb strongly or are mobile.

3.2.3 Biotransformation

Biodegradation/biotransformation is an essential process for the elimination of pharmaceuticals in the water-sediment system. Such elimination is usually carried out by microorganisms through their metabolic and co-metabolic pathways only if the toxicity of the compound does not inhibit the growth of the microbes. Along a river stretch in a typical water-sediment system, there exist aerobic, anaerobic, and anoxic zones, and each zone is characterized by a unique microbial community that can participate in the biotransformation of such compounds. The rate of biotransformation may vary depending upon the ambient temperature, hydrogeology of the river, and physicochemical properties of the pharmaceuticals.

In general, the concentration of pharmaceuticals downstream is expected to be low in comparison with that upstream, due to dilution or in-stream biotic and abiotic removal processes, such as biodegradation or sorption onto sediment. Biodegradation is an important process that aids in attenuation of micropollutants including pharmaceuticals. The rate of biodegradation has been reported to be higher during the summer season compared to the winter season, based on a study conducted in Yamuna river in India (Mutiyar et al. 2018). However, it is very difficult to find any specific trend in any river system from upstream to downstream, particularly when the stream is continually being polluted with additional point or non-point sources. Therefore, a higher concentration of some specific pharmaceuticals, such as that of acetaminophen (9822 ng/L), was reported downstream of river Fuss (Burns et al. 2018). No specific trends in variation in concentration of acetaminophen were noticed from upstream to downstream within the river.

Among the non-steroidal anti-inflammatory drugs (NSAID), biotransformation of diclofenac, ibuprofen, and naproxen has been extensively studied. Diclofenac at an initial concentration of 100 μg/L was reported to be transformed by 97% within five days by previously acclimatized native microbial community present in the river water sample (Paje et al. 2002). Seasonal variation in diclofenac biotransformation was studied by Lawrence et al. (2007), where no significant increase in biofilm (algal, bacterial, and cyanobacteria) thickness was seen during the spring season over a concentration range of 10–100 μg/L. However, the cyanobacterial biomass was significantly reduced during summer. Based on Fluorescent in Situ Hybridization (FISH), it was found that the abundance of Beta, and Gamma-*Proteobacteria,* and Cytophaga-*Flavobacterium* populations were significantly increased at an initial concentration of 100 μg/L. Ibuprofen comes under the category of easily biodegradable pharmaceuticals. Attempts were made to degrade ibuprofen over a concentration range of 20 μg/L to 10 mg/L in river water. While complete biotransformation of ibuprofen was reported to occur within a few hours at a low concentration, several days to several weeks was the time reported for the complete elimination of ibuprofen present at a higher concentration when glucose was used as a carbon source (Chen and Rosazza 1994). Lin et al. (2006b) reported biotransformation of ibuprofen in the laboratory-based on the microbial biofilms collected from river water. Within four to eight days of incubation, biotransformation was noticed. Similarly, *Trametes versicolor*, *Irpex lacteus*, *Ganoderma lucidum*, and *Phanerochaete chrysosporium* were able to degrade ibuprofen at an initial concentration of 10 mg/L within seven days (Marco-Urrea et al. 2009). Alpha- and Gamma-*Proteobacteria* were reported to degrade naproxen at an initial concentration of 6 mg/L. However, the degradation was quite slow, and only 28% removal was achieved at the end of 35 days. However, the same compound was co-metabolically removed up to 78 and 40% in the presence of glucose and phenol, respectively (Wojcieszyńska et al. 2014). The biotransformation of ibuprofen, ofloxacin, venlafaxine, irbesartan, and gemfibrozil was further studied in river water samples where these samples were incubated for a period of 65 days. After 44 days, 40% removal of ofloxacin was observed. and no significant removal was observed for the remaining pharmaceuticals (Boix et al. 2016).

Only limited literature on biotransformation of fluoxetine is reported. The drug is reported to have a half-life in the range of six to ten days in natural surface water when present at an initial concentration of 1 mg/L (Nödler et al. 2014). The most frequently detected antiepileptic drug, carbamazepine, is resistant to degradation and is persistent in nature. It was also reported to substantially reduce the bacterial biomass in a riverine biofilm (Lawrence et al. 2005). Biotransformation of several pharmaceuticals belonging to diverse groups, such as bezafibrate, clofibric acid, ibuprofen, diclofenac, naproxen, metoprolol, propranolol, sulfamethoxazole, and sotalol, along a 12.5 km long river stretch was studied by Kunkel and Radke (2012). Compared to the phototransformation rate, the biotransformation rate was negligible and was restricted to the hyporheic zone only. In contrast, clofibric acid and ibuprofen were reported to be biotransformed by in-stream biofilms growing on submerged macrophytes, and the hyporheic zone had a minimal role to play due to its low hydraulic conductivity (Kunkel and Radke 2011). Additionally, phototransformation and sorption could not contribute to the natural attenuation of these pharmaceuticals. No attenuation was noticed for bezafibrate, diclofenac, metoprolol, and naproxen. Among the antibiotics, biotransformation of sulfamethoxazole was affected by its initial concentration, water temperature, and concentration of humic acid. The biotransformation rate of this compound was significantly increased with increase in temperature from 4 to 25 °C in the water-sediment system. Similarly, with an increase in humic acid concentration from 5 to 30 mg/L, the biotransformation rate was increased from 82.9 to 90.1%, respectively (Xu et al. 2011). Biotransformation of β-blockers in surface water-sediment systems is quite slow. For pindolol and atenolol, 90% removal could be achieved within 0.4–10 days, while more than 100 days were required to eliminate sotalol, propranolol, or celiprolol. However, biotransformation was the primary removal mechanism for such pharmaceuticals compared to sorption (Ramil et al. 2010). In another study, atenolol, acetaminophen, ifenprodil, ibuprofen, carbamazepine, indomethacin, mefenamic acid, and propranolol exhibited low biotransformation in river water (half-life > 24 h), whereas they were more susceptible to phototrasnformation with half-life < 24 h and sorption (Yamamoto et al. 2009). However, biotransformation of ibuprofen along with diclofenac, bezafibrate, and naproxen was significantly increased in the deeper anoxic sediment layer (Fono et al. 2006; Kunkel and Radke 2008). River regions with low flow velocity and flat river beds are more susceptible to the development of anaerobic conditions. Koumaki et al. (2017) studied biotransformation of naproxen, ibuprofen, diclofenac, and ketoprofen under four different redox conditions, i.e., aerobic, anoxic, anaerobic and sulfate-reducing conditions in a lab-scale river water/sediment system. All the pharmaceuticals were significantly biotransformed under aerobic conditions. Biotransformation of naproxen and ketoprofen was enhanced by a factor of two in the absence of oxygen, whereas diclofenac was the most stable pharmaceuticals.

The biotransformation fate of anti-influenza drugs in real surface water samples was studied by Azuma et al. (2017). Among the drugs studied, the biodegradability of laninamivir octanoate and oseltamivir was high followed by laninamivir, amantadine, favipiravir, octanoate, peramivir, and zanamivir. Oseltamivir exhibited slower biotransformation than that of laninamivir with a half-life of 112–139 days, which further reduced to about 80% after one month. Phototransformation for such compounds may be neglected in the water-sediment system.

3.2.4 Phototransformation

In the photolytic process, as the name suggests, one of the most important factors is light. In an engineered system, light is often used artificially. However, for natural attenuation in surface waters, solar radiation serves as the light source. The process of photolysis is catalyzed by light of a specific wavelength or energy, which acts as a selective reagent in breaking chemical bonds, subsequently forming simpler low molecular weight compounds (Gmurek et al. 2017).

Some recent studies have indicated that photochemical or light-induced degradation and transformation of pharmaceuticals are the most important natural attenuation process in surface waters (Baena-nogueras et al. 2017). It is also the simplest method for the degradation of pharmaceuticals in the natural aquatic environment (Gmurek et al. 2017). Although turbidity may partially block sunlight due to inner filter effect, water in the top layer in streams is exposed to substantial amounts of direct sunlight, especially in summer and during noon times (Zhang et al. 2008a, b). In general, the degree and extent of photolysis of pharmaceuticals are influenced by the structure of the pharmaceuticals and also several environmental factors, such as, the intensity of solar radiation, depth of the water column, pH, temperature, salinity, organic matter content, and eutrophic conditions (Baena-nogueras et al. 2017; Jennifer et al. 2017). The intensity of solar radiation and irradiance, in turn, would depend on the existing season and the latitude of the location (Jennifer et al. 2017). Photochemical reactions can degrade pharmaceuticals via both direct and indirect pathways. In direct photolysis pathway, the pharmaceutical absorbs light, usually of a specific wavelength, which triggers its degradation by cleavage of the light-absorbing function group. In indirect pathways, photochemical reactions of oxygen, water, and other organic matter may yield reactive species, which may then attack the pharmaceutical molecule (Avetta et al. 2016). In the indirect pathway, sunlight is absorbed by naturally occurring photosensitizers, such as nitrate, nitrite, and chromophoric dissolved organic matter (cDOM) (Latch et al. 2003; Packer et al. 2003). Photosensitized nitrate and nitrite, in turn, yield hydroxyl radicals ($^{\bullet}$OH), while the irradiated cDOM helps in generating triplet state DOM, which reacts with oxygen to form singlet state oxygen (^{3}cDOM$^{\bullet}$ and $^{1}O_2$, respectively) (Avetta et al. 2016). These processes have been pictorially depicted in Fig. 3.1.

Since phototransformation plays such an important role in the removal of pharmaceutical pollutants from surface waters, it is important to understand the resulting photoproducts that may be formed. It is also imperative to assess whether sunlight assisted photochemical reactions are sufficient to bring about complete mineralization of the compounds. In the case of an indirect pathway, mainly due to the non-selectivity of radicals, various photoproducts formed during the reaction may persist and cause secondary toxic effects (Yin et al. 2017). Unfortunately, due to the myriad of reactions that occur during photolysis, the trace levels of photoproducts formed, and the lack of suitable standards and instrumentation to identify them, it is difficult to quantify them and comment on their nature and toxicity. The formation of such photoproducts is inevitable and thus they cannot be completely eliminated. Hence, the impact of these photoproducts in surface water is a concern that needs to be addressed.

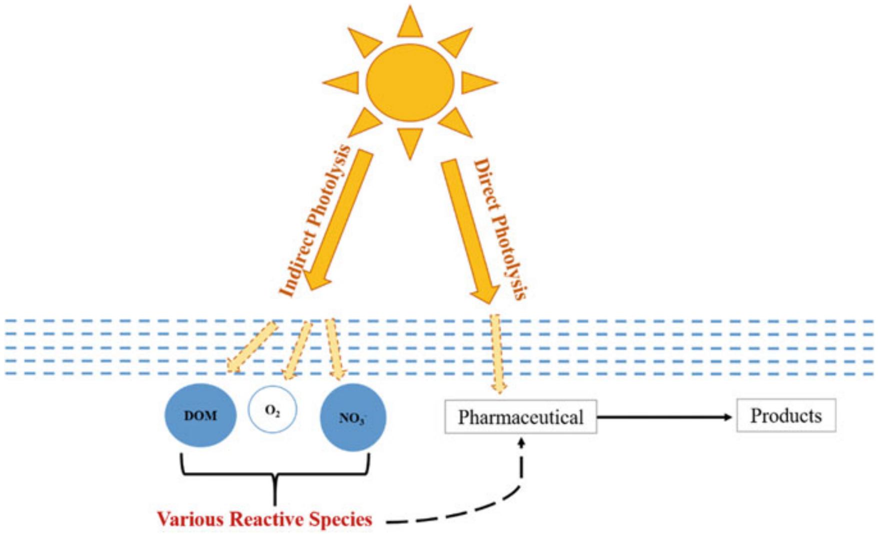

Fig. 3.1 Direct and indirect photochemical pathways prevalent in surface waters for removal of pharmaceuticals (Adapted with permission from Kral et al., copyright American Chemical Society, 2019)

3.2.4.1 Factors Affecting Photolysis in Surface Water

The efficiency of phototransformation of pharmaceuticals depends on many factors, such as the physicochemical properties and initial concentration of pharmaceuticals, the light source, photon flux, and the nature and characteristics of the aqueous phase. Water qulaity parameters, such as, dissolved organic matter (DOM), temperature, and pH of the water can affect photolyis. These factors can be broadly classified as the quality of the solution matrix and the light source and its intensity.

Quality of the Solution Matrix

Water quality, especially dissolved organic matter (DOM) plays a crucial role in photolytic processes of pollutants in sunlit natural waters. Typically, the removal efficiency by photolysis is reported to reduce with an increase in the complexity of the solution matrix. Other factors aside, a high concentration of organic matter in solution tends to act as an inner filter, limiting the amount of light available for the removal of pharmaceuticals (Sornalingam et al. 2016). However, the presence of DOM and other photosensitizers in river water may also have a beneficial effect on the degradation of a host of organic compounds owing to the indirect photolysis pathway (Pal et al. 2010).

DOM usually consists of a complex mixture of organic compounds produced as a result of various natural processes. DOM generated through the decomposition of plants (allochthonous) and microbially produced (autochthonous) DOM (Cottrell et al. 2013) exists in surface water bodies. The absorption of actinic radiation (electromagnetic radiation that can produce photochemical reactions) by DOM results in numerous chemical reactions involving nitrates, nitrites, carbonates and dissolved oxygen, and various reactive species, such as, superoxide/hydroperoxyl radicals ($O_2^{-\bullet}/HO_2^{\bullet}$), singlet oxygen ($^1O_2$), and the hydroxyl radical ($OH^{\bullet}$) are formed (Cottrell et al. 2013). Additionally, photosensitization of DOM due to the absorption of actinic radiation can also generate singlet excited state DOM. Subsequently, this singlet DOM undergoes deactivation, generating triplet excited state DOM ($^3DOM^{\bullet}$), which is also known to play a significant role in the photolysis of pharmaceuticals. However, owing to the complexity of DOM itself, reliable techniques for quantification of $^3DOM^{\bullet}$ are not available (Cottrell et al. 2013). Therefore, the effect of photosensitized excited states of DOM is studied by employing quenchers or by employing DOM proxies, such as benzoquinone (Cottrell et al. 2013). The influence of DOM on indirect phototransformation of pharmaceuticals is dependent on its concentration and chemical components. The combined techniques of excitation-emission matrix spectroscopy (EEMs) and parallel factor analysis (PARAFAC) have successfully been evaluated to understand the composition, source, and fate of DOM in the aquatic environment (Bai et al. 2018). Other than DOM, particulate organic matter (POM) can also cause some, yet not significant, effects on the photolysis of pharmaceuticals in surface waters (Cottrell et al. 2013). Light scattering and partitioning of contaminants on POM influences photochemical degradation of the contaminants by reducing the intensity of actinic radiation available for photolysis of the target compounds.

The effects of $^3DOM^{\bullet}$ are extremely important as they contribute to almost 75% of the aquatic photochemistry of natural waters (Cottrell et al. 2013). $^3DOM^{\bullet}$ may react with pharmaceutical contaminants directly through electron and energy transfer. Moreover, it may also generate other reactive oxygen species, such as singlet oxygen and hydroxyl radicals, leading to other degradation reactions (Bai et al. 2018). Hydroxyl radical has an important effect on the phototransformation of pharmaceuticals in natural waters since it can react with a series of organic contaminants because of its reactivity and non-selectivity (Bai et al. 2018). In contrast, due to the high selectivity of $^1O_2$, the generation of these reactive species is possibly crucial for phototransformation of only a limited number of contaminants. Examples of such compounds include polycyclic aromatic hydrocarbons, furans, dialkyl sulfides, phenolate anions. and pyrroles (Bai et al. 2018).

Light Intensity

Many organic compounds, including pharmaceuticals, can absorb light of wavelength less than 250 nm. This process in surface waters may not play a crucial role as the percentage of sunlight falling within this wavelength range is very small. Therefore, these processes are usually characterized by low quantum yields (Gmurek et al.

2017). However, when sufficient reaction time is provided, direct photolysis in surface waters has the potential to degrade many pharmaceuticals. Typically, it has been reported that the degradation time of most pharmaceuticals in surface water may vary from a few hours to months depending on various environmental parameters (Chowdhury et al. 2011). The specific rate of direct photolysis may vary according to the type of pharmaceutical and surface water quality.

For the sake of understanding the underlying principles of phototransformation of pharmaceuticals, researchers have published results for experiments conducted using various types of irradiation sources with varying intensity. For instance, most bench-scale laboratory experiments conducted with filtered surface water have been irradiated with light sources emitting light over a specific wavelength range, and both monochromatic or polychromatic light sources have been used (Mazellier et al. 2008). The most common irradiation sources include UVC, UVB, UVA, simulated solar light and irradiation using natural sunlight. A rise in light intensity (I) generally increases removal efficiency although the change in pseudo-first-order rate constant varies depending on the pharmaceutical and the light intensity (Sornalingam et al. 2016). Increased rate constants were explained by the higher photon flux, resulting from the increasing intensity.

3.2.4.2 Phototransformation of Specific Pharmaceuticals

Analgesics

Analgesics constitute an important category of pharmaceuticals, which are frequently sold over the counter. Additionally, many medications have these in combination with other pharmaceuticals. Hence, analgesics, including non-steroidal anti-inflammatory drugs (NSAIDs), are frequently detected in wastewater effluents and surface water around the world (Archer et al., 2017; Lee et al. 2003a, b; Shanmugam et al. 2014). These are characterized by extremely low biodegradability index, due to which they pass through the conventional wastewater treatment systems with negligible change in concentration and eventually contaminate surface water bodies (Kim et al. 2007; Valcárcel et al. 2011). Typically, most analgesics and particularly NSAIDs are effectively removed in surface water exposed to sunlight (Matamoros et al. 2009). For most analgesics, photochemical degradation is reported to follow the indirect pathway, and they have much shorter half-lives compared to steroids and other phenolics. Direct photolysis is reported to play an essential role in water exposed to UV radiation, owing to the characteristic UV absorbance of analgesics (Chen et al. 2017). In the natural environment, direct photolysis of analgesics exposed to sunlight is negligible with a few exceptions, such as ketoprofen.

Multiple studies are available on the photochemical degradation of analgesics, such as diclofenac, naproxen, ibuprofen, acetaminophen, and aspirin in sunlit surface waters. For a lake in Singapore exposed to natural sunlight and a solar simulator, Xu et al. (2011) studied the effect of direct and indirect photolytic pathway on degradation of the NSAID, ibuprofen (initial concentration of 100 μg/L). While direct photolytic removal of ibuprofen was negligible, the indirect photolysis rate was reported to increase with an increase in dissolved organic carbon content (DOC), and DOC was predicted to be the most important photosensitizer for ibuprofen degradation. However, a detrimental effect was observed in water containing high amounts of nitrate and nitrite. With an increase in the concentration of nitrate, the formation of nitrated intermediates was found to increase, and these intermediates were resistant to further transformation. Similar observations were made by Winkler et al. (2001) for ibuprofen in German rivers, Elbe and Saale. In the case of naproxen, photosensitization was reported in the presence of fulvic acid-like substances, such that the photolytic removal rate increased in its presence. On the other hand, the presence of humic acids led to a substantial inner filter effect, adversely affecting photolysis (Chen et al. 2017). Chen et al. (2017) reported that the apparent quantum yields for indirect photolytic removal of naproxen in the presence of fulvic acids and humic acids were 2.3×10^{-4} and 2.6×10^{-5}, respectively, whereas the direct photolysis yield (studied in ultrapure water) was 2.1×10^{-2}. The direct photolytic removal was attributed to the decomposition of the excited triplet state of naproxen ($^3NP^*$) and self-sensitization involving $^1O_2$. The mechanism of fulvic acid-mediated photolysis was not completely elucidated as photolytic removal of naproxen was influenced by fulvic acids only at a lower light intensity, ample aeration, and low pollutant concentration. Additionally, a study by la Farré et al. (2008) indicated that some phototransformation by-products of naproxen showed higher toxicity in bacteria, algae, rotifers, and microcrustaceans compared to the parent compound. Similar results were also obtained by Yin et al. (2017), where they found that photoproducts of naproxen exhibited tenfold higher toxicity in *Ceriodaphnia* compared to the parent compound.

Another NSAID viz. ketoprofen has been reported to undergo pseudo-first-order direct photolytic removal in experiments conducted in distilled water irradiated under natural sunlight (half-life of 2.4 min) as well as under a 300 W Xe lamp solar simulator (half-life of 0.54 min) (Matamoros et al. 2009). The short half-lives of ketoprofen can be attributed to its simpler structure; ketoprofen does not have a fused ring structure. However, an inspection of photoproducts of ketoprofen by the researchers also indicated the possibility of the persistence of (3-(1-hydroxyethyl)phenyl)(phenyl) methanone and benzophenone in river waters at the end of 24 days when irradiated under natural sunlight. Under similar conditions, ibuprofen exhibited moderate removal rates with a half-life of about one day (Matamoros et al. 2009).

Phototransformation has been reported as the primary mechanism for the removal of diclofenac in surface waters (Zhang et al. 2008a, b). Diclofenac is also characterized by negligible chemical and biological degradation rates (Baena-nogueras et al. 2017), while almost 90% of it was observed to undergo transformation during exposure to sunlight with a half-life of less than 1 h, at an initial concentration of 100 ng/L (Ebele et al. 2017). Several photoproducts of diclofenac have also been identified. Unlike ketoprofen, none of the photoproducts of diclofenac was persistent although a particular product, i.e., chlorocarbazole was reported to cause cell lysis in red blood cells with significantly higher efficiency than diclofenac itself (Encinas et al. 1998). Surprisingly, the addition of an OH radical quencher (isopropyl alcohol) increased the degradation rate of diclofenac in purified water, deionized water, and Mississippi river water as reported by Packer et al. (2003). The authors proposed that addition of the quencher possibly led to the generation of other radicals or led to photoreduction of the carboxyl group (–COOH) containing diclofenac, with isopropanol serving as the H-source. Such reactions are commonly observed for acidic pharmaceuticals, such as naproxen, ibuprofen, aspirin, and clofibric acid (Packer et al. 2003). Typically, in the case of diclofenac, the presence of humic substances was found to act more as an inner filter, limiting the light reaching the parent compound (Zhang et al. 2008a, b). On the other hand, contradictory results regarding the role of photosensitizers and indirect photolytic pathway have been reported for other NSAIDs.

Acetaminophen or paracetamol was also reported to undergo around 27% removal in surface waters in the summer season by phototransformation for studies conducted in the River Aire, UK (Ebele et al. 2017). In surface waters, the mechanism of phototransformation of acetaminophen was deduced to be via the indirect pathway with a half-life of 29 h (Baena-nogueras et al. 2017). However, similar to the case with naproxen and diclofenac, photoproducts of acetaminophen have been reported to be more complex and more recalcitrant than the parent compound. For instance, 13 photoproducts of acetaminophen were identified in a study. These products were structurally different from microbial biodegradation products or human metabolites (Yin et al. 2017). Studies by Kawabata et al. (2012) also showed that upon exposure to UV light, acetaminophen dimerizes, leading to the formation of a toxic photoproduct as revealed by the bioluminescence inhibition assay.

Antiepileptic and Antidepressants

Antiepileptic drugs and psychoactive drugs are by design highly hydrophobic as they have to cross the blood–brain barrier of the human body. Carbamazepine, a widely used antiepileptic drug, has been most commonly detected at relatively high concentrations in surface waters around the world, along with its metabolites, trans-10,11-dihydro-10,11- dihydroxycarbamazepine (Zhang et al. 2008a, b). These are among the most persistent and recalcitrant pharmaceuticals occurring in surface waters. Negligible removal by direct phototransformation was reported for carbamazepine, fluoxetine, caffeine, and amitriptyline in distilled water exposed to the solar simulator by Baena-nogueras et al. (2017). However, Matamoros et al. (2009) reported degradation at 45 °C with a half-life of 35 h. This was attributed to the thermal disintegration of carbamazepine to iminostilbene. Additionally, carbamazepine was also reported to undergo some removal when spiked water samples were exposed to 500 W Xe lamps, as opposed to 300 W Xenon lamps, usually used in solar simulators (Baena-nogueras et al. 2017). High acidity or salinity can also increase phototransformation rates. For experiments in seawater, tenfold decrease in half-life was observed as compared to that in freshwater (Matamoros et al. 2009). This increase in removal rate was possibly due to photosensitizers that initiated the indirect phototransformation pathway. Similar results were reported for caffeine and amitriptyline, where the former underwent phototransformation only in seawater and the latter showed phototransformation only at high pH (Baena-nogueras et al. 2017). However, natural attenuation of these pharmaceuticals via phototransformation is highly unlikely in the freshwater aquatic environment (Yang et al. 2017).

Indirect photolysis plays an important role in the phototransformation of carbamazepine in natural waters. Presence of nitrate ions and humic constituents of DOM were reported to enhance the transformation of carbamazepine into readily degradable photoproducts in surface water (Lam and Mabury 2005), while under direct photolytic conditions, carbamazepine was found to be extremely persistent. At environmentally relevant concentration at neutral pH, ambient temperature, and sufficient dissolved oxygen, carbamazepine showed a half-life of over 25 days under direct photolysis, while the same was reduced to 4.5 days in the presence of humic substances, acidic pH, and ample dissolved oxygen (Calisto et al. 2011). Gabapentin is another commonly used antiepileptic drug. It is known to be eliminated almost entirely in its native form such that it is present in surface water and even in potable water (Herrmann et al. 2015). The major issue with this pharmaceutical is that under UV treatment in drinking water plants, it forms a large number of persistent and toxic photoproducts. These products are more toxic than the parent compound (Herrmann et al. 2015). These dead-end photoproducts end up in surface water, and they have been reported to be present even after prolonged photolysis. A similar case, wherein more toxic transformation by-products were discharged and detected in surface water, was those of the antidepressant, trimipramine (Khaleel et al. 2017) and antipsychotic drug, quetiapine (Herrmann et al. 2016).

The case of fluoxetine, a selective serotonin uptake inhibitor, is somewhat different. Fluoxetine is extremely photostable under UVA (320–400 nm) irradiation in the presence of humic substances and dissolved organic carbon photosensitizers. However, significant degradation of the compound is observed in the presence of a variety of cations, such as Cu (II), Fe (II), Fe (III), and Al (III) ions (Maalanka et al. 2013). Phototransformation of fluoxetine with metal ions is consistent with the kinetics of a first-order reaction, and the reaction rate constant is the highest in the presence of Cu(II) ions and the slowest in the presence of Al(III) ions. Desipramine was also shown to undergo significantly higher photolytic removal under solar simulator via the indirect pathway, owing to the presence of humic substances (half-life of 12 h, as opposed to 36 h via direct pathway) (Gros et al. 2015; Khaleel et al. 2016). On the other hand, another less commonly prescribed antidepressant, amisulpride was readily degraded through the direct photolysis under simulated sunlight in ultrapure water (half-life of 3 h). Nevertheless, amisulpride was the only pharmaceutical belonging to this class of drugs that underwent complete degradation without the generation of toxic by-products (Gros et al. 2015).

Steroid and Hormones

The similar issue regarding the removal of steroidal pharmaceuticals and hormones is their ability to cause endocrine disruption in aquatic life (Archer et al. 2017). Most steroidal pharmaceuticals, including natural and synthetic hormones and xenoestrogens and androgens, are characterized by the presence of a phenolic ring, enabling these molecules to have considerable solar light absorbance in the 254 nm range (Chowdhury et al. 2011). Also, it is the presence of this phenolic moiety that causes estrogenic activity by enabling them to bind to the estrogen receptor in cells of fishes and other aquatic animals (Mishra et al. 2018). It is believed that the steroidal pharmaceuticals and hormones, such as 17α-ethinylestradiol (EE2) and 17β-estradiol (E2), can undergo direct photolysis, resulting in cleavage of the phenolic ring (Chowdhury et al. 2011). This process is vital as the loss of the phenol ring can reduce the inherent capability of the molecule to cause endocrine-disrupting effects (Li et al. 2016). However, 40–75 days were required for 50% degradation of estrone (E1), E2, estriol (E3), and EE2 (Sornalingam et al. 2016) under direct solar irradiation. For instance, Whidbey et al. (2012) conducted experiments under simulated solar light for the hormones E2, EE2, E1, equilin (EQ), and equilenin (EQN) at a concentration of 10 μg/L each under direct and indirect photolysis conditions. Direct photolysis experiments were conducted at a constant temperature, in a solar simulator, equipped with a Xe lamp and a UV filter to prevent wavelengths <300 nm. Indirect photolysis experiments with added Suwannee River fulvic acid (10 mg/L) led to faster degradation rates for E2, EE2, and EQ via the indirect photolytic pathway. While considerable removal of the steroids was observed through the direct route, results of Yeast Estrogen Screen (YES) assay showed that direct photolysis of E1 caused generation of estrogenic products, such as, Lumiestrone and others that were not identified. On the other hand, in the presence of Suwannee River fulvic acid, E1 underwent degradation via an indirect photolysis pathway and did not produce Lumiestrone or any other estrogenic products. Similarly, androgenic steroidal pharmaceuticals, such as, boldenone and trenbolone have also been reported to undergo direct photolysis, owing to their UV absorbance at 254 nm (Gryglik et al. 2010) and testosterone, due to UV absorbance at 244 nm (Vulliet et al. 2010). Another example is that of estriol (E3). In the presence of humic substances spiked ultrapure water, its half-life varied between 5 and 10 h depending upon the concertation of humic substances. Further, half-life times between 1.6 and 9.5 h were determined in surface water samples, in which it was observed that the matrix composition contributed up to 97% of E3 phototransformation, enabling higher efficiency of the indirect pathway in surface waters (Oliveira et al. 2016). Although steroids are susceptible to direct photolysis, more effective removal with respect to elimination of endocrine disruption effects (Cédat et al. 2016) and faster degradation rates (Leech et al. 2009; Ren et al. 2017) may be achieved via the indirect pathway.

Most of the bench-scale studies showed an increase in photolysis efficiency with variation in the type of irradiation, in the order: sunlight < UVA < UVB < UVC. For example, 91.6% phototransformation of EE2 was achieved in 30 min under UVC (Zhang et al. 2010). The efficiency of photolytic removal of the highly persistent EE2 was compared to its aerobic and anaerobic biodegradation in Lake Quinsigamond, Massachusetts, USA, by Zuo et al. (2013). They reported that EE2 was present in the lake at a concentration of ~ 11 ng/L, a concentration that is sufficient to cause statistically significant feminization of male fishes in the lake. At this concentration, the authors showed that both aerobic and anaerobic biodegradation were more or less ineffective, and they were characterized by long lag phases of 42 days and 63 days, respectively. On the other hand, the photolytic transformation of EE2 was extremely rapid, and almost complete transformation of the parent compound was observed at the end of two days during summer as compared to the dark controls kept over two days. However, the estimation of residual estrogenicity was not in the scope of these studies.

Generally, the photolytic removal of all pharmaceuticals is assumed to follow pseudo-first-order kinetics, with the first-order rate constant being controlled by both direct and indirect photolysis in the case of steroids. Additionally, the rate constant is also indirectly influenced by the light intensity up to a point where mass transfer becomes rate-limiting (Sornalingam et al., 2016). The latter case rarely occurs in dilute surface waters. Typically, the degradation efficiency of steroid hormones was reported to increase as the wavelength of the source moved from visible to UV owing partly to increased photon flux and partly to strong characteristic UV absorbance of hormones (Li Puma et al. 2010). Additionally, it is also reported that the effect of light intensity varied with the nature of the steroid molecule. These inferences were made based on studies conducted using bench-scale reactors employing artificial light sources and concentrations of steroids comparable to that in surface water. For instance, photolytic degradation efficiency under UVA irradiation followed the order EE2 > E1 > E2 (Coleman et al. 2004). While most of the steroids were susceptible to direct photolysis, Whidbey et al. (2012) reported that the half-lives varied from 40 min for E1 to about 8 h for E2 and EE2. Similarly, high pressure (HP) Hg lamp ($\lambda > 365$ nm) did not lead to phototransformation of EE2, while a significant amount of removal occurred in the presence of a UV disinfection lamp ($\lambda = 254$ nm) (Sornalingam et al. 2016). Such variation in the direct photolysis rates of these molecules stems from their different light absorbance characteristics (Mazellier et al. 2008). However, researchers have also shown experimentally that exposure to medium pressure UV light ($\lambda = 254$ nm) for a period of four days was inadequate for the elimination of estrogenicity of E2 and EE2 at an environmentally relevant concentration (Sornalingam et al. 2016). This indicated that even after exposure to UV light sources, the phenolic group of the steroids was unaffected. In addition, irrespective of the nature of the steroid and the type of irradiation (monochromatic or polychromatic light source), the photoproducts were similar (Mazellier et al. 2008). The absorption spectrum of E2 and EE2 is in the range 240–330 nm (Mazellier et al. 2008), where the overlap with natural sunlight is narrow. Hence, a long exposure period may be required for degradation and elimination of estrogenic activity.

While direct photolysis is plausible in the case of steroids, such as E1, E2, E3, and EE2, indirect photolysis plays an equally important role in expediting the removal rates. However, the type and nature of constituents of DOM present are also reported to play a role in the process. For instance, the presence of humic acid and Suwannee River fulvic acid constituents of DOM led to an exponential increase in the free radicals that oxidized the steroids (Sornalingam et al. 2016). On the other hand, Whidbey et al. (2012) attributed the drop in E1 photolysis to the presence of Suwannee River fulvic acid acting as an inner filter. The inhibition of E3 photolysis under elevated light intensity was attributed to the photoactivated humic acid species being more efficient free radical quenchers compared to the parent humic acids (Chen et al. 2013). Other ions, such as nitrate, nitrite, and bicarbonate, may also affect the photolytic pathway of steroids. It was observed that the presence of HCO_3^- ions decreased the rate of photolytic removal of E2 as these acted as quenchers of $OH^\bullet$ radicals, while the presence of NO_3^- and NO_2^- ions significantly increased the generation of $OH^\bullet$ radicals, thereby increasing the rate of removal of E2 (Liu et al. 2017).

The pH of water affected the rate of photolysis of E1 (0.15 h^{-1}), E2 (0.02 h^{-1}), E3 (0.02 h^{-1}), and EE2 (0.02 h^{-1}). Photolysis rate was low below pH 6 and increased gradually up to pH 9. An increase in pH increased the generation of OH^- ions, which in turn created more $OH^\bullet$ radicals that facilitated photolysis. Greater removal efficiency was observed above the pKa values of the estrogens, which is ~ 10.5 for E1, E2, E3, and EE2. As pH increased beyond the pKa, more of the estrogens excited as negatively charged species. Therefore, electrophilic attack by reactive oxygen species resulted in further degradation of the estrogens (Sornalingam et al. 2016). The above trend was also observed by Chen et al. (2013) for E3 phototransformation, which slightly increased with a rise in pH from 6.0 to 8.0 and rapidly increased over the pH range 8 and 10. However, while pH played an important role in determining the photolytic removal of estrogenic steroids, pH had negligible effect on the direct and indirect photolysis of testosterone in spiked surface water samples (Vulliet et al. 2010).

3.3 Modeling of Natural Attenuation

Aymerich et al. (2016) determined the attenuation rate of several pharmaceuticals and their metabolites in a river assuming the river behaved as a plug-flow reactor. Further, they included expressions for lateral flow in the plug-flow reactor to better simulate an actual river system. The mass balance can be expressed as given in Eq. (3.3):

$$(A \cdot \Delta x)\frac{\partial C}{\partial t} = -Q_{\text{out}} \cdot \Delta C - r \cdot (A \cdot \Delta x) \tag{3.3}$$

where A is the river cross-section area (m^2), Δx is the river distance (m), Q_{out} is the river flow (m^3/d), and ΔC is the difference in concentrations (ng/L) between upstream and downstream of the river segment after including lateral flow patterns. Assuming steady-state conditions in the river, attenuation rate constant (*k*, d^{-1}) and half lifetime (HLT, d^{-1}) can be estimated from Eqs. 3.4 and 3.5:

$$\frac{C_{\text{out}}}{C_{\text{in}}} = \frac{e^{(-k \cdot \tau)}}{1+\beta} \tag{3.4}$$

$$\mathrm{HLT} = \ln(2)\frac{1}{\tau} \tag{3.5}$$

Where τ is the hydraulic residence time (d), and β is the dilution factor correction due to flow increase from lateral flows.

Among the pharmaceuticals (acetaminophen, venlafaxine, carbamazepine, ibuprofen, and diclofenac) studied, significant attenuation was observed for ibuprofen (3.3 h) and its metabolites (carboxy-Ibuprofen (9.2 h) and 1-hydroxy-Ibuprofen (2 h)).

Similarly, Acuña et al. (2015) assessed attenuation of 75 pharmaceutical in four rivers of varying physicochemical and molecular properties in different segments with changing environmental conditions. Initially, the dilution coefficient as a result of vertical and lateral dilution due to groundwater and tributaries, respectively, along the river for each pharmaceutical was calculated. Both chloride and sulfate anions were used as tracers. River attenuation was subsequently estimated by comparing the decrease in pharmaceutical and nutrient concentrations relative to the dilution coefficients. First-order degradation constant for each pharmaceutical in the stream was evaluated as per the following equation.

$$k = \frac{1}{t}\ln\left(\frac{C_0}{C_\tau}\right) \tag{3.6}$$

where C_τ and C_0 represent the concentration of pharmaceuticals at time τ and initial concentration of pharmaceuticals, respectively, and τ is the travel time along the river segment.

Furthermore, the non-dimensional mass transfer coefficient (v_f) was estimated using Eq. 3.7 (O'Connor 1988)

$$v_f = \frac{Q}{wv}k \tag{3.7}$$

where Q is the mean river flow rate (m^3/s), w is the mean width (m), and v is the mean velocity (m/s). v_f is a dimensionless parameter that standardizes for river flow rate, velocity, and river width and thus allows comparison of attenuation rates among rivers.

The dilution corrected attenuation rate was highly variable, and this variation may be attributed to both the physicochemical properties of the pharmaceuticals and the local environmental conditions. There was a lack of significant correlation between physicochemical properties and v_f of individual pharmaceuticals. In contrast, previous modeling studies (Gioia and Dachs 2012) on organic chemicals demonstrated a negative correlation between attenuation rate and volatility and hydrophobicity. The attenuation was higher for organics having low to medium volatility ($-4 < \log K_{ow} < -2$) and low hydrophobicity ($0 < K_{ow} < 4.5$). Similarly, no significant correlation was noticed between v_f and pharmaceuticals grouped based on their ring structure

Table 3.2 Half-life of 34 pharmaceuticals measured along the river segments ($N = 4$) (Reprinted with permission from Acuña et al., copyright Elsevier, 2015)

Group of Pharmaceuticals	Pharmaceuticals	Half-life time (h)
Analgesics and anti-inflammatories	Acetaminophen	2 ± 1
	Codeine	3 ± 0.9
	Diclofenac	2 ± 0.5
	Hydrocodone	4 ± 2.2
	Ibuprofen	2 ± 1.1
	Ketoprofen	4 ± 2.9
	Naproxen	8 ± 12.7
	Phenazone	3 ± 2.5
	Propyphenazone	21 ± 29.4
	Salicylic Acid	6 ± 3.3
Antibiotics	Dimetridazole	34 ± 57.7
	Erythromycin	4 ± 2.5
	Metronidazole-OH	4 ± 1.7
	Ronidazole	13 ± 11.1
	Sulfamethoxazole	6 ± 4.9
	Trimethoprim	10 ± 14.4
Antihelminthics	Levamisol	4 ± 4.3
Antihypertensives	Irbesartan	22 ± 32.7
	Losartan	3 ± 0.4
	Valsartan	2 ± 1.0
Ca channel blockers	Verapamil	9 ± 12.8
Antiplatelet agents	Clopidogrel	11 ± 12.2
Diuretics	Furosemide	9.6 ± 15.4
	Hydrochlorothiazide	2.1 ± 1.2
Histamine receptor antagonists	Ranitidine	6.4 ± 4.9
Lipid regulators	Bezafibrate	2.9 ± 1.5
	Gemfibrozil	2.6 ± 0.5
Psychiatric drugs	Carbamazepine	4.1 ± 2.4
	Citalopram	2.8 ± 1.5
	Diazepam	28 ± 45.8
	Lorazepam	7 ± 6.1
	Norfluoxetine	2 ± 0.7
	Venlafaxine	3 ± 1.7
β-Blockers	Atenolol	2 ± 1.4

and functional groups. None of the physicochemical and molecular properties considered correlated with the mean values of v_f. The v_f values of some pharmaceuticals were similar among the various study sites. However, for other pharmaceuticals, significant variability was obtained amongst sites. This may be attributed to varying log K_{ow} values. When hydrophobic compounds sorb onto suspended particles and sediments, they are less susceptible to other biotic and abiotic processes, such as biotransformation, photolysis, and volatilization processes. Additionally, attenuation of carbamazepine, citalopram, irbesartan, valsartan, and venlafaxine was strongly correlated with attenuation of soluble reactive phosphorus (SRP) and concentration of total suspended solids (TSS). The half-lives of various pharmaceuticals ranged from 1.6 to 34 h, and dimetridazole, diazepam, and irbesartan had the highest half-lives, as shown in Table 3.2.

3.4 Conclusions

The self-cleaning ability of a river can substantially attenuate pharmaceuticals discharged from various point and non-point sources. Biotransformation, sorption onto sediment and solid particles, and phototransformation are the important attenuation processes that decide the fate and transport of these compounds in the water-sediment system. Several other factors, such as hydrogeological conditions, concentration and composition of organic matter, and physical parameters, are also responsible. Various physical parameters that affect natural attenuation include river flow rate, reach distance, depth, temperature, mixing, turbulence, and rate of exfiltration, and infiltration. The sorption behavior of any pharmaceutical is affected by sediment organic fraction, type of sediment, surface sorption to mineral constituents, percentage distribution of clay, sand and silt, ion exchange capacity, pH of the system, and ability to form complex metal ions.

Similarly, the extent of biotransformation is dependent upon ambient temperature, hydrogeology of the river, and physicochemical properties of the pharmaceuticals. The rate of biotransformation varies significantly in the aerobic, anaerobic, and anoxic zones of rivers. The intensity of light, quantum yield, the concentration of DOM, rate of formation of reactive oxygen species, and physicochemical properties of individual pharmaceuticals affect the phototransformation of pharmaceuticals in the water-sediment systems. Pharmaceuticals belonging to the same therapeutic class do not necessarily undergo the same degree of sorption, biotransformation, or phototransformation.

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Chapter 4
Impact and Fate of Microplastics in the Riverine Ecosystem

Dhruba Jyoti Sarkar, Soma Das Sarkar, Santanu Mukherjee, and Basanta Kumar Das

4.1 Introduction

In recent times, there has been great interest on ubiquitous occurrence and harmful effect of plastic debris including microplastics (MPs) in the global ecosystems. They have been identified as one of the significant indicators of the anthropocene (Waters et al. 2016; Patel et al. 2019a) and also included in the list of 'contaminant of emerging concern' (CEC) besides other chemical pollutants due to their ability to cause potential threats to the biosphere. The term MPs generally refers to plastic particles with longest diameter of <5 mm (Andrady 2011; Browne et al. 2011). However, recently the term has been suggested to include only plastic particles <1 mm (Lambert et al. 2014). Above this range, the plastic particles were termed as mesoplastic (>1 to ≤5 mm) and macroplastics (>5 mm) (Lambert et al. 2014). But at present, the upper limit of MP is widely accepted to be 5 mm in view of the small size that can be readily ingested by the organisms (GESAMP 2015). The MPs are present in the environments for many years now, as reported by early researchers in 1970s (Carpenter et al. 1972; Colton et al. 1974; Gregory 1977; Singh et al. 2020); however, they have not been studied extensively till early 2000s, thus qualifying them as CEC (Lambert et al. 2014; Wagner et al. 2014; Garthwaite et al. 2010).

In 2018, the world production of plastic reached 359 million tonnes, an increase of 15.43% from 2014 (Plastics Europe 2019). China and Japan are the two top plastic producing countries in world, accounting for 30% and 4% of global plastic production, respectively (Plastics Europe 2019). However, in 2014, it was estimated that the per capita consumption of plastic materials in Asia (China, 45 kg/person; India,

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9.7 kg/person) is low as compared to USA (109 kg/person) and Europe (65 kg/person) (Tata Strategic 2014). However, the Asian countries are suffering most in generating mismanaged plastic waste, and the load of plastic waste in their natural ecosystem is considered to be huge (Jambeck et al. 2015). Thus, it is highly likely that microplastics abundance in the Asian rivers systems is enormous as compared to many other global river systems. A recent predictive model has highlighted that among the rivers, Yangtze River of China contributes the highest annual plastic debris discharge (0.33 million tonnes per year) to marine system followed by Ganga River of Indian subcontinent (0.12 million tonnes per year) (Lebreton et al. 2017; Mukherjee et al. 2020; Singh et al. 2019). The institute, ICAR-Central Inland Fisheries Research Institute, India, explored the abundance of MPs in Ganga River sediment at the eastern part of the country and found that MPs are abundant in the river sediment in the mass range of 11.48–63.79 ng/g sediments (Sarkar et al. 2019; Deka et al. 2015). Similarly, various literature report presence of MPs in marine as well as terrestrial ecosystems, and it is now a well-established fact that MPs are ubiquitously distributed around the world. The occurrence of MPs has been widely studied in the marine ecosystem, including estuaries, lagoon, seafloor, etc. (Cole et al. 2011). However, their abundance study and fate analysis in the freshwater system, especially riverine ecosystem, are still in the infancy stage covering only few major rivers of the world (Klein et al. 2015; Horton et al. 2017; Lebreton et al. 2017; Wang et al. 2017; Sarkar et al. 2019). It was reported that only 3.7% of the total publications on MPs contains the term ‘freshwater’ (Lambert and Wagner 2018).

4.2 Source and Transport of Microplastics in River

MPs including other plastic fragments enter into the riverine ecosystem through various routes, and it was observed that the routes differ with different geographical regions. On the basis of source, the MPs can be classified into two categories, viz. primary MPs and secondary MPs (Fig. 4.1). Primary MPs are produced industrially and utilised either as pellets for further industrial process or in the cosmetic products, viz. facial scrub, tooth paste, etc. (van Wezel et al. 2016; Kumar 2016). The amount of MPs beads used in cosmetics for use in European countries during 2012 was estimated to be 4000 ton (Gouin et al. 2015). However, the primary MPs only represent a little fraction of estimated environmental plastic load, and further, this fraction can be easily addressed, and their use can be minimised (Lassen et al. 2015). The main cause of concern is secondary MPs which are produced in the environment during disintegration of bigger plastic particles in small fragments or debris. The source of secondary MPs includes improper management of plastic waste, discarded to the environment directly or disposed in landfills and ultimately reaching aquatic ecosystem through wind or water-driven transport (Gouin et al. 2015). Further, industrial abrasion process, erosion of synthetic paints and car tyres are important sources of MPs (Lassen et al. 2015; Patel et al. 2019b). Another most important source of

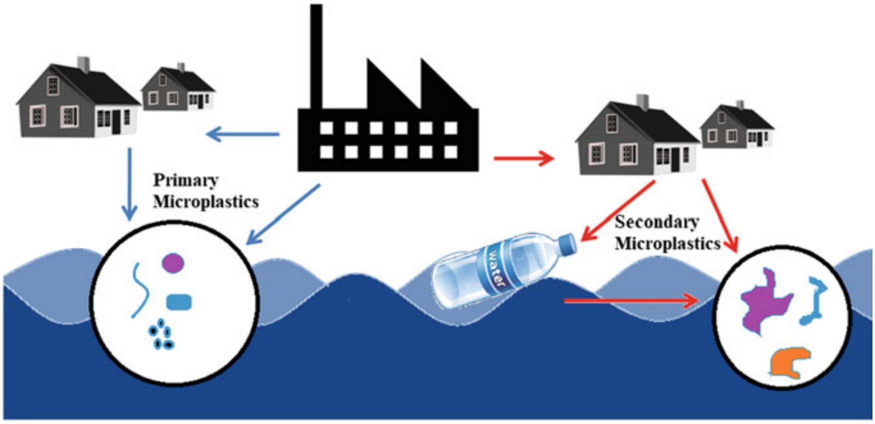

Fig. 4.1 Source of microplastics in river system; primary source (blue arrow), intentional industrial manufacturing and secondary source (red arrow), uncontrolled anthropogenic process. (adapted and modified from Rist and Hartmann 2018)

MPs is synthetic textiles, which releases large amount of microplastic fibres in the wastewater during washing (Napper and Thompson 2016).

In general, the entry of MPs to riverine ecosystem can be listed as (1) passage through wastewater treatment plants (WWTPs) viz. microbeads used in personal care products and release of fibre from textiles during washing, (2) storm water overflow, (3) incidental release, (4) industrial waste, (5) atmospheric deposition. Plastic film for agricultural use is being considered as one of the major sources of MPs in the terrestrial ecosystems (Steinmetz et al. 2016; Qi et al. 2018). The plastic films are increasingly being used in agriculture to control weed, loss of nutrient and moisture, regulation of soil thermal properties, etc. It was estimated that yearly 6.5 million ton of plastic are being used in agriculture for various purposes out of which 10% are being used for soil mulching (Scarascia-Mugnozza et al. 2006; Sarkar et al. 2018, Kumar et al. 2019). After harvesting and subsequent weathering, the plastic films become brittle leading to their journey to aquatic ecosystem through natural stream during rains. After entering to aquatic system, several fundamental processes of fluid mechanics influence the subsequent transport of plastic particles in stream. For example, advective, dispersive and diffusive mass transfer are responsible for combined motion of particles in a fluid. Longitudinal transport through average flow velocity is referred as advection, whereas dispersive mass refers to the spreading of particles from highly concentrated areas to less concentrated areas (Ji 2008). The process of dispersion is multidimensional covering distribution of plastic particles to all flow direction and velocities. The combined transport process of plastic particles due to dispersion and advection can be modelled through one-dimensional advection–dispersion equation (Wallis 2007; Ani et al. 2009). The diffusive mass transfer includes transport of plastic particles (mainly nanoplastics) from high to low concentration through Brownian motion. The settling of non-buoyant plastic particles or aggregated buoyant plastic particles can be described by the Stokes law (Brown and Lawler 2003; Kowalski et al. 2016). The settled plastic particles can also come back to the water column by erosion or resuspension of the riverbed. All these transport processes (Fig. 4.2) are affected by the plastic particle properties viz. shape, size, fractal dimension, density and porosity (McNown and Malaika 1950; Johnson et al. 1996; Khatmullina and Isachenko 2016). Thus, the aggregation of plastic particles with co-pollutants influences their fate significantly. The aggregation process can be modelled using von Smoluchowski particle interaction model where aggregate formation is described kinetically as a function of the concentration, size and densities of colliding particles (Praetorius et al. 2012; Quik et al. 2014). According to the von Smoluchowski particle interaction model, the rate of formation of aggregates is represented by (Elimelech et al. 2013)

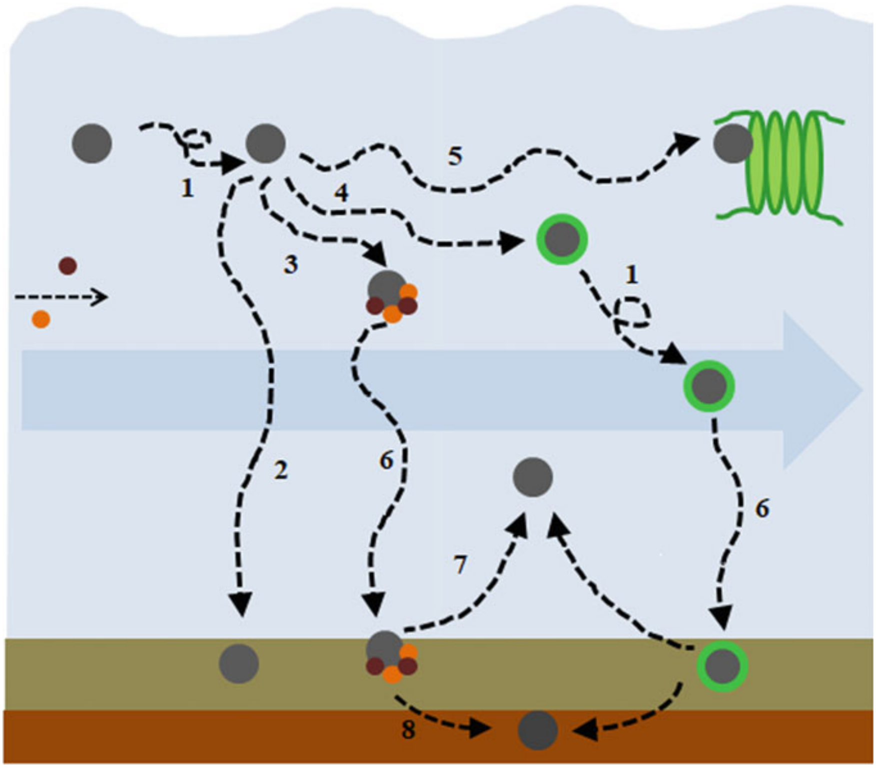

Fig. 4.2 Schematics of different key processes involved in the transport of buoyant and non-buoyant microplastics and nanoplastics in water current. The process includes (1) turbulent transport, (2) settling of non-buoyant MPs, (3) aggregation, (4) surface biofouling of MPs, (5) imbibition of MPs by biota, (6) burial and (7) resuspension. Aggregates are formed with sediment, organic matter, co-pollutants or dissolved substances. Other processes viz. ingestion and excretion by higher aquatic animals (e.g. zooplankton, mussels, fish, etc.) are not included here

$$\frac{\mathrm{d}n_k}{\mathrm{d}t} = \frac{1}{2}\sum_{\substack{i+j\to k\\ i=1}}^{i=j-1} k_{ij}n_i n_j - n_k\sum_{k=1}^{\infty} k_{i,k}n_i$$

where n_i and n_j are the number concentration of aggregates with i and j number of primary particles, respectively. n_k is the number concentration of aggregates with k number of primary particles. In the equation, first expression in the right-hand side represents the rate of formation of k-fold aggregates by collision of any pair of aggregates in a way that summation of i and j becomes k $(i + j = k)$. The second expression represents the loss of k-fold aggregates by collision and aggregation with any other aggregates. k_{ij} and k_{ik} represent the rate constant of formation and loss of k-fold aggregates.

Though in many studies, the shape of particles was considered spherical, the use of fractal dimension brings out the better collision frequency and sedimentation estimates (Lee et al. 2000). The transportation of plastic particles in river is different from other freshwater bodies viz. lakes. Since, river has downward movement due to longitudinal gradient, the time average direction of plastic particles in the river is longitudinal; thus, the advection flow of plastic particles is much higher than dispersive flow (Ji 2008). However, the river often may act as sink for the plastic particles through the process of river sedimentation (Mahmood 1987). Thus, dams in the rivers that enhance the water retention time and reduce the flow velocity may lead to increase deposition of non-buoyant plastic particles. Besides influence of dams, other human uses viz. water treatment plants and irrigation channel also influence the fate of the plastic debris as they are never carried to the marine ecosystem.

4.3 Fate of Microplastics in River

After entering the riverine system, the plastic particles do not remain stationary, and they transport from small streams to large streams and ultimately to marine environments with varying residence time. The transport of plastics including MPs in the riverine ecosystem is governed by its hydrology and morphology at specific river sites (vegetation pattern, presence of groynes and barrages). Synthetic polymers have been greatly studied for their degradation pathways in the natural environment. However, their behaviour may not be same as for plastic in which there are other constituents based on the targeted use besides synthetic polymer as the major ingredient. It is a well-established fact that synthetic polymers are designed to resist environmental degradation factors leading to very slow degradation process and long residence time in the environment. Mainly, the degradation can be classified into biotic and abiotic processes; however, the role of biotic process is reported to very minimal. The abiotic process can be further categorised into mechanical/physical processes, chemical and photochemical processes. At last, the degradation processes lead to development of

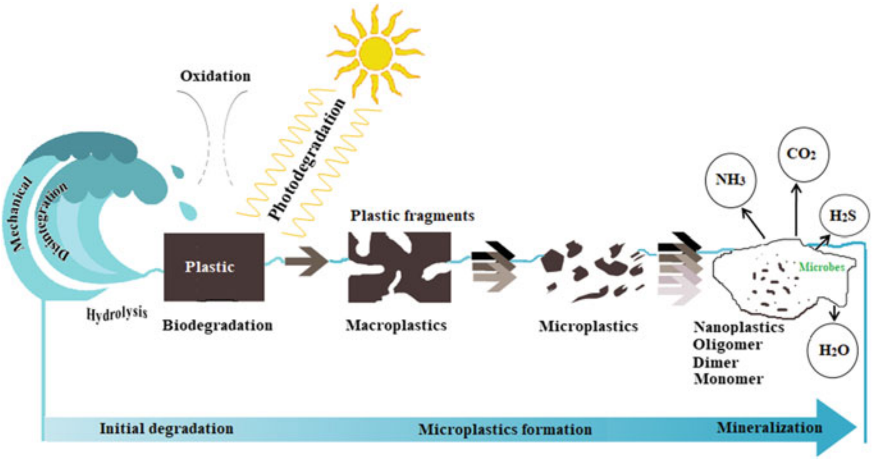

Fig. 4.3 Degradation pathways of plastic materials in flowing water bodies with various degradation processes involved till complete mineralisation

fragments of low molecular weight (viz. oligomers and monomers) and their other chemical derivatives, followed by complete mineralisation (Eubeler et al. 2009).

The important degradation processes of plastic material can be listed as (1) mechanical/physical degradation (abrasive forces due to water current, heating/cooling, wetting and drying); (2) photochemical (UV wavelength); (3) chemical degradation (hydrolysis and oxidation); (4) biodegradation (bacteria, fungi, algae) (Fig. 4.3). The degradation of the plastic is usually started with the photochemical process (photo-oxidation) in the presence of UV light and or through hydrolysis followed by chemical oxidation process (Andrady 2011) depending on the chemical composition of plastic material (polyesters, polyamides, acrylic, etc.). The rate of photo-oxidative degradation of plastic is determined by the type of additives (antioxidant) added into the plastic materials and the vertical positioning of the plastic materials in the water column. Figure 4.4 depicts the abiotic degradation pathways of polyethylene (PE), polypropylene (PP) and polystyrene (PS) describing photolytic cleavage of polymeric backbone (Gewert et al. 2015). The backbone of PE-, PP-, PS- and PVC-based plastics has only carbon–carbon chain and thus vulnerable to photo-oxidative degradation that is divided into three steps viz. initiation, propagation and termination. Initiation step begins with breaking of the polymer chains by light to form free radicals. For photo-induced initiation, the polymer necessities presence of chromophoric groups that absorb light; however in PE, PP, PS and PVC, it may be initiated by presence of small amount external impurities having chromophoric moieties. During propagation step, the free radicals present in the polymer chain react with oxygen to produce peroxy radicals leading to autoxidation and ultimately leading to the chain scissioning or crosslinking. In the termination step, termination of the radical reaction occurs through combination of two radicals. Similarly, photolytic and hydrolytic degradation also occur in polyethylene terepthalate (PET) as

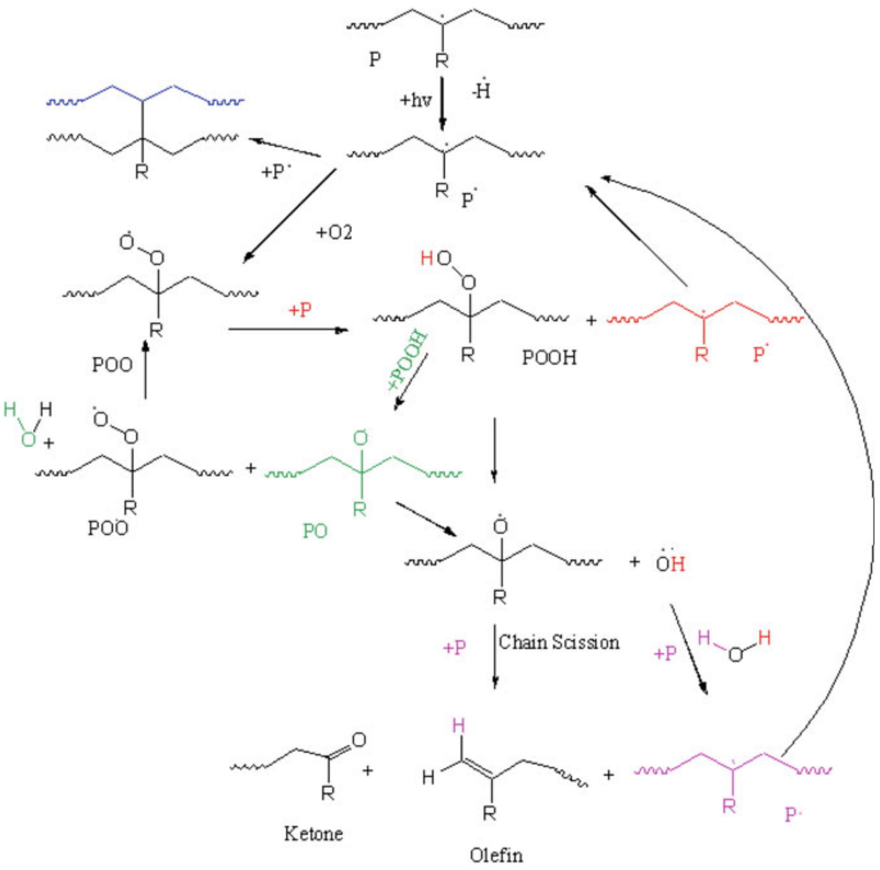

Fig. 4.4 Photodegradation of pathways of the PE (R = H), PP (R = CH3) and PS (R = aromatic ring); P indicates the polymeric backbone (Gewert et al. 2015)

described in Fig. 4.5 which depicts that photo-hydrolytic degradation leads to breaking of the ester linkages forming carboxylic acid end group and vinyl end group or leads to the formation of free radicals which eventually forms carboxylic acid end group (Gewert et al. 2015). Photo-induced autoxidation of the PET leads to the formation of hydro-peroxide at the methylene group leading to the chain scission. Under aquatic environment, PET is also susceptible to hydrolysis leading to reverse esterification forming carboxylic acid and alcohol functional groups. This hydrolysis process is very slow in low temperature; however, it is single most important process of degradation under low temperature (Venkatachalam et al. 2012). It was reported that plastic materials (PE and PS) present on surface water shows quick degradation as compared to partially or completely submerged plastic materials due to reduced light intensity (Grima et al. 2000). Mechanical degradation can be considered as one of the most critical degradation factors for plastic material in flowing

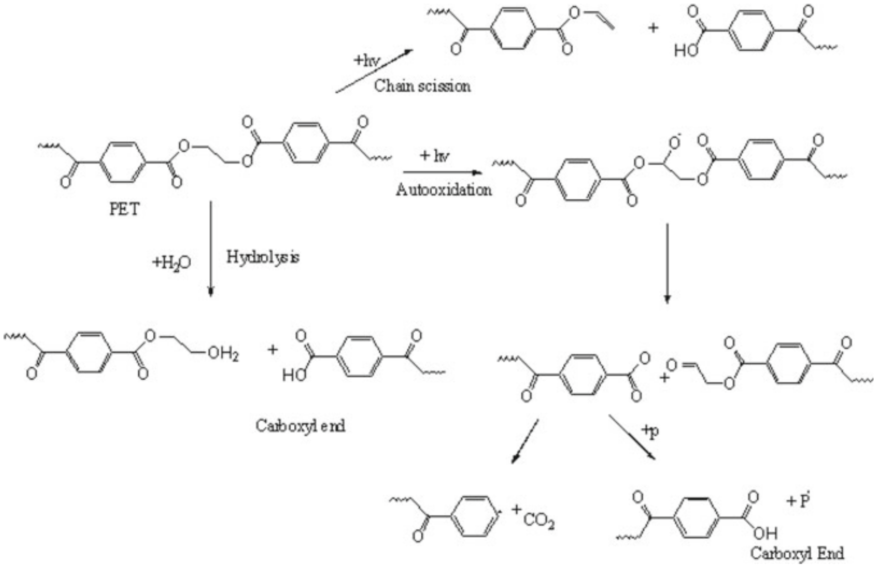

Fig. 4.5 Photolytic and hydrolytic degradation pathways of PET (Gewert et al. 2015)

aquatic bodies. After aging through the chemical and photochemical degradation process, the plastic materials become brittle, and then, it is shredded into small pieces (microplastics/MPs, <5 mm) by friction forces during transportation with the water current. The fragmentation into small pieces is likely to continue endlessly leading to very fine plastic particles in nanometre range (nanoplastics) which could have different physiochemical properties as compared to macroplastic or MPs (Rist and Hartmann 2017).

Since most of the plastics (PE, polypropylene (PP), PS, PET, etc.) are hydrophobic in nature, their degradation by microbes is very slow or rare. Their carbon–carbon backbone is not readily accessible by the microorganism and thus should undergo an abiotic transformation viz. oxidative or photo-oxidative degradation as prerequisite (Weinstein et al. 2016). This abiotic transformation is further delayed by the presence of antioxidants which is added during production step. After the consumption of antioxidants, the photo-oxidative degradation can be started layer by layer followed by microbial degradation (Reddy et al. 2009). Since, plastic materials are composed of long-chain polymers, the microbes must be able to produce enzyme with depolymerisation capacity. These extracellular enzymes are produced to cleave the side chains and polymeric backbone leading to the formation of smaller polymer units (oligomers) which are subsequently consumed to produce monomers. These smaller monomer molecules can be readily absorbed by the microorganism and metabolised.

4.4 Aquatic Ecotoxicity of Microplastics

4.4.1 Toxic Effect of MPs Uptake

After entering to the aquatic system, the mobility and disintegration process generates a blend of parent plastic particles, fragmented particles and other non-polymeric degradation products. Thus, the exposure effect of this complex blend of plastics and associated chemicals to aquatic organisms varies within the time-space. The uptake of MPs by aquatic organisms occurs directly from water column and sediment, and the most important uptake routes include ingestion, dermal uptake or through respiratory surfaces. It was reported that the toxicity of MPs could affect all aquatic organisms through its trophic transfer potential (Farrell and Nelson 2013). It was reported that the freshwater zooplankton *Bosminacoregoni* uptakes PS beads (2–6 μm) when exposed and could not differentiate between MPs and algae (Bern 1990). However, the study also reports that *Daphnia cucullata* can differentiate between PS MPs and preferentially uptook algal cell. In contrast, another study reports that *D. magna* could readily ingest nanobeads and microbeads of PS and retained to greater extent within the organism (Rosenkranz et al. 2009). The chronic effect of secondary MPs (mean size 2.6 μm) against *D. magna* was also studied and found that it leads to elevated mortality, increased inter-brood period, reproduction disability at concentration of 105,000 MPs particles L^{-1} (Ogonowski et al. 2016). The trophic transfer of MPs was observed from blue mussels (*Mytilus edulis*) to crabs (*Carcinusmaenas*) (Farrell and Nelson 2013). The mussels exposed to PS MPs (0.5 μm) at concentration of 1 million particles mL^{-1} was able to transfer PS microsphere to crab haemolymph (15,033 particles mL^{-1}) within 24 h.

The shape and size of MPs play important role in the uptake process to the biota. A smaller particle size of MPs, mimicking food particles, will be better ingested by the organism than larger size. Angular-type MPs are more refrained to dislodge than smooth spherical particles and thus can cause obstruction to gills and digestive tract. Physical effect of microplastics ingestion on the aquatic organisms has been reviewed recently, and the mechanisms include blockages of the digestive system, blockages of feeding appendages, abrasion of tissues, reduction in enzyme production, lower feeding stimulation, embedment in issues, decreased growths, nutrient dilution, lower steroid hormone levels and impaired reproduction (Wright et al. 2013a, b). Biological effect of nano and microplastics against some aquatic organisms is listed in Table 4.1.

4.4.2 Toxic Effect of Leaching Chemicals

Since commercial plastics are made of petroleum resources and consist specifically of synthetic polymers viz. PE, PP, PS, polyvinyl chloride (PVC), etc., they differ in chemical and physical properties such as density, porosity, thermal conductivity

Table 4.1 Biological effect of nano and microplastics against aquatic organism

Damage type	Organism	Reference
Impaired metabolism and cellular stress response	Polychaetes	Wright et al. (2013a, b)
	Echinoderms	Della Torre et al. (2014)
	Bivalves	Avio et al. (2015), Paul-Pont et al. (2016), Sussarellu et al. (2016), Canesi et al. (2015)
	Fish	Cedervall et al. (2012), Greven et al. (2016), Lu et al. (2016)
Tissue damage	Fish	Karami et al. (2016), Lu et al. (2016), Peda et al. (2016)
Tissue transfer	Crustaceans	Rosenkranz et al. (2009)
	Mussels	Browne et al. (2008), von Moos et al. (2012)
	Fish	Kashiwada (2006)
Impaired respiration	Polychaetes	Green et al. (2016)
	Crustaceans	Watts et al. (2016)
	Bivalves	Rist et al. (2016)
Impaired feeding	Polychaetes	Wright et al. (2013a, b), Besseling et al. (2013)
	Crustaceans	Cole et al. (2015), Ogonowski et al. (2016)
	Bivalves	Rist et al. (2016), Wegner et al. (2012), Cole and Galloway (2015)
	Fish	Cedervall et al. (2012)
Impaired development and reproduction	Crustaceans	Cole et al. (2015), Lee et al. (2013), Besseling et al. (2014)
	Echinoderms	Nobre et al. (2015)
	Bivalves	Sussarellu et al. (2016)
	Fish	Lönnstedt and Eklov (2016)
Decreased growth rates and biomass production	Crustaceans	Ogonowski et al. (2016), Besseling et al. (2014)
	Bivalves	Rist et al. (2016)
Behavioural changes	Fish	Cedervall et al. (2012), Lönnstedt and Eklov (2016), de Sá et al. (2015)
Increased mortality	Crustaceans	Ogonowski et al. (2016), Rehse et al. (2016)
	Bivalves	Rist et al. (2016)
	Fish	Mazurais et al. (2015)

Table 4.2 Types of additives used in plastics

Types	Function
Plasticisers	To make the plastic flexible
Flame retardants	To reduce flammability
Crosslinking additives	To link polymer chain
Antioxidants and other stabiliser	To reduced oxidative degradation rate
Sensitisers	To accelerate degradation process
Surfactants	To modify surface properties
Inorganic filler	To reinforce the plastics
Pigments	To induce colour

and additives types. Additives are added in the plastic material to make them suitable for intended purpose. Thus, within a single class of plastics, the performances may differ depending on the type and quantity of additives used. It was reported that additives even may constitute up to 50% of the total mass of plastics and can be of both organic and inorganic origin (Oehlmann et al. 2009). Plastic particles containing biocidal additives, plasticizers or flame retardants are found to be more environmentally hazardous as these substances may leach out to the environment. Types of some chemical additives used in plastics is listed in Table 4.2.

It is always very difficult to assess the effect of leaching chemicals viz. monomers, impurities, byproducts and other additives on the aquatic organisms since the leaching mixture composition depends on the physic-chemical and biological conditions of the environments (Muncke 2009). However, it is being studied under laboratory conditions through the leaching of water-soluble constituents in deionised water (Lithner et al. 2012; Lithner et al. 2009).The effect of leachates (liquid–solid (*L*/*S*) ratio of 10, 24 h) from polyvinyl chloride (PVC), polyurethane (PUR) and polycarbonate (PC) was studied against *D. magna,* and they found to be toxic with EC_{50} values of 5–69 g plastic L^{-1}.With higher *L*/*S* ratio and longer time duration, plasticised PVC and epoxy resin were found to be more toxic with EC_{50} of 2–235 g plastic L^{-1}.

4.4.3 MPs as Vector of Co-pollutants

Through different routes, MPs enter into aquatic bodies and come in contact with other environmental contaminants. It was reported that hydrophobic pollutants with low water solubility sorbed easily on the plastic particles thus improves their transport and ultimately changes their distribution and bioavailability (Teuten et al. 2007). Thus, plastic particles, considered generally as inert and non-toxic material, potentially become a carrier of toxic compounds (Rochman 2015). Different organic chemicals (log K_{OW} from 0.90 to 8.76) were tested for their plastic (HDPE, LDPE, PP, PS, PVC, etc.) to water partitioning coefficients (log K_{PW}), and it was found that good correlation exists between log K_{OW} and log K_{PW} suggesting adsorption of the organic chemicals on to plastic particles is driven by hydrophobic interaction (O'Connor 2016). Further, study shows that plastic particles with smaller size have better capacity to adsorb hydrophobic pollutants (Brandl et al. 2015). Beside these parameters, the properties of surrounding media (e.g. pH, specific conductivity, etc.) also influence the adsorption process and subsequently the dissociation of chemical pollutants from the plastic particles. Not only organic pollutants, it was also reported that heavy metals also get accumulated on the MPs surface (Brennecke et al. 2016). The source of these data is mainly from marine system; however, little report is available on freshwater and terrestrial ecosystem. The accumulation of these pollutants occurs through sorption process which may be physisorption or chemisorptions. Another mechanism is pore-filling process, which happens when the hydrophobic pollutants enter the polymer matrix filling the small pores. The process is highly dependent on the pore diameter and the molecular size of the pollutants. The sorption of pollutants (either physic or chemisorption) on the MPs surface is highly dependent on the environmental parameters viz. pH, temperature, ionic strength, etc., and polymer characteristics. MPs characteristics like polymer type, density and crystallinity, types of additives, etc., influence the sorption kinetics (Brennecke et al. 2016). It was postulated that sorption and diffusion of pollutants occur mostly in the amorphous region of the plastic material as compared to the crystalline region which is more ordered and tightly packed. For these reasons, low-density polyethylene (LDPE) was reported to be used for passive sampling of PAHs, PCBS and other hydrocarbons from the aquatic environments (Bao et al. 2012). As compared to high-density polyethylene (HDPE), the LDPE contains high concentration of branches that prevent the polymer chain to stack side by side resulting low crystallinity and low density (0.90–0.94 g cm^3). Besides these parameters, the most important factor is particle size of MPs which will influence the sorption parameters proportionally.

4.5 Detection of Microplastics in the Aquatic System

The analysis of MPs in the aquatic environmental samples is highly challenging and strongly depends on the compartments viz. water phase (surface water and water column) and solid phase (shoreline sediments, riverbed or lakebed sediments). The process becomes more tedious with high organic loading samples. Due to organic nature, the analytical options of MPs are limited especially when they are present in association of other natural organic matrix. It is easy to extract the large-sized MPs through filtering water samples or through density-based fractionation of sediments. However, it is very difficult to separate smaller MPs or nanoplastics from the water and sediment matrix. Moreover, the microscopic identification becomes tedious for transparent or semi-transparent plastic particles.

4.5.1 FT-IR Analysis

A simple combination of stereomicroscopy and Fourier-transformed infrared (FT-IR) spectroscopy can lead to under or over estimation of MPs due to limitation of identification technique between natural and synthetic polymer or non-detection of transparent plastic particles (Song et al. 2015). MPs identification with standard FT-IR requires visual pre-sorting of potential plastic particles with limitations of prolonging time requirement and error occurrence. Recently, with development of FT-IR combined with microspectoscopy (i.e., μ-FT-IR), the identification of very small-sized MPs (few micrometre) has become possible due to improvement of spatial resolution (Harrison et al. 2012; Löder et al. 2015). In contrast to standard FT-IR machine, μ-FT-IR with focal plane array detectors does not require pre-sorting of MPs with advantages of high throughput analysis of the environmental samples (Harrison et al. 2012; Löder et al. 2015; Tagg et al.2015). Currently, plastic particles more than 10–20 μm size could be identified using this technique (Rist and Hartmann 2018). The only disadvantage of the FT-IR based system is that it has very limited scope for plastics with unknown chemical compositions. The absorbance or transmittance bands of pure plastic materials are included in the library, and they are matched with the extracted plastic materials to detect the chemical composition. Thus, it becomes very difficult to identify unknown plastic fragments from environmental samples, as the FT-IR bands of plastics may change due to the degradation on the plastic surface (Song et al. 2015). Figure 4.6 depicts the infrared spectrum of PE which shows characteristics band of stretching and bending vibration of $–CH_3$ and $–CH_2$ at 2850–3000 cm^{-1} and 1350–1480 cm^{-1}, respectively, whereas the biotically (*Aspergillus niger*)-degraded PE shows the small bands at 1715 and at 940 cm^{-1} corresponding to the ketonic carbonyl group and alkene group (Raghavan and Torma 1992).

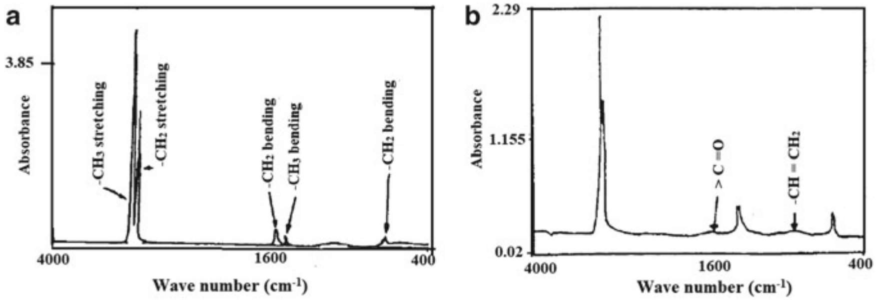

Fig. 4.6 Infrared spectrum of polyethylene film (A), abiotically degraded PE film and biotically (*Aspergillus niger*) degraded PE film

4.5.2 Raman Spectroscopy

Raman spectroscopy was also used to identify plastic particles. Here also, it is combined with microscopy and a spatial resolution of 1 μm can be achieved (Löder and Gerdts 2015). The identification by spectroscopic method (FT-IR and Raman) is affected by the environmental-driven changes on the surface of plastic material or by the presence of additives. Therefore, microbial fouling, humic acid adsorption, presence of colouring pigments, etc., interfere with the absorbance, reflectance or excitation of the plastics and sometimes lead to the misidentification of the particles (Lambert and Wagner 2018).

4.6 Aquatic Risk Assessment of MPs

Since the size of MPs is the most important factor, the risk assessment due to MPs could be based on the same. The MPs of varying particle size possess different risks to the aquatic organisms. Fish may avoid larger plastic particles but have the risk of ingestion of small MPs (<5 mm) while feeding. Through trophic transfer, the plankton eating fish may encounter MPs with size range from nanoscale to 5 mm or more and thus possess a huge effect on ecological health (Tanaka and Takada 2016). It has been described that floating MPs with less density are mostly associated with lower organisms, viz. phytoplankton and zooplankton, whereas benthic invertebrates viz. polychaete worms, amphipods, molluscs and echinoderms show more association with MPs with high density. Thus, higher vertebrates such as fishes also swallow MPs from these lower organisms and benthic vertebrates through prey-predation relationship. Occurrence of MPs was estimated in the sediments of some of major river systems, for example, Rhine River (228–3760 items/kg) (Klein et al. 2015), Beijiang River (178–544 items/kg) (Wang et al. 2017), Thames River (185–660 items/kg) (Horton et al. 2017), Ganga River (99.27–409.86 items/kg) (Sarkar et al. 2019), and it has been found that the dominant plastic debris was found to be PE, PP and PET, which are reported to be the most dominant plastic debris in the rivers of Asia and South East Asia. The most important morphotypes of the plastic particles were found to be the films and fibres. More recently, MPs contamination with fibres is being emphasised as compared to the other morphotypes like films and beads. It was revealed in some reports that the major source of these fine fibres are garments which are released to aquatic system through washing of same (Napper and Thompson 2016).

The differential sources of primary and secondary MPs have huge influences on their risk management and regulatory options. Regulatory measures can successfully minimise the risk associated with industrially produced primary MPs to acceptable levels through regulating their point of production and use. Example of such upstream regulation are US Microbead-Free Waters Act of 2015, which prohibits companies to use microbeads in beauty and health products from 2017 (FDA 2017); UK bans on microbead use from 2018 (GUV.UK 2018), etc. However, managing secondary MPs pollution is much more challenging involving general action against all sort of plastic entering into the ecosystem during all steps viz. production, use and disposal management. To reduce the quantity of mismanaged plastic waste, various government agencies are taking regulatory steps. A recent report by United Nations Environment Program on ‘Single-use plastics: A Roadmap for Sustainability’ underscores the annual environmental damage to the global marine ecosystem at $13 billion (UNEP 2018). Single-use plastics are referred to as disposal plastics which are commonly used for packaging and other plastic items, for example, grocery bags, straws, cups and cutlery, etc., intended to be used only once before they are thrown away or recycled. It was estimated that 47% of global plastic waste generated in 2015 is accounted by plastic packaging waste (UNEP 2018). Many countries including Canada and India had pledged to ban single-use of plastics, such as, straws, drink stirrers, styro foam cups, etc.

4.7 Conclusion

MPs are considered as one of the significant emerging contaminants, and they are being found ubiquitously distributed all over the globe. Their distribution study is being well documented in marine ecosystem; however, the same is still in infancy stage in the river ecosystems at global platform. The rivers are considered as the major source of MPs contamination in the marine ecosystem. The transport of plastic particles and subsequent possible formation of MPs through various processes in river ecosystems will highlight their possible ill effect on the freshwater biota and a vast human population residing on the bank of these river systems. Since each river has its own hydrodynamic characteristics and anthropogenic load on them, modelling MPs abundance and their fate analysis should be viewed critically, and individual approach should be taken for each river ecosystems. Advanced detection tools such as Raman, FT-IR along the microscopes in tandem are considered to be versatile for the detection of microplastic in the river water or sediment samples. However, more smart and sophisticated detection procedure is still awaited since microplastics comprises of many synthetic polymers with gradient of molecular weights and polymeric branching along with the effect of various additives, hence rendering multidimensional array of physical and chemical characteristics.

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Chapter 5
Assessment of Groundwater Quality in Sri Lanka Using Multivariate Statistical Techniques

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5.1 Introduction

Groundwater supplies more than 85% of safe drinking water available for rural communities living in Asian countries including Sri Lanka because no or less treatment is often required and source is located near the consumer (Panabokke 2007). Additionally, groundwater significantly contributes on the agricultural water supply through agro-wells. Population growth, overuse of pesticides and agrochemicals, salt–water intrusion use of water resources for multiple competing uses have caused to fast depletion of groundwater quality and the quantity posing a threat to public health. Groundwater contains various types of pollutants and several other substances, but concentration which is required for human health is defined at a specific limit (Singh et al. 2020). According to the WHO, 80% of diseases are caused by water. Therefore, it is important to evaluate the groundwater quality in order to implement the preventive measures and monitoring procedures.

Groundwater quality is influenced by many natural and anthropogenic factors. Water–rock interactions, aquifer depth, recharge rate and evapotranspiration rate are some of the natural factors (Liu et al. 2003; Panabokke 2007; Panabokke and Perera 2005; Villholth and Rajasooriyar 2010; Singh et al. 2020; Kumar et al. 2010). Anthropogenic activities such as over extraction, inherent contaminants, overuse of agrochemicals and pesticides also affected to change of the water quality. (Villholth

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and Rajasooriyar 2010; Kumar et al. 2016; Das et al. 2015). Elevated concentrations of fluoride in groundwater are one of the well-explored contaminants inherent in Sri Lanka (Villholth and Rajasooriyar 2010; Young et al. 2011; Dissanayake and Chandrajith 2007), while nitrate pollution is a global threat exerted on groundwater (Liu et al. 2003; Villholth and Rajasooriyar 2010; Wongsasuluk et al. 2014). Groundwater quality degradation may make it unusable for human use (Noshadi and Ghafourian 2016). Once a groundwater source is contaminated, its quality cannot be restored back easily (Dohare et al. 2014). Hence, measuring both physical and chemical parameters is important to estimate or predict the quality of groundwater (Liu et al. 2003). Therefore, groundwater quality assessment is a high priority concern under current situation in Sri Lanka.

Mutivariate statistical analysis techniques are widely used to evaluate surface and groundwater quality. Many studies have used cluster analysis (CA), factor analysis (FA), principal component analysis (PCA) and discriminant analysis (DA) for data reduction and classification. These techniques enable us to obtain relationships between parameters and sampling sites and also idea about the degree of similarities and dissimilarities among the various parameters present in sampling sites. This identification can be extended to identify major factors and sources influencing the groundwater quality, hence increasing the viability of groundwater quality monitoring and water resource management (Nosrati and Van Den Eeckhaut 2012; Noshadi and Ghafourian 2016). Although there are several studies conducted on groundwater quality in Sri Lanka, those studies have covered a selected area of the country, either coastal aquifers or a selected area with specific health problems (Dissanayake and Chandrajith 2007; Young et al. 2011; Chandrajith et al. 2014). In this background, this study focused on conducting a groundwater quality assessment representing groundwater wells located within entire country. Hence, water quality analysis was conducted on a total of 1262 groundwater wells distributed all over the country for 18 water quality parameters. Thereafter, multivariate statistical analysis techniques were applied to the data set. Cluster analysis was used to classify the groundwater wells based on their quality. The most influential parameters on the classification were identified through factor analysis and discriminant analysis. Using the evaluation results, finally it is aimed to increase the viability of water resource management and protection in Sri Lanka by providing statistical analysis result as there is no such study carried out for entire country.

5.2 Materials and Methods

5.2.1 Study Area

Sri Lanka is located in the Indian Ocean, close to southeastern coast of Indian subcontinent. Total area of Sri Lanka is 65, 610 km^2 and divided into 25 administrative districts, while 4% is covered by water (Climate Change Secretariat Sri Lanka—Ministry of Mahaweli Development and Environment 2016). The island consists mostly of flat to rolling coastal plains, with mountains rising only in the south–central part. In the lowlands (altitude of 100–150 m), the mean annual temperature varies between 26.5 and 28.5 °C, with an annual temperature of 27.5 °C. In the highlands, the temperature falls quickly as the altitude increases. It is 15.9 °C in Nuwaraeliya. Sri Lanka is influenced by the monsoons, allowing four distinct seasons, as a result of lying in the equatorial and tropical zone. Therefore, monsoons and inter-monsoons are considered as the major rainfall pattern experienced by different regions of Sri Lanka. Rainfall patterns divided Sri Lanka into major three climatic zones; wet zone (annual rainfall >2500 mm), dry zone (annual rainfall 1200–1900 mm) and semi-arid zone (annual rainfall >1200 mm).

5.2.2 Sampling and Data Collection

Groundwater sampling was conducted in 1262 sampling wells distributed in 25 administrative districts and all climatic zones in Sri Lanka from 2010 to 2013. The wells were randomly selected, and the locations were identified by GPS. Samples were filtered on-site and then stored in pre-washed polyethylene bottles using membrane filtering technique (pore size of 0.45 μm) to separate suspended particulate matter from the fluid and soluble component. Thereafter, they were sent to Japan for analysis. Distribution of sampling locations is shown in Fig. 5.1.

The pH value of the water was measured on-site by glass electrode method using a pH metre (Beckman Coulter, Inc. Model Φ260) with the STAR electrode 511,070. Electrical conductivity (EC) was measured by using a conductivity metre (HORIBA B-173; detection limit is 1–19.91 μC/cm). Major anions, fluoride, chloride, nitrate and sulphate were determined by using ion chromatography (For anions: DIONEX ICS 2000, Separation column ionPac AS18, Eluent KOH 23–40 mmol/L (gradient), Suppressor; ASRS 300 4 mm). Cations such as sodium, magnesium and calcium were also measured by using ion chromatography (For cations: DIONEX IC-1500, Separation column ionPac CS12, Eluent MSA 30 mmol/L (isocratic), Suppressor; CSRS 500 4 mm). Detection limit of fluoride is 0.2–2.0 mg/L, while it is 1.0–10.0 mg/L for chloride, nitrate and sulphate. The limit is 0.5–10.0 mg/L for the above anion. Concentration of metals in well water including aluminium (14.1–99.00), cadmium (0.7–7.5), lead (2.4–25.1), zinc (6.9–47.0), nickel (2.6–24.9), copper (5.2–49.9), arsenic (1.5–15.0), chromium (5.0–49.9) and iron (46.7–756.9) were determined by using ICP-OES (Perkin Elmer Optima 5300) or ICP-MS (Agilent 7700) with the detection limits as mention in the brackets in μg/L.

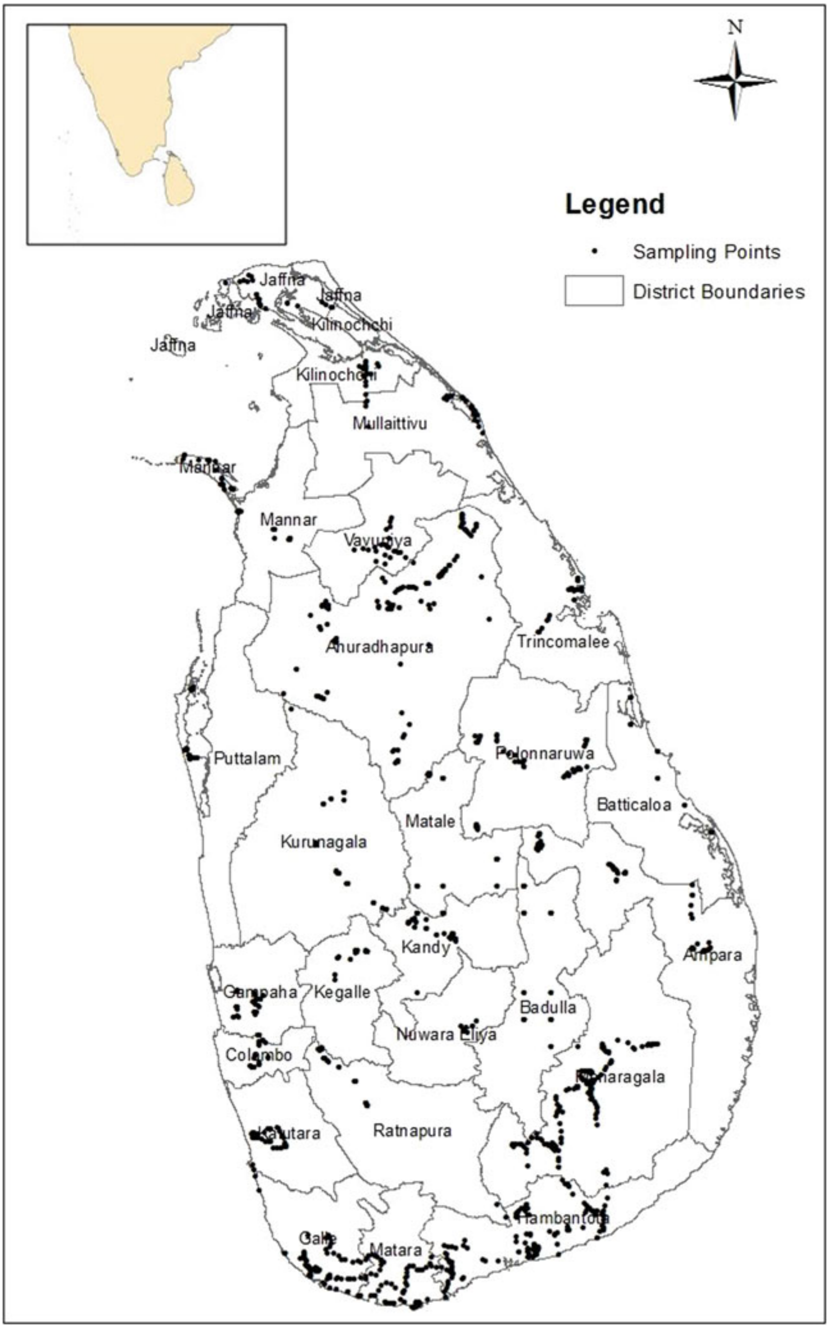

Fig. 5.1 Distribution of groundwater sampling locations ($n = 1262$)

5.2.3 Statistical Analysis

Data were standardized using Z scale transformation (Nosrati and Van Den Eeckhaut 2012).

$$\boldsymbol{Z} = \frac{(\boldsymbol{X} - \boldsymbol{x})}{\boldsymbol{S}}$$

Here, $\boldsymbol{X}$, $\boldsymbol{x}$ and $\boldsymbol{S}$ are representing unedited values of variable, mean and standard deviation, respectively. It is necessary in multivariate cluster analysis to improve homogeneity of data. Further, it ensures that data are in vicinity of the variance and all the variables are weighted equally in hierarchical cluster analysis (Noshadi and Ghafourian 2016 and Daughney et al. 2012).

Statistical analyses of the data were performed using SPSS version 16.0 (SPSS Inc. 2004) and the Statistica version 12.

5.2.4 Cluster Analysis

Cluster analysis (CA) was performed to classify the data set into groups based on the attributes of the objects with respect to a set of special characteristics (Noshadi and Ghafourian 2016). Accordingly, samples having high homogeneity levels are classified under same category, while samples having high heterogeneity levels are classified under different categories (Juahir et al. 2011). Hierarchical agglomerative CA was performed on the standardized data set by means of the Ward's method, using squared Euclidean distances as a measure of similarity.

5.2.5 Factor Analysis

Factor analysis (FA) is used to reduce the contribution of less significant variables by simplifying the data resulting from a principal component analysis (PCA) (Nosrati and Van Den Eeckhaut 2012). PCA was performed on the standardized data set in order to transmute original data set into uncorrelated new variables called principal components (PCs), which are linear combinations of the original data set. In PCA, the eigenvalues are a measure of their associated variances (Meglen 1992). Factors having eigenvalues >1 explain more total variance, while factors having eigenvalue <1 explain less total variance. Therefore, PCs having eigenvalue higher than 1 were retained, while PCs having eigenvalue less than 1 are normally neglected (Juahir et al. 2011).

Varimax rotation was applied to the retained factors. Rotation of PCs is a simple and a meaningful representation of the retaining factors as it decreases the contribution of the variables with minor significance to PCs and increases the more significant parameters (Razmkhah et al. 2010). Further, it redistributes the variance of each factor to enhance the relationship between the independent variables.

5.2.6 Discriminant Analysis

Discriminant analysis (DA) was applied to identify discriminations between two or more groups in terms of the discriminating variables (Usman et al. 2014). DA consists of finding a transform, which gives the maximum ratio of difference between a pair of group multivariate means to multivariate variance within the two groups (Davis 1986). It is concerned with the relationship between a categorical variable and a set of inter-related variables based on the set of measurements. These coefficients represent the maximum distance between the means of the dependent variable (McLachlan 2004).

Eigenvalues, Canonical-R, Wilks' Lambda, Chi-square, and p-value tests are used to produce the discriminant function table. These tests help to determine whether discriminant functions are statistically significant. The eigenvalue is a measure of ratio of importance of the dimensions, which classify cases of the dependent variable. Canonical correlation (R) is a measure of the association between the groups which are formed by the dependent variable and the given discriminant function (Nosrati and Van Den Eeckhaut 2012). If the values are close to 1, it is considered as a strong association. Further, Nosrati and Van Den Eeckhaut (2012) explain the functioning of Wilks Lambda in discriminant analysis. Significance of the discriminant function as a whole will be assessed by Wilks' Lambda test. Wilk's Lambda is an indication of the proportion of the total variance in the discriminant scores which are not explained by differences among the groups. Test values range between 0 and 1. If the value is close to 0, group means are different. A Chi-square transformation of Wilks' Lambda is used along with the degrees of freedom to determine significance of the test. If the value is <0.10, group means differ (Davis 1986).

5.3 Results

5.3.1 Spatial Clustering

All sampling wells were grouped into two major clusters in the analysis; 298 wells were grouped into cluster 1, and 964 wells were grouped into cluster 2 (Fig. 5.2). Almost all of the points in cluster 1 lie on intermediate zone or dry zone of the country, while only two points lie on the wet zone; one is in Galle district, and other one is at the boundary of Matara district. Both points have been grouped into cluster 2 due to the extreme values in some parameters. One sampling well (Galle) had extreme concentrations of chromium (6.07 mg/L) and nickel (14.8 mg/L), while the

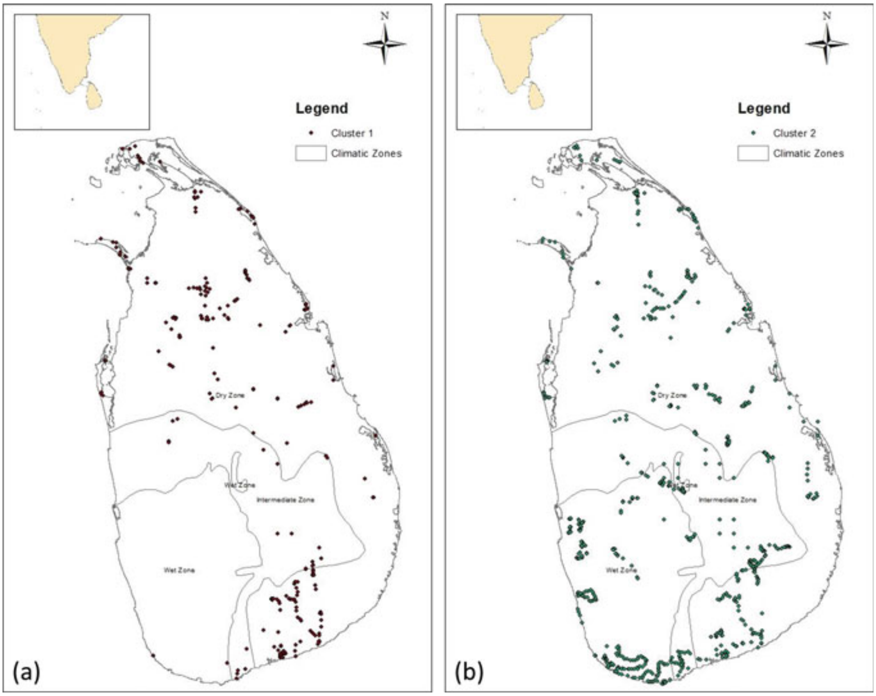

Fig. 5.2 Spatial clustering of sampling wells; cluster 1 **a** and Cluster 2 **b**

other sampling well in Matara had extremely higher nitrate (45.60 mg/L) and calcium (80.50 mg/L) concentrations compared to nearby sampling wells. Groundwater wells grouped into cluster 2 were distributed all over the country.

Average (±SD) values of groundwater quality variables for the two clusters were calculated, and *t* test was carried out for the variables as the average values of measured water quality parameters, except nickel and lead, in two clusters were found to be significantly different (Table 5.1). The average concentrations of fluoride, EC, pH, chloride, nitrate, sulphate, sodium, magnesium, calcium, chromium, nickel, arsenic and cadmium were significantly higher in cluster 1 compared to cluster 2. Other metal ions such as aluminium, iron, copper, zinc and lead showed a higher average value in cluster 2. Regarding fluoride and magnesium, average concentrations in cluster 1 exceeded permissible level for drinking water (SLS 2013). Average concentrations satisfied Sri Lankan Standard for drinking water regarding the other parameters (SLS 2013).

The maximum admissible fluoride concentration is 1.0 mg/L as per the Sri Lankan Standard (SLS), while it is 1.5 mg/L in World Health Organization (WHO) guidelines (WHO 2008). Average value in cluster 1 (1.789 mg/L) exceeded this maximum permissible limit for potable water (51% wells exceeding 1.0 mg/l). In cluster 2, only 81 out of 964 (8%) wells exceeded Sri Lankan standards, while average value is 0.349 mg/L. Regarding magnesium, Sri Lankan standard (SLS 2013) is 30 mg/L,

Table 5.1 Proportion of variance using varimax rotation and communality estimates of groundwater quality parameters in Sri Lanka

Variables	VF1	VF2	VF3	VF4	VF5	VF6	Communality estimates
Fluoride (mg/L)	0.171	−0.035	0.023	**0.571**	−0.241	0.007	0.415
EC (µS/cm)	***0.957***	−0.05	0.001	0.188	0.093	−0.005	0.962
pH	0.319	−0.142	−0.146	**0.71**	0.117	−0.069	0.666
Chloride (mg/L)	***0.904***	0.002	0.046	0.002	0.075	−0.004	0.825
Sulphate (mg/L)	***0.808***	0.029	0.023	−0.097	0.051	0.015	0.666
Nitrate (mg/L)	0.15	0.001	0.078	−0.281	**0.639**	0.121	0.53
Sodium (mg/L)	***0.867***	0	0.014	0.135	−0.006	−0.006	0.77
Magnesium (mg/L)	***0.796***	−0.075	0.008	0.267	−0.038	−0.01	0.713
Calcium (mg/L)	**0.732**	−0.097	−0.022	0.197	0.249	−0.001	0.646
Aluminium (µg/L)	−0.062	***0.879***	0.095	−0.152	0.008	0.019	0.809
Chromium (µg/L)	−0.016	0.158	0.116	0.535	0.451	0.117	0.543
Ferrous (µg/L)	−0.043	***0.884***	−0.017	0.072	0.009	−0.017	0.789
Nickel (µg/L)	0.187	0.135	**0.556**	0.058	−0.004	0.039	0.368
Copper (µg/L)	−0.041	−0.022	**0.695**	0.004	0.008	−0.038	0.487
Zinc (µg/L)	−0.109	−0.056	***0.755***	−0.148	0.112	−0.041	0.621
Arsenic (µg/L)	0.127	−0.019	−0.032	0.142	**0.677**	−0.151	0.518
Cadmium (µg/L)	0.038	0.08	0.377	0.108	−0.21	0.391	0.359
Lead (µg/L)	−0.025	−0.034	−0.089	−0.042	0.05	***0.897***	0.819
Eigenvalue	4.878	1.802	1.441	1.202	1.177	1.005	–
% Total Variance	25.183	9.157	8.709	8.085	7.119	5.666	–
Cumulative % Variance	25.183	34.34	43.04	51.13	58.25	63.92	–

Bold, italic values indicate strong (>0.75), and bold values indicate moderate (0.75–0.50) loadings, respectively and average magnesium concentration in cluster 1 and cluster 2 was 42.470 mg/L and 10.879 mg/L, respectively. Nitrate and arsenic concentrations exceeding Sri Lankan standards (SLS 2013) were found in several districts. Agricultural activities in sandy soils in coastal areas in Puttalam, Mannar, Jaffna, Vavuniya are associated with excessive use of nitrogen fertilizer. Most of the above areas are located on the soil type 'Sandy regosols on recent beach and dune sands' where higher arsenic concentrations (>10 μg/L) were also reported.

5.3.2 Discriminant Analysis

Standard mode, forward stepwise mode and backward stepwise mode of DA were used to obtain classification matrices as shown in Tables 5.2 and 5.3. Then, the Chi-square tests were applied for each mode, and results are shown in Table 5.4. The eigenvalue >1.5, canonical correlation >0.75, Wilks' Lambda <0.4 and Chi-square transformation of Wilks' Lambda show that the clusters are significantly different. Finally, 14 parameters were remained in the forward stepwise mode, while it was reduced to ten in the backward stepwise mode (Table 5.2).

In all analyses, classification matrices assigned 93% of the cases accurately (Table 5.3). However, in the backward stepwise mode, data set was classified into two clusters by using only ten water quality parameters (Tables 5.2 and 5.3). Hence, fluoride, EC, sulphate, nitrate, sodium, magnesium, chromium, nickel, arsenic and cadmium were identified as the most significant parameters to discriminate the two clusters. Therefore, DA was able to substantially reduce the number of parameters necessary for categorization. Box and whisker plots were constructed to evaluate different patterns associated with spatial variations in groundwater quality in two clusters (Fig. 5.3). As shown in the Fig. 5.3, Z scale transformed values (Y-axis) clearly indicated the differences in mean values between two main clusters for each parameter.

5.3.3 Factor Analysis

Factor analysis was able to explain >69% of variability by first six varimax factors (VFs) in terms of measured groundwater quality parameters, in which eigenvalue >1. They were able to explain >96% of variance in EC; >82% in chloride; 81% > in lead; 80% > in aluminium; >70% in sodium, magnesium and iron; 60% pH, sulphate, calcium and zinc; 50% in nitrate, chromium and arsenic; <50% in fluoride, nickel, copper and cadmium (Table 5.5).

According to Liu, factor loadings can be classified as 'strong', 'moderate', 'weak' corresponding to absolute loading values; >0.75, 0.75–0.50, 0.50–0.30, respectively. The highest proportion (25.18%) of the total variance was explained by VF1. It had strong positive loadings on EC, chloride, sulphate, sodium, magnesium and calcium.

Table 5.2 Classification functions resulting from discriminant analysis applied to the clusters of groundwater wells in Sri Lanka

Variables	Standard mode $F = 110.62$			Forward mode $F = 142.52$			Backward mode $F = 196.90$		
	$p < 0.000$			$p < 0.000$			$p < 0.000$		
	Cluster 1	Cluster 2	p value	Cluster 1	Cluster 2	p value	Cluster 1	Cluster 2	p value
Fluoride	1.045	−0.339	0.000	1.045	−0.339	0.000	1.081	−0.351	0.000
EC	1.424	−0.462	0.003	1.431	−0.466	0.002	1.175	−0.418	0.000
pH	−0.294	0.073	0.017	−0.300	0.076	0.011	–	–	–
Chloride	−0.543	0.155	0.018	−0.546	0.158	0.017	–	–	–
Sulphate	−0.752	0.229	0.000	-0.756	0.231	0.000	−0.597	0.186	0.000
Nitrate	0.537	−0.174	0.000	0.536	-0.174	0.000	0.571	−0.181	0.000
Sodium	1.085	−0.314	0.001	1.086	−0.315	0.001	0.749	−0.203	0.001
Magnesium	1.534	−0.447	0.000	1.533	−0.447	0.000	1.529	−0.444	0.000
Calcium	0.261	−0.084	0.142	0.265	−0.085	0.136	–	–	–
Aluminium	0.002	−0.005	0.964	–	–	–	–	–	–
Chromium	0.424	-0.121	0.000	0.424	−0.120	0.000	0.393	−0.113	0.000
Ferrous	−0.044	0.018	0.654	–	–	–	–	–	–
Nickel	−0.322	0.099	0.000	−0.327	0.100	0.000	−0.367	0.113	0.000
Copper	−0.068	0.017	0.460	–	–	–	–	–	–
Zinc	−0.137	0.043	0.135	−0.158	0.048	0.069	–	–	–
Arsenic	0.603	−0.182	0.000	0.601	−0.181	0.000	0.590	−0.179	0.000
Cadmium	0.585	−0.177	0.000	0.577	−0.175	0.000	0.580	−0.175	0.000
Lead	0.013	−0.005	0.868	–	–	–	–	–	–
(Constant)	−4.015	−0.519	–	−4.012	−0.519	–	−3.968	−0.515	–

Table 5.3 Classification matrix resulting from discriminant analysis applied to the clusters of groundwater wells in Sri Lanka

Sampling sites	% Correct	Sampling sites assigned by DA	
		Cluster 1	Cluster 2
Standard mode			
Cluster 1	73.913	221	78
Cluster 2	98.961	10	953
Total	93.026	231	1031
Forward mode			
Cluster 1	73.913	221	78
Cluster 2	98.961	10	953
Total	93.026	231	1031
Backward mode			
Cluster 1	72.909	218	81
Cluster 2	99.273	7	956
Total	93.026	225	1037

Table 5.4 Chi-square tests for discriminant analysis applied to the clusters of groundwater wells in Sri Lanka

Function	Eigen value	Canonical-*R*	Wilks' Lambda	Chi-square	Df	Sig.
Standard mode	1.601	0.784	0.384	1196.261	18	0.00
Forward mode	1.600	0.784	0.384	1197.265	14	0.00
Backward mode	1.573	0.781	0.388	1186.516	10	0.00

VF2 and VF3 explain approximately 9% of the total variance by each component. VF2 had strong positive loading on aluminium and iron, while VF3 had a strong positive loading on zinc and moderate positive loadings on nickel and copper. VF4, explaining 8% of the total variance, had a moderate positive loadings on fluoride, pH and chromium. Further, chromium had an approximately similar loading on VF5 also. VF5 accounted for 7.1% of total variance, had a moderate positive loading on nitrate and arsenic, chromium. Finally, VF6 explained 5.7% of total variance with a strong positive loading on lead only. Cadmium had no strong or moderate correlation with any VF, while it has weak loading on VF3 and VF6.

5.4 Discussion

There are six main types of aquifers in Sri Lanka. Depth of groundwater table and recharge rate vary with the type of aquifer and the climatic zone (Panabokke 2007).

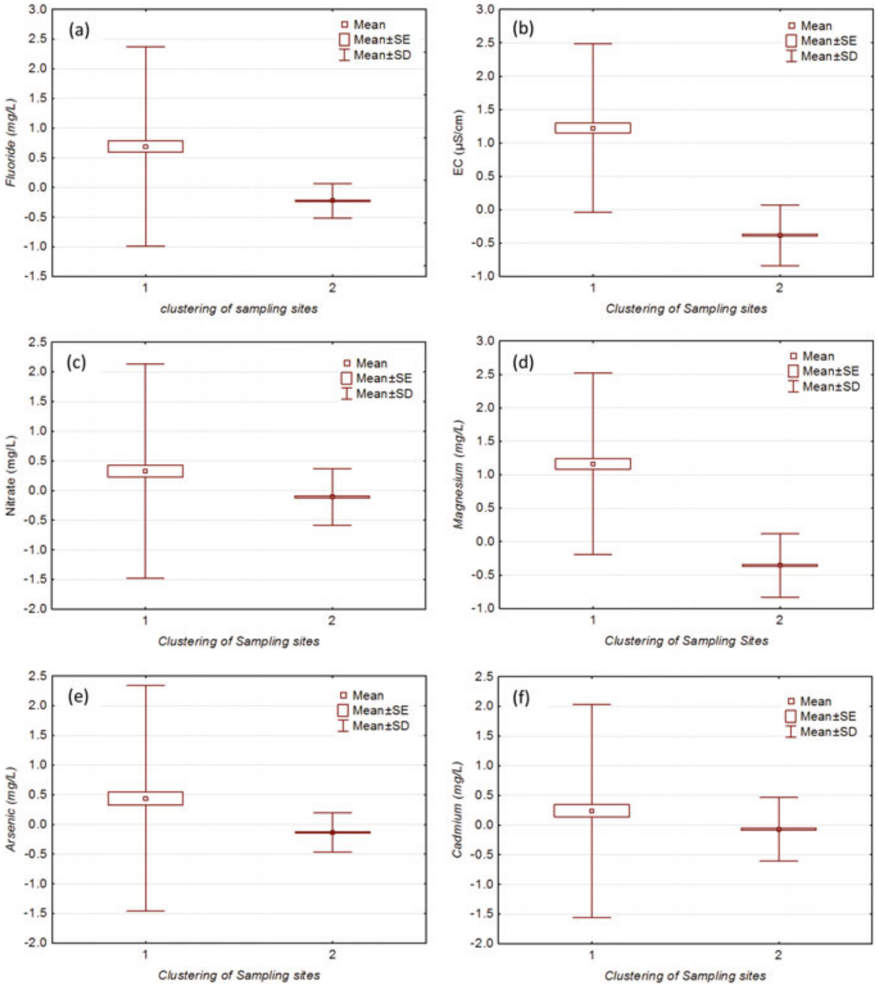

Fig. 5.3 Box and whisker plots of discriminating parameters (parameter values in Y-axis are Z scale transformed values.); Fluoride **a** EC **b** Nitrate **c** Magnesium **d** Arsenic **e** and Cadmium **f**

Consequently, these variables cause variations in the groundwater quality. According to spatial cluster analysis, 298 sampled wells were grouped into cluster, 1 and those wells had high mineral concentrations compared to cluster 2. Wells grouped in cluster 1 (except two sampling wells) were located in intermediate (intermediate zone is the area sandwiched between the wet and dry zones receiving a mean annual rainfall of 1750–2500 mm.) and dry zone of Sri Lanka, while 964 wells located in all three climatic zones were clustered under cluster 2. Shallow karstic aquifer, shallow aquifers on coastal sands, deep confined aquifer, alluvium aquifer and regolith aquifer of hard metamorphic rock region are the main types of aquifers located in intermediate and dry climatic zones (Panabokke 2007). Shallow karstic aquifer is limited to the western

Table 5.5 Mean (±SD) and significant values of groundwater quality variables in two clusters obtained by cluster analysis in Sri Lanka

Variable	Cluster 1 (n = 298)			Cluster 2 (n = 964)			t test value	p value	SLS for Drinking water
Fluoride (mg/L)	**1.79**	±	0.161	0.349	±	0.014	8.901	0.00	1.0
EC (μS/cm)	1441	±	47.4	404	±	9.50	21.423	0.00	1500[a]
pH	7.93	±	0.016	7.32	±	0.025	20.416	0.00	6.5–8.5
Chloride (mg/L)	200	±	11.7	34.6	±	1.41	14.019	0.00	250
Sulphate (mg/L)	104	±	10.2	16.9	±	0.666	8.526	0.00	250
Nitrate (mg/L)	14.42	±	2.07	5.37	±	0.299	4.326	0.00	50
Sodium (mg/L)	168	±	8.61	33.0	±	1.02	15.61	0.00	200
Magnesium (mg/L)	**42.4**	±	1.64	10.9	±	0.321	18.884	0.00	30
Calcium (mg/L)	79.7	±	2.89	33.5	±	0.882	15.32	0.00	100
Aluminium (μg/L)	3.99	±	1.00	25.9	±	3.67	−5.752	0.00	200
Chromium (μg/L)	0.58	±	0.06	0.250	±	0.014	4.834	0.00	50
Ferrous (μg/L)	8.45	±	0.94	17.2	±	2.01	−3.955	0.00	300
Nickel (μg/L)	1.08	±	0.09	0.942	±	0.043	1.504	0.464	20
Copper (μg/L)	1.68	±	0.18	3.07	±	0.755	−1.777	0.017	1000
Zinc (μg/L)	4.81	±	0.64	16.3	±	1.67	−6.401	0.00	3000
Arsenic (μg/L)	1.78	±	0.27	0.375	±	0.026	5.14	0.00	10
Cadmium (μg/L)	0.013	±	0.002	0.005	±	0.000	2.82	0.00	3
Lead (μg/L)	0.104	±	0.026	0.426	±	0.299	−0.599	0.287	10

n is the number of wells in each classification cluster. Concentrations exceed SLS are highlighted in bold

[a] EC as per the salinity standard

part of Jaffna peninsula (it is underlain by Miocene limestone formations), and eastern part is dominated by sandy regosols on recent beach and dune sands (Panabokke and Perera 2005). Sandy regosols support a different type of aquifer. Therefore, quality of the groundwater obtained from shallow coastal aquifers is different compared to the karstic aquifers (Panabokke 2007). Shallow aquifers on coastal sands are freshwater bulbs floating on saline water and recharge mainly from the 3 to 4 months of rain received from north to eastern monsoon (Chandrajith et al. 2014). Deep confined aquifers located within sedimentary limestone and sandstone formations of the north–western and northern coastal plains, and they are relatively deep and have a relatively high recharge rate (Panabokke and Perera 2005). However, a few alluvial aquifers are also found in the area. Alluvial aquifers are associated with alluvial landforms such as coastal and inland rivers and inland valleys. Deeper and larger alluvial aquifers are associated with Mahaweli ganga, Kirindi oya, Kelani ganga, Daduru oya, etc. (Panabokke and Perera 2005). Metamorphic hard rock regions cover around 80% of the island and weathered and fractured crystalline rocks bear water (Panabokke and Perera 2005). However, groundwater potential in the hard rock regions is limited. South–western lateritic aquifers confined to the wet zone of Sri Lanka (Panabokke and Perera 2005). It has considerably high water holding capacity due to its vascular nature, and this aquifer is relatively shallow. In the meantime, the water level is rapidly fluctuating in response to the precipitation patterns (Panabokke and Perera 2005). Overexploitation and contamination tremendously pressurize these aquifers (Villholth and Rajasooriyar 2010). Lateritic aquifers, alluvial aquifers and coastal sand aquifers have comparatively higher recharge rate due to their shallow nature (Panabokke 2007; Villholth and Rajasooriyar 2010). Further, they receive freshwater frequently, and hence, mineral ion concentration is lower. In contrast, shallow nature makes them contaminate easily by anthropogenic pollutants dissolved in rainwater runoffs (Villholth and Rajasooriyar 2010). Therefore, depending on the aquifers in which they are located, groundwater wells located in dry and intermediate zones are grouped into either cluster 1 or 2. Since several types of aquifers are available in adjacent areas, clear boundaries with different groundwater quality controlled by soil distribution or climatic condition are not identifiable in Sri Lanka. However, groundwater in wet zone is generally similar in quality hence clustering under cluster 2 only. Furthermore, relatively high precipitation and associated recharge may govern the water quality in the wet zone of Sri Lanka. Most of the heavy metal ions are proven to be entered into the surface and groundwater due to anthropogenic activities (Tchounwou et al. 2012; Azizullah et al. 2011). In agreement with that, higher concentrations of above metal ions were observed in districts such as Colombo, Kandy, Gampaha, Kalutara, Nuwaraeliya and Galle (Fig. 5.1) those are considered as highly urbanized and industrialized districts in Sri Lanka. Further, all these districts are located in wet zone of Sri Lanka, which receives plenty of rainfall during north–western monsoon.

Water quality parameters retained in the backward stepwise DA are fluoride, EC, sulphate, nitrate, sodium, magnesium, chromium, nickel, arsenic and cadmium. Among them, nitrate, chromium, nickel, arsenic and cadmium are identified as anthropogenic pollutants (Leung and Jiao 2006; Wongsasuluk et al. 2014), while others mineral ions are supposed to enter into groundwater through natural phenomena. Hence, discrimination of clusters had based on dissolved constituents enter into groundwater by anthropogenic and natural phenomena both.

Regarding the factor analysis, VF1 had strong positive loadings on EC, chloride, sulphate, sodium, magnesium and calcium. Gathering of above ions in one factor usually reflects the effect of natural processes such as dissolution of carbonate, dolomitic and evaporative minerals in the groundwater (Bencer et al. 2016; Noshardi and Ghafourian 2016). Jiang et al. (2009) also hypothesize that high positive loadings on EC, calcium and magnesium together due to water–rock interactions. Further, dissolution of sulphide bearing minerals and chloride bearing minerals may add those ions into water. Although sodium, chloride and sulphate are liable to enter into groundwater through sewage effluents and chemical fertilizers, then they should show a correlation with nitrate (Jiang et al. 2009). In our analysis, nitrate occupies separate factor. Hence, VF1 is assumed to reflect natural geological interactions with groundwater.

VF2 and VF3 are occupied by two groups of metal ions; VF2 is by aluminium and iron, and VF3 is by zinc, nickel and copper. Aluminium and iron may leach into groundwater during mineral weathering of hard rocks such as feldspars and granites (Braga et al. 2002; Leung and Jiao 2006), and biotite and granite occur in hard metamorphic rocks, and regolith aquifers are associated with that (Young et al. 2011). Further, numerous anthropogenic activities, such as industrial effluent discharge, sewerage and landfill leachate, may also contribute to increase aluminium and iron in groundwater (Leung and Jiao 2006). Further, storm water contains high concentrations of aluminium, iron, zinc, copper, chromium, cadmium, nickel and lead (if leaded petrol still in use) (Leung and Jiao 2006). In our analysis, higher average value of all five metal ions is shown in cluster 2. Therefore, it can be assumed that aluminium and iron in groundwater are entered through anthropogenic activities and natural rock–water interactions both because other three common metal ions (zinc, nickel and copper) found to enter into groundwater through industrial effluents and runoff are occupying a separate factor. Although zinc, nickel and copper can be entered into groundwater through natural processes, the dominant phenomenon of their availability in groundwater in Sri Lanka may be industrial activities.

There are a lot of studies carried out regarding fluoride concentration in Sri Lankan groundwater (Young et al. 2011). Fluoride can enter into groundwater easily from rocks and soils, which are rich in fluoride-bearing minerals. Severe weathering of these rocks and minerals in the tropical climate enhances the entry of fluoride into the groundwater and is therefore leached out from the fluoride-bearing minerals (Young et al. 2011). In the factor analysis, fluoride and pH occupy a separate factor. Wang et al. (2002) states that ‘The adsorption of fluoride in soils decreased from humid areas to arid areas and from acidic soils to alkaline soils’. This may explain the positive relationship observed between pH and fluoride dissolved in groundwater (VF4 in factor analysis). Further, easy leachability of fluoride in the wet zone may cause lower fluoride in wet zone, while dry zone has fluoride rich groundwater (Dissanayake and Chandrajith 2007).

VF5 had a moderate positive loading on nitrate and arsenic, chromium. Nitrogenous fertilizers, organic manures, human and animal wastes and the effluent from industrial activities are the major sources of nitrate in groundwater (Villholth and Rajasooriyar 2010, Jiang et al. 2009, Noshardi and Ghafourian 2016). Arsenic and nitrate occupy same factor in the factor analysis. However, arsenic concentrations exceeding 10 ug/l [Sri Lankan standard for drinking water (SLS 2013)] were found in groundwater wells associated with the soil type of 'sandy regosols on recent beach and dune sands' only. Coincidently, these areas are agricultural areas, and farmers use high amount of nitrogen fertilizers for papaya, onion, vegetables and tobacco (Specifically in Kalpitiya peninsula) cultivations in the coastal belt. Further, nitrate pollution in different levels was observed in all agricultural areas in Sri Lanka, while some of them observed to exceed 50 mg/l, Sri Lankan standard for drinking water (SLS 2013). For example, Anuradhapura and Badulla districts located in the middle of the country also showed high nitrate concentrations at some locations, but arsenic concentrations were less than 10 ug/l Sri Lankan standard for drinking water (SLS 2013) in Badulla or Anuradhapura district. Therefore, arsenic has no relationship with nitrate, which is strong enough to indicate that arsenic may come from fertilizer. However, there are reports that arsenic, chromium and other heavy metals may enter into the groundwater through agrochemicals and retain in groundwater since sandy soils are poor in adsorption. However, clayey soils in other agricultural areas may adsorb arsenic hence cannot observe in groundwater in dissolved forms (Wongsasuluk et al. 2014, Liu et al. 2006). Correlation of chromium with nitrate may also explain the agrochemical usage (Liu et al. 2003).

The sources of lead in groundwater are soil, air, used lead products and the use of lead pipes and roofing material (WHO 2011). Dissolution of residues of vehicle emission in the groundwater through precipitation may be the way of addition of lead into water bodies and to increase the concentration of lead in groundwater (Leung and Jiao 2006). According to the Annual Performance and Accounts Report of Ministry of Environment, Sri Lanka (2001), vehicle gas emission is very high in Colombo, Galle and Kandy districts, in which higher concentrations of lead in groundwater were observed. The groundwater table is higher in above districts, since they locate in wet zone of Sri Lanka, hence storm water runoff may easily filtrate to the groundwater (Villholth and Rajasooriyar 2010). Hence, lead may enter into groundwater through vehicle emission, and this hypothesize is supported by the higher values of lead in wet zone and occupying separate factor; VF6.

5.5 Conclusion

In this study, spatial variations in groundwater quality in Sri Lanka were evaluated using multivariate statistical analysis techniques. Sampled groundwater wells ($n = 1262$) were clustered into two different clusters based on the attributes of the groundwater quality parameters. The average concentrations of fluoride, EC, pH, chloride, nitrate, sulphate, sodium, magnesium, calcium, chromium, nickel, arsenic and cadmium were significantly higher in cluster 1 compared to cluster 2. Other metal ions such as aluminium, iron, copper, zinc and lead showed a higher average value in cluster 2. Regarding fluoride and magnesium, average concentrations in cluster 1 exceeded permissible level for drinking water (SLS 2013). Average concentrations satisfied Sri Lankan standard for drinking water regarding the other parameters (SLS 2013). Groundwater wells located in dry and intermediate zones, which were rich in mineral ions due to rock–water interactions and lower recharge rates, were clustered into cluster 1. Shallow aquifers in wet zone and coastal areas and wells located on alluvial aquifers were clustered into cluster 2, and they were located in all three climatic zones of the country. Shallow wells in the country, specifically wells located in wet zone, were found to be liable to pollute by anthropogenic pollutants (heavy metals). Nitrate pollution and liability to nitrate pollution are high in agricultural areas, especially dry and intermediate zones are at high risk, because they receive low precipitation, hence recharge rate is low. Shallow wells located in karstic aquifer in Jaffna peninsula and coastal aquifers in Kalpitiya peninsula are some examples.

Discriminant analysis (backward stepwise mode) reduced the number of discriminating parameters into ten, but they were a mixture of ions dissolved in groundwater by anthropogenic activities and natural interactions. Since several types of aquifers are available in adjacent areas, clear boundaries with different groundwater quality controlled by soil distribution or climatic condition are not identifiable in Sri Lanka.

Further, factor analysis resulted in six factors, which may influence on groundwater quality of Sri Lanka. Factors analysis was able to explain >69% of variability in measured groundwater quality parameters. Factor 1 was accounted for natural rock–water interactions, while factor 2 and 3 were identified as dissolution of heavy metals due to natural processes and anthropogenic activities both. VF4 was occupied by fluoride and pH. Fluoride is encountered in minerals and geochemical deposits. Fluoride removal efficiency depends on the pH where the value is getting decreased from acidic soil to basic soils. VF5 had a moderate positive loading on nitrate and arsenic, chromium and fertilizer, and agrochemical usage may govern this factor. VF6 was occupied by lead only and hypothesized that it may due to dissolution of vehicle emission in runoff and entering into shallow aquifers. Finally, it can be concluded that anthropogenic activities such as agrochemical usage, fertilizer usage and industrialization have an influence on Sri Lankan groundwater already though have not exceeded beyond the acceptable levels. However, it is noteworthy that discriminant analysis resulted in a mixture of ten parameters to discriminate groundwater quality in two clusters, hence the influence of anthropogenic pollutants on groundwater is not negligible, and continuous assessment of groundwater quality is a necessity to avoid groundwater contamination in Sri Lanka.

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Chapter 6
Source and Fate of Perchlorate in the Environment: A Grave Concern for World

Paulami Sahu

6.1 Prologue

Perchlorate is an emerging contaminant and considered as a worldwide health issue as it disrupts normal functioning of human thyroid gland by interfering in iodide uptake by it and poses serious threat to overall growth of human, dominantly of foetus and children, by affecting the regulation of metabolism and brain development (Plummer et al. 2006). Perchlorate (ClO_4^-) is a naturally occurring inorganic anion of oxyhalide salts that is frequently detected in the environment (Rajagopalan et al. 2006), and though ClO_4^- of ammonium (NH_4^+), potassium (K^+), magnesium (Mg_2^+) and sodium (Na^+) remain inert at solid state, it can pollute water and soil when dissolved in water (Duncan et al. 2005). Perchloric acid ($HClO_4$) also contaminates soil and water. As chlorine in ClO_4^- has a maximal +7 oxidation state, it shows a very strong oxidizing character, and it is highly soluble too (Kumarathilaka et al. 2016). In terms of kinetics, at ambient condition, ClO_4^- is relatively stable, and this stability is due to the tetrahedral arrangement of oxygen atoms around central chlorine atom, and these oxygen atoms restrict central chlorine to react with reductants (Xu et al. 2015). Due to this stable nature, ClO_4^- may persist for very long period of time, may be decades, in surface and groundwater (Sturchio et al. 2014). This persistent behaviour of the ClO_4^- compelled many environmentalists to determine the fate of ClO_4^- in the environment. At ambient temperature, common ClO_4^- compounds are mainly solid in nature and appeared as white or clear crystals. Their physical properties and uses are given in Table 6.1.

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Table 6.1 Characteristics and uses of some perchlorate compounds

Compound	Formula	Molecular weight (g/inol)	Deusity (g/cm^3)	Physical appearance	Aqueous solubility at 20 °C (10^3 mg/L)	Decomposition temp. (°C)/Reaction	Uses
Ammonium perchlorate	NH_4ClO_4	117.488	1.952	Colourless or white orthorombhic and regular crystals	217–220	150	Energetic booster in rocket fuel
Sodium perchlorate	$NaClO_4$	122.439	2.02–2.499	Hygroscopic/deliquescent, white orthorombhic crystals	2010	492	Strong oxidizing agent used in explosive and chemical industries
Potassium perchlorate	$KClO_4$	138.547	2.5298	Colourless crystal to white crystalline powder, hygroscopic	7.5–16.8	440	Solid oxidant for rocket production
Lithium perchlorate	$LiclO_4$	106.3906	2.428–2.429	Deliquescent, white crystal	375	<250–400	Electrolyte in voltaic cells, synthesis of organic chemicals
Perchloric acid	$HClO_4 2H_2O$	223.21	2.21	White, hygroscopic powder	Very soluble	250	Analytical, oxidizing and dehydrating agent

Source Modified table after Sturchio et al. (2003) (Srinivasan and Viraraghavan 2009)

In this chapter, different aspects of ClO_4^- such as (a) brief history of ClO_4^- contamination; (b) sources of ClO_4^-: natural and anthropogenic; (c) fate of ClO_4^- in water; (d) probable effect of ClO_4^- on different life forms; (e) standard and measuring methods for ClO_4^- and (f) its degradation and remediation strategies have been discussed.

6.2 Brief History of Perchlorate Contamination

In 1985, ClO_4^- was first detected in wells at industrial sites in California, USA. But it was first observed as a chemical of concern in 1996, when fertilizers containing $NaClO_4$ and $KClO_4$ have negative health impact on certain agricultural crops (Nzengung et al. 1999). From 1997 onwards, with advancement of more sophisticated analytical methods, detection and identification of ClO_4^- in groundwater, surface water, soil and food become easier (Rice et al. 2007).

6.3 Origin and Sources of Perchlorate

By origin, ClO_4^- is either natural or synthetic and is either naturally occurring chemical substance or chemical derivative of anthropogenic activities. Natural ClO_4^- assemblages are mostly found in arid and semi-arid regions of earth (Rao et al. 2007) and are of atmospheric or geogenic in origin (Cao et al. 2019). In arid and semi-arid regions, due to less precipitation, net infiltration is also less, and therefore, mobilization of ClO_4^- to groundwater is restricted. In addition, higher evapotranspiration rate leads to higher ClO_4^- accumulation on the ground of semi-arid and desert parts of the world compared to other regions (Albright et al. 2008).

6.3.1 Natural Perchlorate

6.3.1.1 Origin and Occurrence

Natural atmospheric process is responsible for formation of natural ClO_4^-. Most probably the chloride in the form of NaCl from sea or terrestrial chloride composites blown towards atmosphere, and photochemically reacts with atmospheric ozone to produce ClO_4^- (Trumpolt et al. 2005). In the marine environment, the photolysis of ozone occurs in the presence of sea salt which is expected to create chlorine (Cl_2) and hypochlorous acid (HOCl) (Oum et al. 1998). In the course of time, the chlorate (ClO_3^-) formation has been predicted in the stratosphere (Von Clarmann 2013). The formation of hypochlorite radicals (OCl^-) occurs when molecular chlorine (Cl_2) dissolute in water (Siddiqui 1996). The addition of oxygen molecule to chlorate (ClO_3^-) or fractionation of hypochlorite may possibly result in the formation of ClO_4^- radical. All the above-mentioned reactions are thermodynamically favourable, but the major cause intended for not forming considerable amounts of perchlorate may be kinetic. It should be feasible to influence the formation of perchlorate by providing the precursor ingredients and adequately energetic environments. With the reference to a recent theory, it is suggested that, additionally, there is a probability that lightning may show an important capacity to create some atmospherically produced perchlorate. Furthermore, ClO_4^- formation is also influenced by UV-mediated photo-oxidation (Dasgupta et al. 2005). Another natural source of increased atmospheric ClO_4^- is volcanic eruptions (Furdui et al. 2018). Following its formation in atmosphere, ClO_4^- returns to the earth's surface in dissolved form along with precipitation. In arid and semi-arid regions, its rate of deposition is much more than its rate of dissolution during precipitation, and therefore, with time, ClO_4^- is integrated and becomes a part of specific geologic formations (Urbanski et al. 2001). Terrestrial soil ClO_4^- concentrations ranging from10^{-1} to 106 $\mu g\ kg^{-1}$ have been estimated in the Atacama Desert (Chile), southwestern United States, southern Africa, United Arab Emirates, northwestern China and Antarctica (Jackson et al.; Lybrand et al. 2016). The ClO_4^- accumulation in soils/caliche relies on its deposition rate and on site-specific geologic, hydrologic and biogeochemical conditions (Cao et al. 2019). Occasional precipitation in arid regions reduces the chances for ClO_4^- in potash deposits to dissolve and migrate to groundwater. Therefore, ClO_4^- would remain in these deposits in higher quantities than other locations with higher precipitation (Srinivasan and Viraraghavan 2009).

6.3.1.2 Environmental Release of Natural ClO_4^- by Human Activities

The anthropogenic pathway of introduction of ClO_4^- into the environment is more dominant than the geogenic sources. ClO_4^- containing products are the main anthropogenic sources for ClO_4^- contamination. For example, Colorado River water and Lake Mead water are highly polluted by rocket fuel production unit in Henderson, Nevada, and it is a big anthropogenically ClO_4^- contaminated site. Paleogeochemical deposits of sodium nitrate and ClO_4^- of the Atacama Desert are considered as a rich source of naturally occurring ClO_4^-. Anthropogenic activities like mining and application for agricultural and industrial purposes released ClO_4^- in the environment. From 1830 onwards, Chilean nitrate was exported to the USA, France and England for agricultural uses. But during World War I, consumption pattern of Chilean nitrate is completely transformed from agricultural use towards gunpowder and explosives production. As a consequence, the Chilean nitrate production raised by many fold, almost upto 3 million tons, to meet the increased demand of explosives during World War I and therefore, it is introduced into environment (Cao et al. 2019). During the World War I, European countries and the USA together consumed about 97% of the total Chilean nitrate produced (Ericksen 1981; Wisniak and Garcés 2001). Besides anthropogenic uses of Chilean nitrates, due to intensive agriculture in arid and semi-arid environments, natural ClO_4^- accumulating in unsaturated areas can be readily flushed and mobilized by introduction of percolation process. Continuous irrigation has displaced accumulated salts to a greater depth of several meters, and ClO_4^- is migrated from unsaturated zone to groundwater regime (Rao et al. 2007; Scanlon et al. 2010). Recent study of Furdui et al. (2018) indicates that anthropogenic activities trigger another atmospheric input to ClO_4^- sources that are chlorinated solvents (e.g. methyl chloroform).

6.3.2 Synthetic Perchlorate

6.3.2.1 Production and Uses

In the 1890s, synthetic ClO_4^- was manufactured commercially for the first time in Masebo, Sweden (Trumpolt et al. 2005). Most common industrial process used for synthetic ClO_4^- production is use of electrolytic method using sodium chloride as feedstock (Brown and Gu 2006). Since World War II, ClO_4^- was extensively used as explosives and propellants. In the USA, 90% of ammonium perchlorate consumption is accounted for the military uses (Duncan et al. 2005). Synthetic NH_4ClO_4 is used as a propellant in solid rocket fuels (Mendiratta et al. 1996), and as a consequence, synthetic ClO_4^- producing industries are substantial industry in the USA and Europe nowadays. Some other uses of ClO_4^- are fireworks, signal flares, white smoke generators, matches, artillery traces, electroplating solutions, railway torpedoes, gas drying agents, lubricating oils, cloud seeding, tanning, finished leather, electronic tubes, fabric fixes, dyes, electroplating, aluminium refining, signal and road flares, rubber manufacture, paint and enamel production, cattle feeds and magnesium batteries (Backus et al. 2005; Cao et al. 2019; Cheng et al. 2004; Dean et al. 2004; Wilkin et al. 2007).

6.4 Fate of Perchlorate in Water

After entering into the natural water systems, fate of ClO_4^- depends on physicochemical properties of that aqueous system. Generally, ClO_4^- ions are highly soluble in water and stable in environment. Perchlorate degrading anaerobic bacteria may degrade ClO_4^- if the anaerobic system has exhausted electron donors as oxygen or nitrate is depleted, and sufficient organic carbon is present. ClO_4^- accumulation at various horizons of soil at shallow depths is observed in arid and semi-arid regions, due to high rate of evaporation of infiltrating rainfall containing leached ClO_4^-. ClO_4^- does not bind to soil particles, and therefore, ClO_4^- movement in soil is largely dependent on the presence and circulation of water. If sufficient rainfall is available, ClO_4^- may completely be leached from the soil (Trumpolt et al. 2005) and contaminate groundwater, and ClO_4^- ions will follow the groundwater gradient and migrate towards discharge locations (Clausen et al. 2004). But to understand the ClO_4^- contamination pattern and movement of ClO_4^- contaminated groundwater front, knowledge about local groundwater flow gradients and directions and hydrogeological properties of the aquifer is essential (Cao et al. 2019).

6.4.1 Flow, Transport and Transformation Pathways of Perchlorate

Nowadays, ClO_4^- can be identified and measured in micromolar range in the environment, particularly in groundwater, very easily compared to that of the past (Wagner et al. 2006; Wendelken et al. 2006). ClO_4^- is already detected in water, soil and food, in nanogram to milligram range, in many countries like USA, Canada, China, South Korea and India (Her et al. 2011; Kalinski et al. 2007; Kannan et al. 2009; Nadaraja et al. 2015; Poghosyan et al. 2014; Smith et al. 2006; Ye et al. 2012).

6.4.2 Perchlorate in Water

ClO_4^- is found even much away from its source area as sufficient rainfall may transport ClO_4^- due to its higher water solubility. Military operations, fireworks and industrial uses are major causes of ClO_4^- contamination of rainwater, groundwater, surface water and drinking water.

6.4.2.1 Rainwater

Rainwater samples collected from Ireland and China show different concentrations of ClO_4^- (Barron et al. 2006). It is observed that ClO_4^- concentrations in rainwater of urban area are more than that of rural area, probably for air pollution (Qin et al. 2014). In areas where rainwater is the main contributor of surface water, rainwater becomes important source of ClO_4^- contamination of surface water (Qin et al. 2014).

6.4.2.2 Surface Water

Chilean nitrate fertilizer, having high quantities of ClO_4^-, is intensively used in agriculture, and it is a proven source of ClO_4^- contamination of surface water. Different foods are also contributor of ClO_4^- in surface water. Low concentrations (0.1–0.5 mg L^{-1}) of ClO_4^- existed even under natural conditions as background ClO_4^- across various environments. For example, ClO_4^- detected in Great Lakes like Lake Ontario, Superior and Michigan of the USA is dominantly natural (Poghosyan et al.

2014). ClO_4^- salts of potassium and ammonium are the primary oxidants in pyrotechnic mixtures, and many cases of surface water contamination by ClO_4^- residue from firework displays (Fram and Belitz 2011) are reported. For example, high concentration of ClO_4^- is observed in surface water samples in Harbour (Canada), even four days after a firework display (Backus et al. 2005). Study of Tan et al. (2005) reveals that ClO_4^- contamination of stream water (up to 400 $\mu g\ L^{-1}$) and sediment pore water (up to 30 $\mu g\ L^{-1}$) in Texas (USA) attributed to a solid fuel rocket motor manufacture that closed in 1995.

6.4.2.3 Groundwater

Soil ClO_4^- is considered as chief source of ClO_4^- in groundwater. Capillary forces and surface tension compel dissolved ClO_4^- to be trapped within soil pores but not to sorb to soil particle due to electrostatic repulsion (Albright et al. 2008). Biological degradation of ClO_4^- while percolation through soil is restricted up to shallow depth as organic matter generally decreases with greater depth, and this lack of degradation leads to direct infiltration of ClO_4^- into the groundwater zone (Ridley and Tock 2005). For example, unsaturated zones of the arid and semi-arid southwestern United States are an important source of ClO_4^- contamination in groundwater (Jackson et al. 2005; Parker et al. 2008; Rajagopalan et al. 2006; Rao et al. 2007). Groundwater even shows seasonal variation in ClO_4^- levels in groundwater of Harbin, North China (Ye et al. 2013). ClO_4^- of groundwater even has geogenic origin too. For example, groundwater from upstream parts in the Middle Rio Grande Basin of North-Central New Mexico contains ClO_4^- which is attributed by natural deposition (Plummer et al. 2006). On the contrary, source of ClO_4^- contamination in groundwater of the Po River Delta plain, Italy, is Chilean nitrate fertilizer (Mastrocicco et al. 2017). Substantial accumulation of natural or synthetic ClO_4^- in the unsaturated zone is of high threat as it may cause rapid increase in ClO_4^- concentration in groundwater if artificial recharge from irrigation exceeds recharge from precipitation (Fram and Belitz 2011).

6.4.2.4 Drinking Water

Hypochlorite solutions are used as a disinfectant in the water treatment process, and this ClO_4^- may subsequently contaminate drinking water. For example, Aranda-Rodriguez et al. (Aranda-Rodriguez et al. 2017) have detected ClO_4^- concentration in a range of 0.06 and 5.7 $\mu g\ L^{-1}$ in treated water from Canadian drinking water treatment plants. The presence of ClO_4^- in soil may lead to acceleration in mineral dissolution process and therefore, probably enhance the concentration of toxic heavy and/or trace metals into the soil and groundwater. Therefore, sites having high ClO_4^- contamination in soil or groundwater generally have substantial amounts of heavy/trace metals in it, and it could be a possible path of releasing metals to the surface water and groundwater and finally, accumulated in living organisms both in agricultural product and livestock products, via food chain (Kumarathilaka et al. 2016). Various concentrations of ClO_4^- are detected in various food types such as dairy products, beverages, meats, fruit and vegetables (Kim et al. 2014), and it depends on various factors such as species types, age of plant, presence and concentration of other nutrients and ions in the medium and transpiration efficiency (Smith et al. 2004).

6.5 Potential Impact of Perchlorate on Living Organisms

6.5.1 Impacts of Perchlorate Toxicity on Animal and Human

To understand the health impacts of ClO_4^- in humans, many animal toxicity studies have been carried out. Generally, the dosage used for animal is much more than that of potential human exposure (Keil et al. 1998). Study reveals that in presence of ClO_4^-, treated rodents suffer from hypertrophy and hyperplasia (Caldwell et al. 1995; Lewandowski et al. 2004), and long exposures may convert some lesions to cancerous thyroid tumours (Kessler and Kruskemper 1966; Pajer and Kalisnik 1991). In fish, thyroid hormones partially or fully control certain biological processes such as reproduction, ovarian maturation and oogenesis, temperature tolerance, formation of the stomach and muscular development and highly affected in the presence of ClO_4^- (Blanton and Specker 2007). It is proved that ClO_4^- is carcinogenic, and its high dose application on rats for a long period causes tumour formations. As rats and human thyroid functions in similar way, information revealed from rat toxicity studies are considered as relevant to human also.

In case of human, after consumption of ClO_4^- through drinking water or by ClO_4^- contaminated food, ClO_4^- is adsorbed very fast and reaches to the bloodstream through stomach and intestines. Study of Dasgupta et al. (2006) has been reported that ClO_4^- is present in different human body fluids such as urine, breast milk, saliva and blood, and it is mainly due to the ingestion of ClO_4^- contaminated water and food (Smith et al. 2006). The half-life of ClO_4^- in human serum is about 6–8 h, and it remains unchanged during this tenure, and then, it is rapidly eliminated from the body through urination. Various studies have described that the presence of ClO_4^- in human body may lead to inhibition of iodine uptake as iodide into thyroid gland of healthy adult humans (Brabant et al. 1992; Dasgupta et al. 2006). Due to same ionic charge and almost same ionic radius of ClO_4^- ions and iodide ion, iodide uptake by the thyroid follicle cells is hinderer by ingestion of ClO_4^- (Tietge et al. 2005). This substitution of iodide by ClO_4^- decreases thyroid hormone production. As a result, reduction of serum T3 and T4 and increase in TSH levels are observed in the adult. Thyroid hormones are the main growth controlling hormone which helps in normal growth, particularly of infants and children, as well as controlling proper brain development and metabolic activities (Goleman and Carr 2006). This hormonal disbalance results hyperplasia, which ultimately may lead to hypothyroidism. This iodine uptake inhibition is very detrimental for the foetus in the mother's womb too. ClO_4^- occurrence in pregnant women reduces the synthesis of thyroid hormones, and consequently, placental transfer of iodine is decreased in the foetus. It may cause neurobehavioural problems in infant and children in future (Bansal et al. 2009; Leung et al. 2010). Clinical studies and studies conducted on animals indicate that effect of ClO_4^- depends on dosage, and thyroid function of human may be disrupted by large doses of ClO_4^- only (Srinivasan and Viraraghavan 2009).

6.5.2 Impacts of Perchlorate Toxicity on Environment

Very few ecological data are available on the exposure and impacts of perchlorate toxicity on the environment (Smith et al. 2001). For example, to understand impact of toxicity of ClO_4^- on fishes, five-day acute toxicity test was carried out on mosquitofish (*Gambusia holbrooki*) adults; they were exposed to aqueous sodium perchlorate at 1, 10 and 100 mg/L, and their growth was studied (Park et al. 2006). Growth was enhanced at 1 mg/L but seized at 10 mg/L. Study carried out on zebrafish in water containing ammonium perchlorate at 0, 18 and 677 mg/L for up to eight weeks reveals that ClO_4^- does not accumulate in whole fish, and impact of extrathyroidal toxicity results in thyroid follicle hypertrophy, angiogenesis hyperplasia and colloid depletion (Patino et al. 2003). These results suggest that, at environmentally relevant concentrations, ClO_4^- does not induce acutely toxic effects, but higher dosage for longer period may lead to hormonal effects on health of species.

6.6 Standard and Measurement of Perchlorate in Water

6.6.1 Standard of Perchlorate in Water

The current health advisory level for ClO_4^- is set at 15 μg/L based on the reference dose recommended by US EPA (Wilkin et al. 2007). EPA calculated a tap water screening level of 11 μg/L for perchlorate and perchlorate salts as per EPA, 2013. The World Health Organization (WHO) established provisional maximum tolerable daily intake (PMTDI) of 0.01 mg/kg body weight for ClO_4^- (Coates et al. 1999). The current California regulatory standard for perchlorate in water is 6 ppb. (http://www.waterboards.ca.gov/drinking_water/certlic/drinkingwater/Perchlorate.shtml).

6.6.2 Analytical Methods

The USEPA has developed methods to detect ClO_4^- based on selectivity, sensitivity, precision, accuracy and method robustness (Wagner et al. 2007). After the USEPA established Method 314.0 for analysing ClO_4^- (Wagner et al. 2006), numerous standard methods (i.e. 314.1, 314.2, 331.0 and 332.0) have been established that can detect ClO_4^- concentrations in the ng/L range.

Ion chromatography is considered as the basic method of analysing ClO_4^- in drinking water and environmental samples. Standard Method 314 (ion chromatography) had been established and released by EPA's Office of Ground Water and Drinking Water for the analysis of drinking water (Hautman et al. 1999) and can be applied for aqueous samples of ClO_4^- having a concentration of 4 μg/L. This method has been validated in drinking water only, and no guidance is provided for use with soils and biota. For aqueous and soil samples, similar Method 9058 (ion chromatography) has been issued by the EPA's Office of Solid Waste and Emergency Response (USEPA 2000). The reporting limit of 0.5–1 μg/L for ClO_4^- is achievable. Many forensic approaches have been proposed regarding ClO_4^- source identification and age dating. Stable isotope analysis is also carried out to identify the sources of ClO_4^-. Triple-oxygen isotope ratios $^{17}O/^{16}O$ and $^{18}O/^{16}O$ ratios and $^{37}Cl/^{35}Cl$ ratio are used to distinguish anthropogenic and naturally occurring sources of ClO_4^- (Coleman and Coates 2004; Sturchio et al. 2003). To confirm the origin of ClO_4^- in soil, whether evaporate or marine, scanning electron microscopy and/or X-ray diffraction method may be used (Srinivasan and Viraraghavan 2009).

6.7 Remediation of Perchlorate

Many biological and physicochemical processes are available for the remediation of ClO_4^- in contaminated environments. Some of the important processes are briefly described in the following sections.

6.7.1 Biological Treatment Methods

To remove ClO_4^-, biological treatment methods are used very frequently as they are efficient as well as eco-friendly. This may be of two types: in situ and ex situ. In situ mechanism includes biodegradation and phytoremediation, whereas the use of bioreactor for ClO_4^- removal is an ex situ mechanism.

6.7.1.1 Natural Biodegradation

Natural biodegradation is an in situ biodegradation (ISB) process which is used to reduce contaminant at source (Faris and Vlassopoulus 2003). Though, in many environmental conditions, the stable nature of ClO_4^- makes its remediation difficult, still natural biodegradation of ClO_4^- is possible under certain conditions and in the presence of respiring microorganisms, available in different environments such as freshwater of ponds and rivers as well as wastewaters, soils and sediments (Rice et al. 1996; Van Ginkel et al. 1995). Many bacterial isolates such as *Dechloromonas* and *Azospira* species have the capacity to reduce ClO_4^- to chloride for cell respiration (Raj and Muruganandam 2012). If ClO_4^- respiring microorganisms exist naturally in the system and can compete for the existing sources of organic matter, then only in situ remediation of ClO_4^- contaminated site is possible. Otherwise, if nutrients are added to the contaminated sites, ClO_4^- reduction may be enhanced. Microbial reduction of perchlorate progresses in the following steps:

$ClO^-_{4\,(aq)} \rightarrow ClO^-_{3(aq)} \rightarrow ClO^-_{2\,(aq)} \rightarrow Cl^-_{(aq)} + O_{2(g)}$. Perchlorate reductase catalyses reduction of $ClO^-_{4\,(aq)} \rightarrow ClO^-_{3\,(aq)} \rightarrow ClO^-_{2(aq)}$, while chlorate dismutase catalyses $ClO^-_{2(aq)} \rightarrow Cl^-_{(aq)} + O_2(g)$ (Nadaraja et al. 2013; Ye et al. 2012). Therefore, bio-reduction or natural biodegradation can successfully remove perchlorate, and this technology can be applied for treatment of wastewater in large-scale treatment plants (Kumarathilaka et al. 2016).

6.7.1.2 Phytoremediation

Another important in situ mechanism for treating ClO_4^- is phytoremediation where vegetations like French tarragon, cottonwood, willow, etc., are used successfully to remove ClO_4^-. Study reveals that willows, under hydroponic conditions, can degrade ClO_4^- from 10,000 µg/L to below detection limit within 53 days (Nzengung et al. 1999). Some vascular plant species such as sweetgum (*Liquidambar styraciflua*), black willow (*Salix nigra*), pickleweed (*Allenrolfea occidentalis*), smartweed (*Polygonum punctatum*), water-lily (*Nymphaea odorata*) and duckmeat (*Spirodela polyrrhiza*) also have the capacity to remediate ClO_4^- (Susarla et al. 2000) from water (Fig. 6.1).

6.7.1.3 Bioreactor

Along with already discussed in situ ClO_4^- treatment technology, some ex situ treatment systems are also developed which can degrade ClO_4^- from contaminated water. Bioreactor is one of them, in which microorganisms like certain bacteria degrade ClO_4^- from contaminated groundwater and surface water, soil, etc., under certain anaerobic conditions. In addition to the electron sink, these organisms require carbon sources such as ethanol, methanol or acetic acid for their growth (Coates et al.

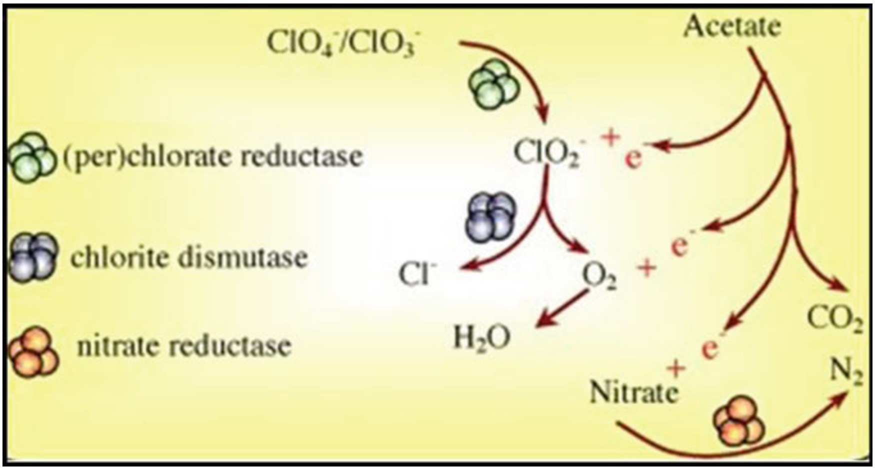

Fig. 6.1 Schematic diagram of perchlorate degradation and pathways (Xu et al. 2015)

1999). To remove ClO_4^-, two types of bioreactors, i.e. fluidized bed reactors (FBR) and packed bed reactors (PBR) are commonly used. Recent studies reveal that three-step processes and two enzymes are involved in ClO_4^- reduction. A perchlorate reductase enzyme catalyses reduction of ClO_4^- to chlorate and then to chlorite. A chlorite dismutase enzyme causes further breakdown of chlorite to chloride and oxygen (Polk et al. 2001; Sartain and Craig 2003). Perchlorate reducing strains reported in the literature includes *Wolinella succinogenes* HAP-1, isolates GR-1, *Dichlorosoma* sp. (Kim et al. 2014; Wendelken et al. 2006), etc.

6.7.2 Physicochemical Treatment Methods

6.7.2.1 Chemical Reduction

At ambient conditions, ClO_4^- is unstable from thermodynamic point of view and may results in chloride as per the reaction shown below:

$$ClO^-_{4\,(aq)} + 8H^+(aq) + 8e^- \rightarrow Cl^-_{(aq)} + 4H_2O_{(1)}\ E^\circ = +1.389\,V$$

Due to chlorine–oxygen bond stability, there is a high activation energy barrier of $ClO^-_{4,}$ and as a result, ClO_4^- behaves as inert substance with most of the reducing agents. Complexes of Sn (II), Ti (III), V (II) and (III), and Ru (II) can reduce ClO_4^- at very slow rate (Earley and Kallen 1971; Kumarathilaka et al. 2016). To remediate ClO_4^- in water, some strong reducing agents such as zero-valent iron (Fe (0)) can be used as per the reaction below (Cao et al. 2005):

$$ClO^{-}_{4\,(aq)} + 4Fe(0)_{(s)} + 8H^{+}_{(aq)} + 8e^{-} \rightarrow Cl^{-}_{(aq)} + 4Fe^{2}_{(aq)} + 4H_2O \qquad (6.1)$$

ClO_4^- can be removed by nanoscale zero-valent iron (10 mg L^{-1}) at different rates at different temperatures. For example, ClO_4^- can successfully remove at a rate of 0.013 mg g^{-1} hr^{-1} and 1.52 mg g^{-1} hr^{-1} at temperatures such as 25 °C and 75 °C, respectively (Cao et al. 2005). But this process has a drawback as residual iron will remain present in treated medium, and therefore, further treatment is required to remove iron from the medium (Kumarathilaka et al. 2016).

6.7.2.2 Adsorption

In adsorption process, some adsorbent media such as granular activated carbon (GAC) or activated alumina are used to remove ClO_4^-. Generally, the three influencing factors of adsorption capability of a particular adsorbent are structural characteristics of adsorbent, solution pH and surface properties of an adsorbent. In USA, granular activated carbon is widely used to adsorb ClO_4^- during water treatment process. (Ye et al. 2012). Recently, a group of researchers identified some other modified adsorbents such as granular ferric hydroxide to remove ClO_4^- from the water within 60 min (Kumarathilaka et al. 2016). The maximum adsorption capacity of granular ferric hydroxide was 20 mg/g at pH 6.0–6.5 at 25 °C. Optimum removal occurred in the pH range of 3–7 (Baidas et al. 2011).

6.7.2.3 Membrane Filtration

Pressure-driven membrane filtration by using reverse osmosis, nanofiltration, ultrafiltration and electrodialysis (ED) are considered as promising technologies for removing ClO_4^-. Both size exclusion and electrostatic exclusion are prominent pathways for removing inorganic contaminants using such a membrane. Moreover, solution pH and conductivity determine the degree of rejection by controlling the membrane charge. To remove ClO_4^- from groundwater, mainly three types of semi-permeable membranes are used: (i) high-pressure RO membrane, (ii) nanofiltration membrane and (iii) low-pressure RO membrane. High-pressure RO membranes (>150 psi) have been observed to remove about 99.9% of ClO_4^- (Morss 2003). Study of Yoon et al. (2009) reveals that ClO_4^- removal is directly proportional to the pH and indirectly proportional to the conductivity. In addition, when the ratio of solute radius to the effective membrane pore radius is greater than 0.4, ClO_4^- removal was higher than 70% in the reverse osmosis membrane. According to study of Roach and Tush (2008) 95% of ClO_4^- can be separated by polyelectrolyte-enhanced ultrafiltration even in the presence of tenfold excesses of competing ions such as chloride, sulphate and carbonate. Electrostatic attraction properties between ClO_4^- and positively charged NH_3^+ is an important mechanism which can be used for removing ClO_4^- during hybrid/ultrafiltration process using chitosan as an adsorbent, and its equilibrium will be reached in 3 min. (Darracq et al. 2014; Xie et al. 2011). But this mechanism has some drawbacks such as scaling and fouling, which need maintenance or replacement, and due to non-selective nature of this membrane filtration technologies, demineralization of target water can take place.

6.7.2.4 Ion Exchange

Another ex situ technology that is used to eliminate ClO_4^- from groundwater and surface water is ion exchange technology. Synthetic ion exchange resins are generally used as strongly basic ion exchange media. The removal efficiency of the media depends on stability of media, its exchange capacity and its regeneration capacity. For example, strongly basic ion exchange media are very effective to remove ClO_4^- from ClO_4^- contaminated water if concentration of ClO_4^- is <50 mg/L. Positively charged functional groups of perchlorate resins are initially dosed with anions like chloride ion. These positively charged functional groups attract ClO_4^- anion present in perchlorate contaminated water, due to its stronger attractive force and replaces ClO_4^- anion with Cl^- (Mihelcic 1999), and thus, ion exchange process removes the ClO_4^- ion, populating the treated water with chloride ions. But coexisting anions of ClO_4^- may occupy the available sites, and as a consequence, perchlorate removal efficiency will be reduced (Ye et al. 2012). Study of Darracq et al. (2014) reveals that out of five different resins that are A532E, A520E, A400E, PWA-5 and PSR-2, A532E and PSR-2 show the best performance in removing ClO_4^- from groundwater and drinking water systems. They can treat ClO_4^-contaminated water containing 10–10,000 μg/L ClO_4^- (Table 6.2). Problems associated with this technology are of two folds (i) high cost and (ii) disposal after a single use.

6.7.2.5 Electrochemical Reduction

Nontoxic chloride ions are produced by electrochemical reduction of ClO_4^- (Logan 2001). Electrochemical reduction of ClO_4^- anion has been conducted in a cell with Ni electrode and a Pt counter electrode in concentrated solutions of hypochlorous acid (Rusanova et al. 2006). Electrodes such as Ti, Rh, Pt, Ir, Ru and Sn are also capable of reducing ClO_4^- ions (Brown 1986; Lang et al. 2008). For example, study of Wang et al. (2009) reveals that in the presence of Ti anode, ClO_4^- in aqueous solutions shows significant reduction from 200 mg/L to 20 mg/L within 8 h. The presence of titanium metal as a chemical reductant can remove ClO_4^- in water (Lee and Kramer 2007). The activity of titanium was enhanced by eliminating the localized surface oxide film using electrochemically induced pitting corrosion. The activity of pitting corrosion is enhanced by higher current. Higher current dissolves more transitory titanium metal ions near the pits, and it results in a higher rate of ClO_4^- reduction. The surface of the bare Ti(0) inside the pits induces further electrochemical reactions, increasing the current. This increased current causes faster conversion of chloride to chlorine (Srinivasan and Viraraghavan 2009).

Table 6.2 A summary of performance of ion exchange used for treatment of perchlorate

	Description	Performance	Reference
Ground water (Presence of nitrates and chlorinated solvents).	A non-regenerable Perchlorate-selective resin is used. The system operating flow rate 400 gpm	Initial concentration 50 μg/L. Effluent concentration <4 μg/L	Cal EPA (California Environmental Protection Agency) (2004)
Drinking water	A fixed bed, non-regenerable anion-exchange resin is used	NA	ITRC (2005)
Groundwater (Plant Ion Exchange System (PIES) and Wash Ion Exchange System (WTES))	The PIES included twelve single-use anion exchange columns in 4 parallel trains. The WIES included three single-use ion exchange columns in series	Initial concentration 80,000–350,000 μg/L. Effluent concentration 500–2,000 μg/L	Cal EPA (California Environmental Protection Agency) (2004)
Drinking water	A fixed bed, non-regenerable anion exchange system is used. The system consists of 10 ion exchange vessels, each loaded with a strong-base, quarternary amine resin, operating at 6,000 gpm	Initial concentration 20–50 μg/L. Effluent concentration <4 μg/L	Cal EPA (California Environmental Protection Agency) (2004)
Groundwater	A non-regenerable, nitrate-selective anion exchange system is used. Operating flow rate 10,000 gpm	Initial concentration 15 μg/L. Effluent concentrations <4 μg/L	Cal EPA (California Environmental Protection Agency) (2004)
Groundwater (other contaminant—trichloroethane)	Six fixed bed, non-regenerable anion exchange systems are used	Initial concentration 20 μg/L. Effluent concentration <μg\L	Cal EPA (California Environmental Protection Agency) (2004)

Source Sturchio et al. (2003) (Srinivasan and Viraraghavan 2009)

6.7.2.6 Removal by Iron Nanoparticles

Study has been carried out to understand the performance of stabilized elemental iron nanoparticles in removing ClO_4^- (Xiong and Zhao 2006) in water. It can convert 100% of ClO_4^- to chloride during ClO_4^- degradation process without any intermediate products. Elevated temperature is required for this reaction, and temperature has a high control on this process. During ClO_4^- reduction by elemental iron at elevated temperatures, microwave heating or conventional block heating is used for rising temperature, and both of them results in 98% removal of ClO_4^-. This indicates removal of ClO_4^- by elemental iron which was mostly due to heat energy at higher temperature (Oh et al. 2006).

6.7.2.7 Catalytic Reactors

In the presence of methyl thrioxorhenium to a combination of 5% Pd-carbon powder as catalyst, hydrogen gas can reduce ClO_4^- and convert it completely to chloride (Hurley and Shapley 2006).

6.8 Conclusion

Perchlorate contamination in surface and groundwater causes health issues in various parts of the world (Böhlke et al. 2015). It is already proved that thyroid gland is the most affected human body part by perchlorate toxicity, and continuous consumption of ClO_4^- -contaminated water may result in abnormal decrease in human body weight and growth. Along with oral ingestion via drinking water and food, ClO_4^- bearing dust is another prevailing source of perchlorate. Though removal of ClO_4^- from environment is very difficult due to its persistent nature, with advancement of new technologies, it is possible now. Among physical, chemical and biological ClO_4^- removal methods, biological one is considered as the cheapest and eco-friendly technology. For example, production of ClO_4^- adsorbing biochar by converting waste organic materials is a promising biological technology to remediate ClO_4^- from environment. Though other methods have higher efficiency in ClO_4^- removal, due to their higher cost and requirement of high skill and scientific understanding, biological method is considered as the sustainable ClO_4^- removal technology.

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Chapter 7
Carcinogenic Nature of Emerging Contaminants: Havoc for Present and Gateway of Unhealthy Future

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7.1 Introduction

Cancer is a threat to the mankind, and it is growing at a rapid rate (Peto 2001). Environmental pollution is one such major contributor to this disease, and hence, it is demand of the time to eliminate these environmental factors in order to minimize the occurrence of this disease. The concerned authorities reported that 90% of the human cancer is originated due to environmental pollution (Fiore et al. 2019). The factors responsible include radiation, smoking, occupational exposure, viruses, commercial chemicals, etc. (Williams 2019). Water is the life-giving assets and one of the major carriers of diseases to food chain, ultimately reaching to human beings. Due to rapid urbanization, commercialization, industrial activities, etc., a large number of hazardous contaminants have found its way into water bodies, thereby leading to great havoc on the ecosystem (Arora et al. 2018). Carcinogenic emerging contaminants in water bodies are a major reason to increase the risk to the disease on regular exposure and utilization of this contaminated water. Water contamination is a serious problem and gateway of an unhealthy future (Kunwar 2019; Dagdeviren and Robertson 2009). Human activities for their luxurious life are adding poisonous chemicals of varieties of range into the water. On evaluation of the possibility of connection between the cancer and drinking water, it can be identified that there are enough contaminated chemicals to trigger these dreadful diseases (Tsuji et al. 2019). Before reaching the tap, water can get contaminated at any point. Various kinds and amounts of carcinogenic contaminants occurring in water may be due to many reasons like contamination at the source, during treatment process, etc. (Chowdhary et al. 2020).

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Source water may be contaminated by many carcinogens, but they are present in lower concentration. Further, contaminants introduced during treatments process are limited in number, but their frequency is far more in comparison with the source contaminants (Turner 2019). Finally, water while moving through pipes, fixtures and joints or other distribution systems may get contaminated by the compounds present in them before reaching to the consumer (Fawell and Nieuwenhuijsen 2003). This chapter discusses various sources and pathways of these contaminants and various types of contaminants of emerging concern like pharmaceuticals, personal care products, plasticizers, pesticides, steroids, perfluorochemicals, food additives, artificial sweeteners and surfactants. Carcinogenic emerging contaminants like arsenic, asbestos, radon, parabens, alkylphenol, fluoride, nitrate, disinfection by-products, microbes, etc., are also discussed throwing light on its toxicity and the range of cancer they initiate within human beings through water contamination. Further, carcinogenic mechanism induced by these carcinogenic contaminants is also discussed (Singh et al. 2019, 2020). The aim of this chapter is to discuss various types of emerging contaminants causing cancer, their harmful effects and how it invades the human body through the medium of water, thus leading to dreadful diseases. The concluding remarks focus on the need to eliminate these toxic substances from the environment by adopting suitable measures.

7.2 Contaminants of Emerging Concern

As discussed, contaminants of emerging concern are the class of chemicals which have been present in the surrounding for decades, but their significance and presence are presently elucidated. Information and data regarding these contaminants are limited, and hence, research and treatment of these substances face difficulties. Network of reference laboratories, related organizations and research centres for monitoring of emerging environmental substances like NORMAN reported a list of contaminants of emerging concern based on the literature studies (Siddique et al. 2016). US environmental protection agency (USEPA) defined emerging contaminant as a material which is characterized by real or potential danger to environment and human health (Halden 2015). According to US geological Survey (USGS), contaminants of emerging concern are naturally occurring or synthetically available microorganisms or chemical which is not monitored by environment but are capable enough to pollute the environment and adverse human health and ecological effects (Klaper and Welch 2011). Some of the selected contaminants of emerging concern are discussed below. In Table 7.1, some of the contaminants, their toxicity and sources are shown.

Table 7.1 Anthropogenic sources for common heavy metal pollutants along with their provisional guideline limits according to WHO and their toxicity (Kobielska et al. 2018)

Heavy metal	Anthropogenic sources	Toxicity
Cu	Water pipes, chemicals and pharmaceutical equipment, kitchenware, roofing, alloys, pigments	Relatively not detrimental, narrow tolerance for plants
Hg	Amalgamation(the process of metal extraction), electrical and measuring apparatus, catalysts, dental fillings, Hg vapour lamps, solders, X-ray tubes, pharmaceuticals, fungicides scientific instruments, electrodes, rectifiers, oscillators, chloralkali cell's mobile cathode	Biomagnification in aquatic environments, Minamata disease
As	Animal feed additive, algaecides, herbicides, insecticides fungicides, pesticides, rodenticides sheep dip, tanning and textile, pigments, veterinary medicine, ceramics, special glasses, metallurgy, electronic components, non-ferrous smelters, electrical generation(coal and geothermal), light filters, fireworks	Phytotoxic(toxic to plants), arsenicosis (i.e. blackfoot disease), keratosis, possible vascular complications, carcinogenic
Cr	Data storage, plating, ferroalloys manufacturing, textiles and leather tanning, wood treatment, passivation of corrosion cooling circuits, pigments	Cr3 + not detrimental to mammals, Cr6 + very toxic, carcinogenic
Zn	Zn alloys, PVC stabilizers, gold precipitation from cyanide solution, in chemicals and medicines, anti-corrosion coating, cans, barriers, rubber industry, welding and soldering fluxes, paints	Relatively not detrimental to mammals (may affect cholesterol metabolism in humans)
Pb	Alloys, ceramics, plastics, glassware, lead–acid batteries, cable sheathings, sheets, solder, pipes and tubing, sheets, ordinance, antiknock agents, tetraethyllead, pigments	Pb poisoning (a worldwide issue) through gasoline, plumbing and paints
Cd	Neutron absorbers(within nuclear reactors), nickel–cadmium batteries, anti-corrosive metal coatings, alloys, plastic stabilizers, coal combustion, pigments	Phytotoxic, bio-accumulative, itoi-itoi disease, carcinogenic
Ni	An alloy in the steel industry, computer components, catalysts, ceramic and glass moulds, electroplating, nickel–cadmium batteries, dental and surgical prostheses, arc-welding, pigments	Contact dermatitis, asthma, chronic respiratory infections carcinogenic

7.3 Pharmaceutical and Personal Care Products

These substances maintain their chemical characteristics and vary in a wide range as they generally contain a non-polar centre with a polar functional group. The products formed on the transformations of these substances remain persistently in environment as reported by Fent and his team in the year 2006 and Clarke and Smith in the year 2011 (Clarke and Smith 2011; Caminada et al. 2006). In 2003, Diaz-Cruz and team reported that the environmental existence of Fenofibrate and Clofibrate which are the metabolite of blood lipid is twenty one years (Silvia Díaz-Cruz et al. 2003). Additionally, this medicinal waste carries unknown and dangerous side effects on various species, mostly after a long period of exposure. It also initiates resistance to bacteria by releasing antibiotics into the surroundings. Till now, the overall and detailed impact of these metabolites among the organisms in the environment is unpredictable as reported by Hernando and team in the year 2011 (Hernando et al. 2011). Pharmaceutical and personal care products and their transformed products, i.e. metabolites, are collectively known to as effluent-derived contaminants which are available mostly in the wastewater. To name a few, some of the structural categories of antibiotics are macrolides, sulphonamides, tetracyclines, cephalosporins, penicillin, fluoroquinolones and nitroimidazoles as reported by Clarke and Smith and Jury and team in the year 2011 (Clarke and Smith 2011; Jury et al. 2011). All the pharmaceuticals, their metabolite, personal care products and antibiotics have the property to remain persistent, and only a part of it is degraded during the treatment process and hence makes its way into the drinking water supplies, thereby causing harmful effect on environment and health as reported by Clarke and Smith in the year 2011 (Clarke and Smith 2011).

7.4 Steroids

Synthetic steroids and natural endrogenous like mestranol and estrone, respectively, are primarily released from wastewater treatment plant, and excretion of human body enters into the ecosystem (Thomaidis et al. 2012). This results in harmful effect on the environment as well as human beings. Either natural or synthetic, steroids are released from human body in the form of polar inactive conjugates, but they remain in sewage effluent as active and free substance. This is due to enzymatic or chemical dissociation by the bacterial sludge present in the sewage effluent which converts these inactive conjugates of steroids into active steroids as reported by Fan and team in the year 2011 (Fan et al. 2011).

7.5 Perfluorochemicals

These are defined as the class of anthropogenic chemicals which are used to prepare products that bear resistance to water, grease, stains, oil and heat. These chemicals remain suspended persistently in the ecosystem. Perfluorochemicals are unique compounds which comprise lipophobic and as well as hydrophobic nature, and they also consist of carbon–fluorine bond which is one of the strongest bonds known (Thomaidis et al. 2012). According to Clarke and smith in the year 2011 and Martin and team in the year 2010 reported that toxic impact of exposure to these chemicals on human health and environment is not known but expected to cause endocrine disruption (Clarke and Smith 2011; Martin et al. 2010). The degradation of perfluorochemicals is obstructed due to their chemical structures. The common class of perfluorochemicals is perfluorooctanesulphonate and perfluoroalkylsulphonates which are detected and measured in the environment.

7.6 Pesticides

In the year 2012, Stuart and team reported that evaluation of the pesticides has been done by numerous research agencies and regulatory organizations (Stuart et al. 2012). The metabolites of the pesticides are reported by Lapworth and team in the year 2012 for their high degree of toxic effect in the groundwater (Lapworth et al. 2012). As a result of this, pesticides have been included in the category of the emerging contaminants. Some of the metabolites are captan, acephate, clethodum, acetochloroxanilic acid, etc. (Naidu et al. 2016).

7.7 Plasticizers

It consists of naphthalene sulphonates, ortho-phthalic acid and numerous different substances which are combined to materials like gypsum, clays, concrete, plastic, etc., in order to enhance the rheological characteristics and plasticity. The harmful feature of the plasticizers includes endocrine disruptors. For example, BPA, a part of polycarbonate plastics, has diversified uses such as paper coatings, lenses, adhesives and food containers as reported by Vandenberg and team in the year 2007 and Bang and team in the year 2012 (Bang et al. 2012; Vandenberg et al. 2007). It is the highest among the chemicals produced in the world as reported by Dow in the year 2012 (Pal et al. 2014). BPA leach into the water cycle via various media like in plastic production plants, at the time of degradation of plastics naturally, discharges from wastewater effluents, etc.

7.8 Surfactants

Perfluorooctanoic acid and perfluorinatedsulphonates, etc., are applied since decades in cookware coatings, packaging, surfactants, paints, etc. According to Ahrens and team in the year 2009 and Poynton and Vulpe, in the year 2009 (Ahrens et al. 2009; Poynton and Vulpe 2009), it was reported that this substance occurs in sewage treatment effluents, groundwater and persistently remains in the surrounding. According to Montgomery—Brown and Reinhard in the year 2003 reported that the degradation product of alkyl phenol, ethoxylate and corresponding metabolites remains dispersed in aquatic surrounding (Montgomery-Brown and Reinhard 2003).

7.9 Food Additives and Artificial Sweeteners

In 2009, Buerge and team reported the occurrence of sweeteners like sucralose, saccharin and acesulfame, etc., in domestic wastewater through human excreta (Buerge et al. 2009). Scheurer and team, in the year 2008, reported detection of parabens (food preservative) in the groundwater (Scheurer et al. 2009). Few other lists of food additives are terpineol, triacetin, eucalyptol, hexanoic acid, etc. Out of these, some are endocrine disruptors or oxidants (Thomaidis et al. 2012). Nowadays, artificial sweeteners are preferred over normal sugar due to their low-calorie content, and as they do not have response to insulin, it can be consumed also by people suffering from diabetes. These substances remain immune to fermentation caused by microbes which cause dental plaques. The chemicals like sucralose, aspartame, cyclamate, etc., are omnipresent in the surface water. In the year 2009, Loos and his team reported that ninety eight per cent of consumed sucralose by human beings gets released in the same form with long half-life and remains dispersed in the aquatic environment (Loos 2009).

7.10 Carcinogenic Contaminants

7.10.1 Asbestos

Asbestos is defined as the hydrated silicate minerals occurring in nature and possess fibrous structure and used commercially (Polissar et al. 1984; Howe et al. 1989). The fibres of asbestos occur in water bodies due to the process of weathering, mining, run-off from asbestos cement pipes (Toft et al. 1984). In water, these substances get altered after undergoing various physiochemical modifications, and the cancer caused to human depends on concentration as well as the crystal structure, shape and size of the fibres of the asbestos (Mossman et al. 1983). It is a matter of concern that the asbestos present in the drinking water is capable of inducing harmful effect on health. These fibres when ingested are capable of causing an increase in the risk of gastrointestinal cancer (Edelman 1988). The short asbestos fibres when ingested penetrate into wall of intestine and may be removed through urine or get accumulated on different organs and tissues. On long-term exposure to this substance, by the workers, there may be maximum chances of colon cancer (Gerhardsson De Verdier et al. 1992).

7.10.2 Arsenic

It is Class-A category of carcinogenic contaminant which occurs in nature as metalloid. Worldwide, the consumption of either arsenic-contaminated crops or water is considered to be dangerous for life as it is capable of triggering many health risks (Chan and Huff 1997). More than hundred millions of people all around, one hundred five countries are affected by the consumption of arsenic-contaminated drinking water. Both inorganic and organic forms of arsenic prevail in contaminated water. According to Smedley and Kinniburgh in the year 2002 and Basu and team in the year 2014, approximately ten milligram per kilogram amount of arsenic concentration is found in soil (Smedley and Kinniburgh 2002; Basu et al. 2014). The concentration of As in groundwater is in between 0.5 and 5000 Âμg per litre, reported by Ravenscroft and team in the year 2009 and Kippler and team in the year 2016 (Brammer and Ravenscroft 2009; Pournara et al. 2016). Orpiment, arsenopyrite and realgar are some of the major mineral sources for arsenic in groundwater (Islam et al. 2013). There are four oxidation states in which arsenic occurs; they are arsine (trivalent arsenic), elemental arsenic (zerovalent arsenic), arsenite (trivalent) and arsenate (pentavalent) as reported by Sharma and team in the year 2014 (Sharma et al. 2014). The mobility and solubility of arsenic are mainly dependent on redox reactions and pH. Arsenite predominately exists in deep groundwater, i.e. reduced condition at high pH, and pentavalent arsenic exists at low pH in oxidized surrounding, i.e. shallow groundwater, as reported by Abdallah and Gagnon in the year 2009, Bundschuch and team in the year 2012 and Jackson and team in the year 2012 (Abdallah 2009; Bundschuh et al. 2012; Jackson et al. 2012).

7.10.3 Radon

It is a radioactive gas which is naturally produced due to degradation of uranium present in rocks and soil (Arnold 2006). Every year, in the USA, more than twenty thousand people die due to lung carcinoma due to exposure to radon (Edling and Axelson 1983). This gas is responsible for more than fifty per cent of natural radioactivity exposure, thereby causing health issue to general people as well as miners because it is a universal contaminant of environment and water (Shuko 1986). From the epidemiologic studies of the miners, the relation between lung cancer and radon is established (Samet and Eradze 2000). On further research reported that nearly 70% death due to lung cancer among mining people is because of exposure to radon, and it was also reported that in comparison with other occupation non-smokers, miners are in more risk zone of lung cancer (Samet 1989). Reports are there stating that thirty per cent of people who neither smoke nor work in mining are affected by lung cancer due to exposure to radon. The permissible level of exposure to this gas in many countries is 200 Becquerel per metre cube, but there are reports showing results of increase risk of lung cancer due to radon even at the level of 100 Becquerel per metre cube (Mehra et al. 2006).

7.10.4 Fluoride

Among all the elements, fluorine is most reactive and electronegative and found in the form of fluoride in nature (Deshmukh et al. 1995). According to Totsche and team in the year 2000, fluoride washes into the water due to the weathering of fluoride ion containing minerals (Totsche et al. 2000). Fluoride in small proportion is vital for the strength of the enamel and providing minerals to bones as reported by Bell and Ludwig in the year 1970 (Bell and Ludwig 1970). But, overexposure to this fluoride leads to fluorosis of skeleton and teeth as reported by Sorg and Logsdon in the year 1978 (Arif et al. 2012). According to Mameri and team in the year 1998, it was reported that the diseases of fluorosis have become common all over the world apart from India especially in developing countries like New Zealand, Thailand, Canada, Sri Lanka, Iraq, Kenya, South Africa, Turkey, Libya, Algeria, USA, Japan, Argentina, etc. (Mameri et al. 1998). The major source for human consumption of fluoride is groundwater. In groundwater, the prime sources of fluoride are minerals containing fluoride like hydroxylapatite in rocks, cryolite, fluorapatite and fluorspar as reported by Farooqi and team in the year 2007 (Prevedouros et al. 2004). Groundwater contamination by fluoride is a major issue as it carries major health as well as environmental hazard in many areas.

7.10.5 Polycyclic Aromatic Hydrocarbon (PAH)

In the year 2004, Prevedouros and team reported that this substance is a part of the group of compounds known as POPs, i.e. persistent organic pollutants, that generally exist as complicated mixtures consisting of two or more benzene rings, and the resultant compound consists of only hydrogen and carbon (Prevedouros et al. 2004). According to Harvey in the year 1997, there are around sixteen PAHs which are considered as priority pollutants capable of causing risk of cancer reported by United States Environmental Protection Agency (Krupadam et al. 2010). These substances are present in natural gas and oil, wood smoke, cigarette smoke, diesel engine, gasoline exhaust, etc., as reported by Li and Chen in the year 2002, Guteirrez-Dabanasnd team in the year 2005 (Gutiérrez-Dabán et al. 2005; Li and Chen 2002). These PAHs get washed in the water bodies through agricultural run-off, industrial effluents, atmospheric deposition sewage, etc. According to Matsui and team in the year 2000 and Flotron and team in the year 2003, it was reported that many of the PAHs up to some extent get reduced by the existing wastewater treatment plants but fail to minimize the level below the permissible limit for aquatic organism (Matsui et al. 2000; Flotron et al. 2003). According to Madras and team in the year 1998, Ko and team in team in the year 2000 and Zheng and team in the year 2007, it was reported that techniques which can be promising in effectively reducing the PAHs and its removal in wastewater treatment plant are adsorption by activated carbon, reverse osmosis, membrane filtration, UV radiation and ozonation, etc. (Zheng et al. 2007; Madras et al. 1994; Ko et al. 2000). But, establishing these techniques will enhance the cost in the treatment plants. Hence, it is necessary to find pathways which will be equally efficient, selective as well as economical for removal of polycyclic aromatic hydrocarbon from the wastewater.

7.10.6 Microbiologic Agents

The principal microbes existing in drinking water which can be ingested are protozoa, bacteria and viruses (Gerba and Smith 2005). Depending on various raw water sources, the concentration of these microbes varies. Schistosoma haematobium is a microorganism originating in water and capable of causing risk of bladder cancer in many subtropical and tropical regions where the native disease is schistosomiasis (Gerba and Pepper 2019). The infection caused due to Helicobacter pylori leads to chances of gastric lymphoma, stomach cancer and many other (Kim 2011). Moreover, the reason behind growth of infections due to Helicobacter pylori in drinking water is lack of hygiene, overpopulation, etc. (Kakelar 2019).

7.10.7 Nitrate

Over the last decades, the degree of deposition of nitrogen has been doubled on the surface of the land mainly due to a wide range of utilization of nitrogen-containing fertilizers, burning of fossil fuels and opting nitrogen fixation crops over natural vegetation (Jenkinson 2001). This heavy amount of nitrogen-based compounds on surface of land gets converted into nitrate, and a major part of it gets washed into the groundwater. From the data reported from Geological Survey of USA of private wells, it was observed that 9% of studied sample crossed the maximum contaminant level which is 10 mg/L. In order to prevent methemoglobinemia, susceptible to infants, the permissible amount of nitrate in drinking water is set to be ten milligram per litre by US Environmental Protection Agency (Kumar 2013).

7.11 Disinfection By-Products

The process of disinfection of drinking water is a successful measure for treating wastewater (Simpson and Hayes 1998). From the literature survey, it is reported that there is minimization of rate of mortality and morbidity by using chlorine during the process of disinfection process of the drinking water (Li 2018). On long-term use of chlorine in swimming pool water during disinfection, there is reaction between organic materials present in untreated water and chlorine which leads to release of toxic substances which increases the chances of cancer (Florentin et al. 2011). Many disinfection by-products are reported like haloacetic acid, trihalomethanes and chloroform (Richardson 2003). The by-products produced from the process of disinfection remain suspended in treated water system in which compounds like chloroform can remain at level of hundred parts per billion if they are not properly controlled. The lower molecular weight compounds primarily enter body through dermal adsorption, while bathing and inhalation, swimming in pools which are chlorinated. The substances bearing higher molecular weight affect when it is consumed. Some of the common cancers occurring due to exposure to these disinfection by-products are cancer of rectum, colon and bladder (Melnick et al. 2007).

7.11.1 Alkyl Phenol

These are utilized as the precursor material in the manufacture of surfactants and detergents in industries and also used as antioxidants for producing rubber polymers and plastic. These are also used in personal care products like hair products. Some examples includes 4-tertiary butylphenol, 4-tertiary octylphenol and 4-nonylphenol. Alkyl phenol are the second largest class of non-ionic commercially used surfactants (Dekant and Völkel 2008). These are utilized in a large scale in textile, paper, plastics, lubricating oils, detergents industries, etc. In the year 2002, its production worldwide was approximately estimated to be around seven lakh tons (Choi et al. 2009). Sixty per cent substances enter the sewage treatment plant and aquatic environment and aerobically degraded with breakage of ethyl substrate sequentially into small chain and into forms which remain persistently in environment (White et al. 1994). The alkyl phenol metabolites get accumulated in sediments of river and sewage sludge because they are hydrophobic in nature. They remain dispersed in soil, air and into water bodies in sufficient amount to cause harmful impact on human health as well as animals and environment (Dekant and Völkel 2008; Choi et al. 2009; Ying 2006). Nonylphenol has been reported to enhance the growth of MCF-7 breast cancer cell and simultaneously enhances the proliferation and development of mammary glands. In addition, alkyl phenol is responsible to trigger the risk of cancer such as breast cancer which is hormone dependent (Guenther et al. 2002).

7.12 Carcinogenic Mechanism Triggered by Some Emerging Contaminants

7.12.1 Arsenic

The mechanism of carcinogenesis induced by arsenic involves process of biotransformation. Inside the body, the heavy metal Arsenic initiates a number of methylation, oxidation and reduction reaction (Ebert et al. 2011). Arsenical species undergoes reduction from pentavalent state to trivalent state during glutathione-dependent reaction (Németi et al. 2010). After that oxidative methylation occurs where dimethylarsenate, methylarsonate and monomethylarsonous acid are produced (Drobna et al. 2009; Rossman 2003; Rossman and Klein 2011). Arsenic triggers a fast depolarization of membrane of mitochondria, collectively causing deleation and depletion of Deoxyribonucleic acid (DNA) resulting in cancer among human beings (Partridge et al. 2007; Ruiz-Ramos et al. 2009).

7.12.2 Asbestos

If the asbestos fibres which are inhaled are longer, i.e. around five micrometre, then it is not removed by the process of phagocytosis effectively. As a result of this, a series of molecular reactions occur, leading to inflammation, carcinogenesis and fibrosis (Xu et al. 2007; Choe et al. 1998). Moreover, the asbestos fibres which are completely phagocytized can cause interference in mitosis, thereby causing chromosomal missegregation (Ault et al. 1995). During the incomplete procedure of phagocytosis of asbestos fibres, reactive nitrogen and oxygen species are released which causes damage to the DNA (Hei et al. 2006). The reactive oxygen species is hydrogen peroxide (Xu et al. 2007). Asbestos fibres which are rich in iron like amosite and crocidolite generate higher amount of reactive oxygen species (Srivastava et al. 2010). Alike arsenic, asbestos also causes damage to mitochondrial DNA and results in reactive oxygen species derived from mitochondria leading to trigger base oxidation, breakage of single strands (Panduri et al. 2004; Aljandali et al. 2001). Hence, carcinogenis induced by asbestos is expected to happen by causing chronic inflammation via oxidative stress which effectively damages DNA.

7.12.3 Radon

Though, inert chemically, radon is capable of decaying in electrically charged active progenies and on attachment with aerosols, it can be inhaled and finally reaches epithelial cells of lungs. On the final deposition, radon undergoes decay, releasing alpha particles and free radicals which ultimately harm DNA (Samet et al. 2009).

These alpha particles start decaying leading to eject electrons from water and produce a number of reactive substances which cause damage to cell by the attack of hydroxyl radical (Hubaux et al. 2012; Riley 1994). Non-irradiated cells can also get damaged due to the release of harmful by-products from the irradiated cells (Zhou et al. 2000). There are facts which reflect that the reason behind the occurring of injury to lung tissue cells by alpha particles is mainly because of chromosomal damage occurring in nearby non-irradiated cells. Moreover, in carcinogenesis induced by radon, there are noticeable levels of cytokines in the alpha particle radiation-affected cells (Kobielska et al. 2018).

7.13 Conclusion

Many hazardous chemicals are available which cause interference in the natural and biological processes and seriously affect balance of the nature. Human beings when exposed to these chemicals cause the growth and risk of cancer. Water is lifeline for all the living beings. The growing rate of population and pollution has already caused scarcity of pure drinking water. Discharge of heavy metal and contaminants of emerging concern has injected poison to it, thereby triggering the risk of various kinds of life-threatening cancers. Sustainable techniques are needed in order to ensure water purification and protecting the future generation by saving the available water sources. A wide range of emerging contaminants are available globally which has tarnished the natural beauty and purity of the environment like personal care products, lifestyle, ionic liquid, food additive, by-products generated from water treatment techniques, pesticides, pharmaceuticals, etc. It is highly needed to develop methods in order to identify carcinogenic activity of the chemical before disposal. The contaminants of emerging concern need to be managed by minimizing toxic discharges directly to freshwater sources, generation of less amount of wastes, proper waste disposal and more research and development in properly enhancing the quality and effectiveness of the existing wastewater treatment systems.

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Part II

Advanced Technologies for the Removal of Contaminants of Emerging Concern

Chapter 8
Reappraisal of Permeable Reactive Barrier as a Sustainable Groundwater Remediation Technology

Alok Kumar Thakur and Manish Kumar

8.1 Introduction

Groundwater contamination has become a serious problem throughout the world due to the release of various contaminants from different sectors, both industrial and non-industrial. As per the United Nations, around 3 million people die each year around the globe due to consumption of contaminated water, diseases being diarrhea, typhoid, viral hepatitis and cholera being most common. Alone in India, this death toll rises to one lakh, and here, acute diarrheal diseases constitute 60% of the total deaths. Registered cases as per 2018 data of Ministry of Health and Family welfare in the last five years are equivalent to the population of the United Kingdom. India is at top of the chart in groundwater abstraction with an estimated volume of 251 km^3/year (Gun 2012). As per world report, groundwater of one-third of India's 725 districts is not fit for drinking due to the contaminants being more than the permissible limit be it arsenic, fluoride or salinity (Singh et al. 2019, 2020; Kumar et al. 2010, 2016; Das et al. 2015). Conditions in the state of Uttar Pradesh, West Bengal, Assam, Odisha and Madhya Pradesh are being severely criticized. As per NITI Aayog report of 2019, India stands at 120th rank out of 122 countries in water quality index report, which is not to be improved anytime soon, looking at the country's demand increasing each year.

Groundwater contamination exists when a man-made pollutant originating from sources like combustion of fossils fuels, road salts and other dreadful chemicals gets leached into the groundwater and ravage the water quality making its unsafe for human or animals use as shown in Fig. (8.1). The contribution of groundwater in every field is of critical importance be it irrigation, drinking, mining or industrial. More than two billion people around the world depend on the groundwater aquifers

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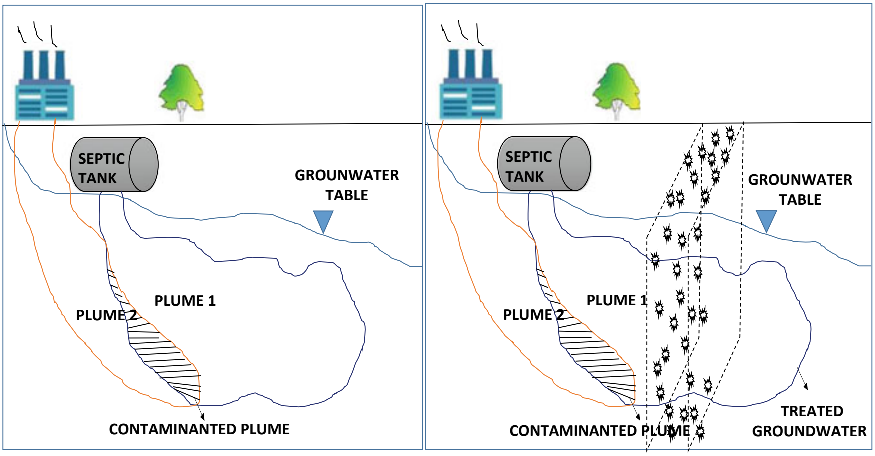

Fig. 8.1 Leaks from septic tank and leaching of pollutants from industrial site forming contaminated plume in the aquifer

for drinking purpose (Thiruvenkatachari et al. 2008). Because such a huge number of population around the globe depends on it, a little bit of toxicity also in the water quality standards can affect a large number of living beings.

The sources of groundwater contaminations are a varied range of source that includes storage tanks *if gets cracked or leaked ends up polluting groundwater*, septic systems *improperly designed systems can leak down pathogens below*, uncontrolled hazardous wastes *if improperly kept also leads to groundwater contamination*, landfills *if not shielded from bottom can contaminate groundwater*, chemical and road salts *different types of pest control or salt to melt ice can get leeched down to pollute groundwater*, and last but not the least atmospheric contaminants (Groundwater Foundation, National Groundwater Association). Groundwater is a constituent of the hydrological cycle, and thus, the contaminants from other areas of the cycle can find their way to the surface water and finally the groundwater. Figure (8.1) shows the application of PRB to remediate the contaminated groundwater.

The current review will discuss the following aspects in great details (i) what are the groundwater contamination sources (ii) what are the methods employed to remediate groundwater and how PRB is more efficient than the conventional methods used (iii) also, we will discuss the nature of different reactive materials used for the different contaminants and discuss their degradation phenomenon (iv) also we will discuss case studies to check it is in field implications and problems we encounter.

8.2 Groundwater Contamination

Sources

Groundwater contamination has been mostly due to human activities but also some part of it is due to the naturally occurring minerals. The contaminants once produced due to any anthropogenic activities leak down the aquifer pollute the groundwater, and it becomes very difficult as well as costly to remediate. The conventional remediation technologies like the pump and treat systems used to have high operational and maintenance costs. The contaminants according to their physical, chemical or biological nature sometimes travel with the flow of groundwater, sometimes they do not, forming a contaminated plume.

The sources of groundwater contamination can be broadly divided into two main categories

1. Natural Sources
2. Anthropogenic Sources
   (a) Point Sources
   (b) Non-Point Sources.

If you walk through a mountain valley and you see a cascading river stream, which may seem clear at first but same may not be the case, it would have been contaminated with naturally occurring minerals like hydrogen sulfide (H_2S), chromium (Cr(VI)), arsenic (As), iron (Fe), fluorides (F), radon gas (Rn), etc., which generally comes from the disintegration of Uranium (U), another natural radioactive contaminant. Anthropogenic sources include Pointy and Non-Point sources. Point sources include those sources which contaminate groundwater directly. It may include a varied range of sources from leaking chemical tanks or septic storage tanks situated just below the ground. On the other hand, Non-Point sources include sources which do not pollute groundwater directly but usually due to the runoff from a contaminated site. These contaminated sites include an agricultural field where pesticides and fertilizers are sprayed regularly or the chemical factories where the pollutants are not disposed of properly or untreated. There are a new set of contaminants coming into the picture of groundwater contamination known as 'Emerging Organic Contaminants' (EOCs), and these include pharmaceutical products, body care products also known PPCP. These are the contaminant usually present in the range of (ng/L or μg/L) (Lapworth et al. 2012). These contaminants are not only lacking a proper categorization but also do not have enough data, to make a universal decision for their permissible limits. Till 2012, there were more than 180 EOCs detected in groundwater.

Coming to India, it has a varied range of hydrogeological conditions which is a result of different amount of pattern of rainfall, wide range of geological conditions and also the topographical features in the entire county, the natural contaminants like fluoride, arsenic, chlorides vary vividly throughout the entire country, for example, there is high arsenic concentration in eastern states and high fluoride concentrations in western states of India. The various contaminants exceeding the permissible WHO

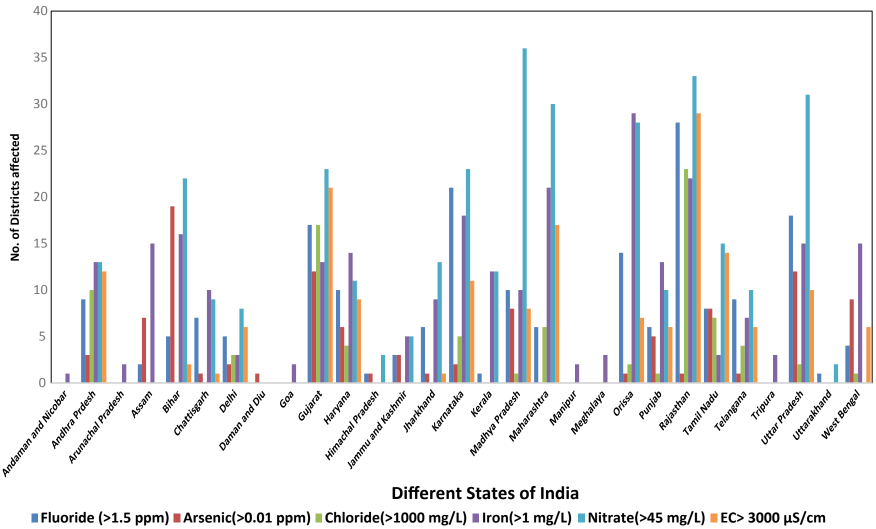

Fig. 8.2 Number of districts in India affected by Prime groundwater contaminants

limits are shown in Fig. (8.2) (Groundwater Quality in Shallow Aquifers in India, Central Ground Water Board 2018). The anthropogenic contaminants, on the other hand, involve the influxes from the agricultural and industrial sector. The intense use of the fertilizers has already caused a severe increase in nitrate concentration beyond permissible limit in more than 90 districts covering a territory of 11 states. Most common being used in India is dichloro-diphenyl-trichloroethane (DDT), benzene hexachloride (BHC). These contaminants have severe effects on human health ranging from mutagenic to carcinogenic shown in Table (8.1). The survey conducted by Central Pollution Control Board (CPCB) has identified more than 22 industrial sites responsible for contaminating the groundwater (CPCB 1995). The other main reason being the digging of wells in the coastal areas has contaminated the groundwater due to the intrusion of seawater in the aquifers. Landfill leachate is also one of the major constituents of groundwater contamination containing organic matters, ammonium and metals (Nooten et al. 2008). Nitrate contamination, which is mainly the result of the agricultural activities, is pervasive worldwide. Around 3/4th of India is having more than 45 ppm of nitrate in its shallow aquifers (CGWB(Central Groundwater Board) 2012).

Metal demands are increasing yearly, all the metals do have their diverse areas of uses, in spite of this, there are four to five primary constituents which requires metals most than the others like constructions, transport, types of machinery and chemical products. A study by Elshkaki et al. (2018) compared the primary metals productions and consumptions over the last 3–4 decades ranging from 1970 to 2010. These metals include iron (Fe), manganese (Mn), aluminum (Al), zinc (Zn), lead (Pb), copper (Cu) and nickel (Ni). Table (8.2) shows the comparison for the same.

Table 8.1 Groundwater contaminants and their health implications

Contaminants	Health effects		References
	Carcinogenic organs affected/symptoms		
Vinyl chloride	Cancer Group (1)	Liver	Lee et al. (1978)
Tetra chloro ethylene	Bladder cancer, non-Hodgkin lymphoma (NHL), multiple myeloma	Erythema and Blistering on the skin surface, depression, liver injury, eye irritation	Hake and Stewart (1977)
Tri-chloro ethylene	Kidney cancer, liver cancer, NHL	Autoimmune disease (Scleroderma), respiratory tract toxicity, delayed motor function, change in vestibular function and trigeminal nerve function	Scott and Jinot (2011)
BTEX	Inhalation carcinogenic effect	Reduced fetal growth, asthma, respiratory dysfunction, abnormalities in semen	EPA IRIS data Bolden et al. (2015)
Methylene chloride	Mammary tumors, Leukemia, Pheochromocytomas, Pheochromoblastomas	Irritation in lungs and Bronchi, Decrease in the number of RBCs and Hemoglobin, Eyes irritation and respiratory systems	Moskowitz and Shapiro (1952)
1, 1, 1-trichloroethane	Metastasis of carcinosarcoma to lymph nodes	Deposition of fats, hydropic degeneration, centrilobular necrosis, Cirhossis	Hodgson et al. (1989), Thiele et al. (1982)
Di (2-ethylhexyl) phthalate	Maybe carcinogenic (based on experiments on mice)	Autism spectrum disorders (ASDs), liver damage, sexual maturity delayed	Testa et al. (2012) Department of Health and Human Services, ATSDR (Agency for Toxic Substances and Disease Registration) data

(continued)

Table 8.1 (continued)

Contaminants	Health effects		References
	Carcinogenic	organs affected/symptoms	
1, 1 dichloroethane	No study reported	Adrenal cortical atrophy and hepatic damage (dogs), neurological, renal immunological, genotoxic and cardiovascular effects	Nelson et al. (1979) ATSDR data
1, 1 dichloroethene	Breast cancer risks involved	Hepatic, urinary and kidney system effected, nose to lungs tracts can become problematic and neurological dysfunction	Falck et al. (1992) ATSDR data
1, 2 dichloroethane (0.005 ppm)	Inadequate results	Hepatic and renal system effected	ATSDR data Department of Health and Human Services
1, 2 dichloroethene	Male breast cancer risks associated with its tans form	Blood forming affected and problems in Liver, Mutation Problems like sex chromosomes loss	ATSDR Data, Pub Chem (US National Library of Medicine), NIOSH data
Chloroform	Probable group B2 carcinogenic	Skin and eyes irritation, cytogenetic damages, mammary glands, liver, etc., affected	EPA, NIOSH and IARC data
Arsenic	Cancer of bladder, kidney, skin, lung, prostate and liver	Vascular diseases (peripheral, cardio and cerebral), causes of death due to nasopharynx and esophagus also reported	Wu et al. (1989)
Barium	No data	Endocrine, nervous, renal, hematological, hepatobiliary, reproductive system affected	Tardiff et al. (1980), Ohgami et al. (2012)

(continued)

Table 8.1 (continued)

Contaminants	Health effects		References
	Carcinogenic organs affected/symptoms		
Cadmium	Lungs and livers, pulmonary carcinogen	Aortic and coronary atherosclerosis, increase in the level of cholesterol and blood pressure, renal tubular dysfunction, proteinuria, chronic renal insufficiency	Kopp et al. (1982), Brzoska et al. (2000)
Chromium	Stomach cancer reported	Gastrointestinal effects Decrease in hemoglobin concentration, hepatic effects	Meyers (1950), Mancuso (1951)
Copper	No studies	Wilson disease, progressive lenticular degeneration, Alzheimer's disease, Parkinson's disease	Bandmann et al. (2015)
Fluoride	Bone cancer, respiratory cancer	Metabolic bone disease, gastrointestinal symptoms like nausea, vomiting. Loss in weight also reported	Hallanger Johnson et al. (2007), Grandjean et al. (1992)
Lead	Risk of tumorigenesis	Chronic kidney disease, tubulointerstitial nephritis, diabetes, hypertension	Ekong et al. (2006), Silbergeld et al. (1993)
Manganese	Risk of breast cancer	Neurological effects, damage of lung tissues, respiratory effects	Mergler et al. (1999), Kagamimori et al. (1973)
Nickel	Lung and nasal cancer, respiratory tracts related cancer	Hemorrhagic gastritis, decrease in bone marrow cell generation. Effects like vomiting, headache, diarrhea are common	Grimsrud and Peto (2006), Daldrup et al. (1983)

(continued)

Table 8.1 (continued)

Contaminants	Health effects		References
	Carcinogenic organs affected/symptoms		
Nitrate	Bladder, brain, colorectal, kidney, ovary thyroid	Type 1 childhood diabetes, high blood pressures, respiratory tract infections	Ward et al. (2005, 2007, 2010)
Zinc	Prostate cancer	Nausea and loss of appetite, diarrhea	Institute of medicine, nutrition and food board (2001)

Table 8.2 Major heavy metals and their increased production in anthropogenic age

Metal	Earlier demand 1975 (Tg)	Present demand 1975 (Tg)	Major area where metal is used
Iron (Fe)	350	800	Construction
Manganese (Mn)	3	8	Iron and steel
Aluminum (Al)	4	18	Transportation
Zinc (Zn)	2.5	6.5	Galvanizing
Lead (Pb)	2	5	Batteries
Copper (Cu)	2	5.5	Infrastructure
Nickel (Ni)	0.25	0.55	Industrial, machinery

Acid mine drainage is another problem associated with groundwater contamination. It generally occurs in the mining areas (Nordstrom et al. 2000). Whenever there is an entry of oxygen or water into sulfur-containing minerals or rocks, it gets transformed to sulfate solutions which in turn contaminates the groundwater and aquifers (kcil and Koldas 2006). Volatile organic compounds (VOCs) are also gaining interest as more dreadful contaminants, as their production has been exponentially in the last two decades (Geller et al. 2000). The contaminants like tri-chloro ethylene (TCE), etc., are carcinogenic and pose a bigger threat when leached into the aquifers near the industrial sites (Chiu et al. 2013). The urban waters already suffering with the issues of metals and VOCs have also been started contaminating with emerging contaminants like PPCPs (Pharmaceutical and Personal Care Products), ARBs (Antibiotic Resistance Bacteria), and ARGs (Antibiotic Resistance Gene) (Kumar et al. 2019).

8.3 Groundwater remediation technologies

Groundwater remediation has always proved to be a costly affair. The remediation technologies are mainly divided into three main categories namely (Hashim et al. 2011)

Chemical—Reduction, chemical flushing, in situ chemical fixation
Biological—Biological activity, bio-sorption, enhanced bio-restoration
Physical–chemical processes—PRBs, electro-kinetics, adsorptions.

The major processes involved in the remediation of groundwater involved from the last few decades are (Vallero 2011)

Pump and Treat: It employs more than one pumping wells, and the contaminants are cleaned up using physical or biological mechanisms. Not use in the case of low permeable aquifers (Zhang).
Air Stripping: It transfers all the volatile compounds from water to air.
Air Sparging: Here, the air is pumped into the water below to aerate it.
Bioremediation: It uses lively microorganisms to degrade or render the toxic materials harmless.
Filter through GAC: These granular activated carbons (GACs) help in the containment of the contaminants.
Natural Attenuation: It is the secondary form of bioremediation. The contaminants degrade over time with the help of microbes present instead of employing some pieces of machinery.
Bio-filtration: It is generally used to treat vapor-phase pollutants. It has a medium which is porous and contains microbes inside of it.
Adsorptions: It is most applicable for organic compounds but has also shown promising results for inorganic ones. Both the type of adsorptions, i.e., physical and chemical arises due to the electrostatic interactions (Muralikrishna and Manickam 2017).

The chemical treatment mainly involves detoxifying the contaminant by redox reactions or some time the only lone process of reduction or oxidation occurs (Evanko and Dzombak 1997). The chemical in situ application of permeable reactive barrier (PRB) has gained a lot of interest due to the low operational cost, media longevity and its hydraulic performance. PRB uses the hydraulic gradient (natural or induced) for remediating the contaminated groundwater, and the upgradient contaminated water gets decontaminated after reaching down gradient (Starr and Cherry 1994).

8.4 Permeable Reactive Barriers (PRBs)

Permeable reactive barrier has been defined as a trench filled with a certain amount of reactive material to remediate the contaminated groundwater contained in the aquifers

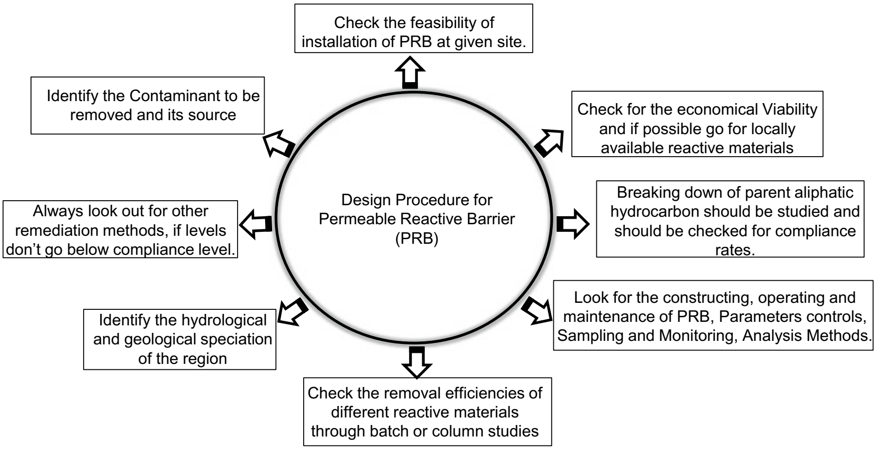

Fig. 8.3 Design procedure before permeable reactive barrier at any site

(Indraratna et al. 2015). PRB is recognized as passive remediation techniques for contaminated groundwater (Blowes et al. 2000). The concept on which PRB works is quite simple, PRB uses the hydraulic gradient of the groundwater flow, and the reaction occurs between the reactive material kept in PRB and influent contaminant upstream. Figure (8.3) shows the various pre-designing tasks before actually setting up the PRB at any contaminated site.

The very first conceptual idea about PRBs was given by McMutry and Elton (1985). Their idea revolved around three main constituents, i.e., (a) Treatment methodology (physical or chemical). (b) The hydraulic data and (c) The geotechnical designs. This groundwater remediation technique can be installed in either temporary or permanent basis. A large number of PRBs installed in the last three decades follows two types of setups (i) continuous trench (ii) funnel and gate. In the former type, the trench provided for the reactive filler is perpendicular to the groundwater plume flow and in the later one, walls (funnel) are emplaced to direct the plume toward the gate. The modified techniques involve the construction of subsurface PRBs with injection and fracturing models. A lab scale demonstration of PRB using hydraulic gradient to remediate groundwater is shown in Fig. (8.4).

Hydrological and Geological conditions for In Situ PRB applications.

8.4.1 Hydrological Characteristics

In the year 2015, US Geological Survey analyzed the several hydrological parameters of PRB which was remediating groundwater nitrogen in Cape god, Massachusetts by Barbaro et al. (2019) The factors that were used to evaluate the site characteristics were as follows:

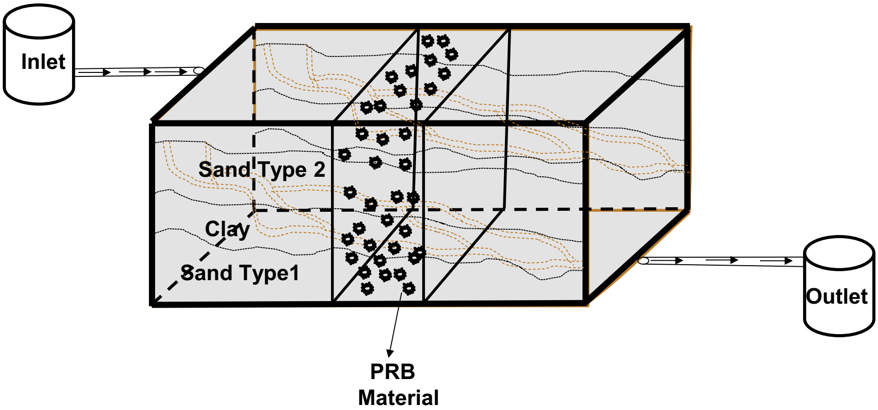

Fig. 8.4 Lab-scale demonstration of treatment of contaminant groundwater under the influence of hydraulic gradient

The direction of flow and groundwater flow rates
Level of the groundwater table
Value of hydraulic conductivity
Nature of aquifer (homogenous or heterogeneous)
Concentration and distribution of contaminant (in this case nitrate)
Dimensions of PRB (mainly thickness and length)
Accessibility of drilling/digging and installing PRB
The sensitivity of the reactive materials and targeted contaminant for redox reactions.

8.4.2 Geological Characteristics

Geological site characterization is divided into two major characteristics, i.e., geochemical and geotechnical characterization. The first one includes the monitoring of the parameters like pH, oxygen reduction potential (ORP) and dissolved oxygen (DO). The evaluation of these parameters will be helpful in the determination of the inorganic compound formation which may be due to the reaction between the reactive fillers and contaminants targeted. These parameters vary seasonally and also under depth. For thin aquifers, the changes are taken as negligible most of the time. The geochemical study also helps us identify the species that would react with our reactive media. Various works of the literature have identified the species like manganese, calcium, etc., to have lower down the efficacy of PRBs.

On the other hand, geotechnical aspect includes both the factors, i.e., above ground as well as beneath the ground. The former includes the easiness by which any equipment can use at the particular site. The later factor includes the presence of undersurface lithology that may cause the hindrances later, e.g., rocks and sediments.

8.5 The Software Involved in the Design of PRBs

As the numerical simulations play a most important role in determining the fate and transport of the contaminants, software like MODFLOW, FE FLOW are important so that the places of installation of injection and extraction wells can be selected. The PRB once placed in between the groundwater flows, goes through several issues like formation of metal hydroxides and carbonates precipitates, which ends up filling the pore and in turn decreases the hydraulic conductivity. To remove this kind of problems, we need more numerical software-based approaches which can help us with the modeling of reactions occurring inside PRB and determinable mass balance equations (Courcelles et al. 2011). Software programs like PHREEQC (Parkhurst and Appelo 1999), ORCHESTRA (Meeussen 2003), MINTEQ (KTH, Dept. of Land and Water Resources Engineering 2010), TOUGHREACT (Xu et al. 2004), CHESS (L'Assistant Informatique per Chimistes et Ingénieurs 2010), PHT3D (Prommer et al. 2003) help one in replicating the complex chemical reactions.

All these simulation-based softwares in Table (8.3) are user-friendly and are used according to the data management and outputs are needed, i.e., numerically or graphically.

8.6 Design of PRBs

The foremost design when PRB is ever talked about comes out to be continuous and funnel and gate system. (Pérez et al. 2018) analyzed the performance of two differently designed permeable barriers for zinc and sulfate remediation. It uses the two stainless sheets of steel reactors with a volume of 2.1 L volume, one for homogeneous substrate and other for diffusive exchange. The first one contains a mixture of all the materials, and the later one contains two layers namely reactive and conductive (sand). Reactive materials used were (i) pine compost (439.8 g) (ii) anaerobic sludge (54.98 g) (iii) nZVI (54.98 g) (iv) sand (0.5–5 mm, 2316.19 g) (v) gypsum (23.37 g). The change in concentration of Zn was 65.5–0.01 ppm in 60 days.

Permeable reactive barrier wells are the new innovative design of PRBs which we can implement for the remediation of VOCs in the low permeability aquifers (Bekel et al. 2019).

A series of total 12 wells, each in the category of extraction wells (1.5 m) and re-injection wells (1.2 m), were installed along the gradient of the plume. The depth of these wells was 15–16 m. The wells were constructed using rig fitted with 1.2 and 1.5 m augers. The PRB materials were filled after a UPVC raiser was placed

Table 8.3 Different software for the hydrological and geochemical analysis of groundwater

Catagory of software	Name of software	Application
Aquifer and Pump Testing	Aquifer Win32	Analysis of (pumping test + slug test)
	Aquifer Test Pro	Analysis graphically (all kind of aquifers)
	Infinite Extent	Analysis (pumping test)
	Chem graph	Storage of monitoring data of groundwater
	Enviro Base Pro	Database of standards of soil and water, their properties
	EquIS Geology	Database for environmental geology
	Hydro Geo Analyst	Data management of groundwater and borehole data
Geochemical Software	AquaChem	Geochemical analysis of water quality data graphically
	Hydrogeochem	Hydrological transport and geochemical analysis combined
	MINETQA2	Calculate the equilibrium between the absorbed and dissolved phases
Public Domain Software	BALANCE	Analyze mass transfer calculations
	GEOPARK	Analysis of spatial variability of functions
	HST3D	Simulation of heat and solute transport, in 3D flow
	MOC	2D solute transport
	MOCDENSE	Simulation of flows in the cross-sectional plane
	MODFLOW	A 3D groundwater flow model
	PEST	Parameter estimation for nonlinear models
	PESTAN	Analyze transport of organic solutes passing through Vadose zone
	PHREEQC	Model geochemical reactions
	PLOTCHEM	Plotting of water quality data
	RECESS	Estimate groundwater recharge and discharge with help of old records
	RETC	Retention curve program for unsaturated soils
	VLEACH	Leaching model for Vadose zone
	VS2DT	Analysis of solute and flow transport in single-phase flow in a porous medium
USGS Groundwater Software	AQTESTSS	Data management of aquifer and slug test

(continued)

Table 8.3 (continued)

Catagory of software	Name of software	Application
	DDestimate	Estimate drawdowns
	GSFLOW	Helps to model precipitations and runoffs
	GW_CHART	Graphical analysis of other software
	HST3D	Heat and solute transport model
	HYDRO THERM	Simulate GW flow and heat transport in a range of (0–1200 °C)
	INFIL 3.0	Estimate the infiltration below the root zone
	MODFLOW 2000	Groundwater management through optimization
	MF2K-VSF	Analysis with variably saturated flow
	MOC3D	Transport model of groundwater flow
	MODFLOW 2005	3D finite difference model
	MODOPTIM	Optimization of the groundwater flow model
	PHAST	Simulate multicomponent geochemical reactions
	PULSE	Predict hydrograph of groundwater discharge to streams
	SEAWAT	3D variable density groundwater flow
	SHARP	Simulate freshwater and saltwater flow in coastal aquifers system
	SUTRA	Variable density solute and energy Transport
	VS2DT	Simulates solute transport
	WTAQ	Calculate drawdowns and hydraulic properties
	ZONBDGT	Computes subregional water budgets

Source (Kumar 2012)

in the mid of drilled holes. There are six cases in which the design of PRB can be summarized (Gautam C Ijoor 1999) which are shown in Fig. (8.5).

8.7 Mechanisms Inside PRB

Permeable reactive barrier's one foremost advantage over the pump and treats system is its passive method of working, i.e., without any labor or energy input. The barrier

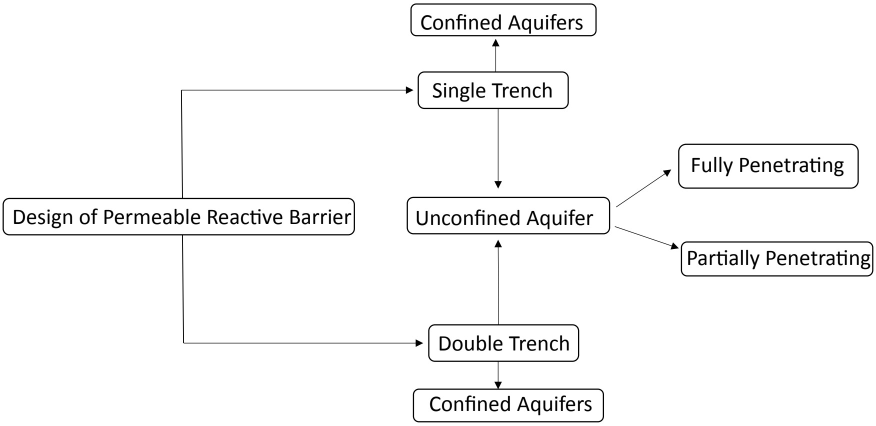

Fig. 8.5 Design consideration of any PRB in different kind of aquifers

before being set up has to go through (i) preliminary site assessment (types and concentration of contaminants, the velocity of groundwater) (ii) characterization of site (aquifer) and distribution of plume (iii) reaction rates and half-lives of contaminants (iv) barrier location and configuration (Gavaskar 1999). Modeling in 3D rather than 1D and 2D helps us to simulate the entire flow style of groundwater in the aquifers and also of the plume (Gupta and Fox 1999). The study by Bastiaens et al. (2008) has shown the use of lab-scale multifunctional permeable reactive barriers to remediate ammonium, halogenated hydrocarbons and chemical oxygen demand (CODs) from a 40-year-old landfill in Belgium. The different mechanism on which PRB works is shown in Fig. (8.6).

Gravel is generally added in between the reactive materials to improve the permeability of PRBs, and in the same, limestone is added as sulfate reducing bacteria can have controlled growth (Jarvis et al. 2006) have tested the mixture of organic materials for the removal of sulfate and cadmium ions, and the processes he noticed wer bioreduction and sorption by SRB and organic matter, respectively.

8.8 Reactive Materials

The study by Pérez et al. (2018) has shown that by using the straw and chicken manure as reactive material, it kind of lost its reactivity after six months of operation. Hashim et al. (2011) already suggested that the only drawback might be was a decrease in the number of bioavailable nutrients which would otherwise is constantly required for sulfate remediation. There have been many other material used for the remediation of heavy metals removal. Some of them are Cadmium by Burmese Grape Leaf Extract (Borah et al. 2018), Lead and Cadmium by Murraya Koengii powder (Mukherjee et al. 2020). There have been also the use of MnO_2 with alginate beads and Activated

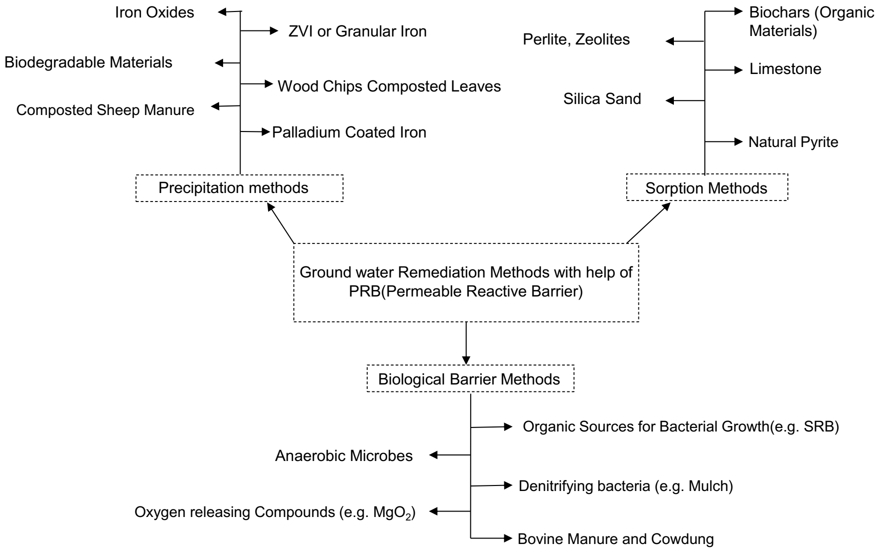

Fig. 8.6 Different mechanism inside permeable reactive material for different types of reactive materials

Carbon for the remediation of organic contaminants (p-cresol, tylosin) and inorganic contaminants (Arsenic, Cadmium) (Shim et al. 2019a, b).

Sulfate-Reducing Bacteria: It was first collected by Prof, (Groudev et al.) at Bulgaria. The area was located near a uranium mine deposit and was contaminated with radiogenic and heavy metals. The collected sample was cultivated through a process given in Fig. (8.7). The reaction involved in the sulfate-reducing bacteria constitutes two equations, first is the reduction of sulfate

$$SO_4^{2-} + 2CH_2O \rightarrow H_2S + 2HCO_3^-$$

Secondly, the sulfide formed reduces the metals

$$H_2S + \mathrm{Metal}^{2+} \rightarrow \mathrm{Metal}\ \mathbf{x}\ S_{(s)} + 2H^+$$

Nano-Zero Valent Iron (nZVI): Zero valent iron has shown promising results for several types of groundwater contaminants. Limitation for PRB having ZVI as its reactive material was incomplete removal of halogenated hydrocarbons as there is no change in their aromatic structures (Choi et al. 2007). Kumari et al. (2018a) studied the remediation of Chromium with the help of nZVI fused into magnetic corn cob silica. ZVI over a while turns into an agglomerate due to which its effectiveness might decrease, so a combination of ZVI with fibrous palygorskite was tried, which had an increased effective surface area and also acted as a catalyst (Frost et al. 2010). ZVI Synthesis has seen a long way from its inception from precision milling method,

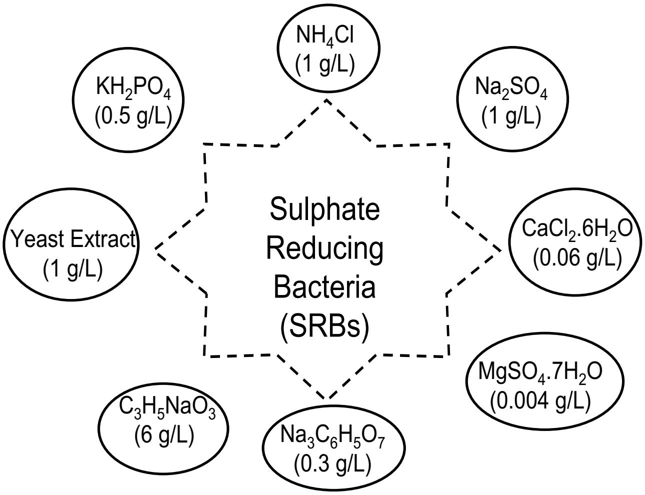

Fig. 8.7 Constituents of sulfate-reducing bacteria in lab

to extracting it via reduction of hydrous Fe^{2+} with the help of reducing agents.

$$Fe^{2+} + 2BH_4^- + 6H_2O \rightarrow Fe^0 + 2B(OH)_3 + 7H_2O \uparrow$$

There are multiple methods for the synthesis of nZVI shown in Fig. (8.8), and applications are also shown for the same.

Permeable Reactive Concrete (PRC): This is a PRB which uses concrete as reactive material. This study was done by Holms et al., and in this, he has used the more porous form of regular concrete which helps in adsorption of metals due to more number of removals sites. The PRC consists of cement, fly ash, aggregate and water. The modifications can be done on top of it by applying a chemical paste on top it, which will depend on the contaminant we want to remove. PRC uses a wide range of processes to remediate contaminants, i.e., from filtration to sorption, from ion-exchange to precipitation (Anderson et al. 2013; Sañudo-Fontaneda et al. 2014). The removal reason is still needed to be studied, but the high pH of pore water may be the reason for the removal, as the solubility of Pb, Cd and Zn decreases with increase in pH. The cost estimation by Holmes suggested \$1.2 million for Pb removal and \$80 thousand removals for Zn removal. Alighardashi et al. (2018) studied the implications of nano-silica on previous PRC for remediating nitrate removal. Nano-silica in order of 6% and fine aggregates in the order of (20%) was the optimum design for removal of nitrates.

Fly Ash: Fly ash, a by-product of any thermal power plant that uses coal as a source of energy, has proved to be the best heavy metal adsorbent according to various pieces of literature. In a batch test by Wantanaphong et al. (2005), it was found to have removed Pb(10 mg/L), Cd(1 mg/L), Cu (10 mg/L) and Zn (10 mg/L) completely, having the % metal removed equivalent to 100%. Fly ash, despite serving as the

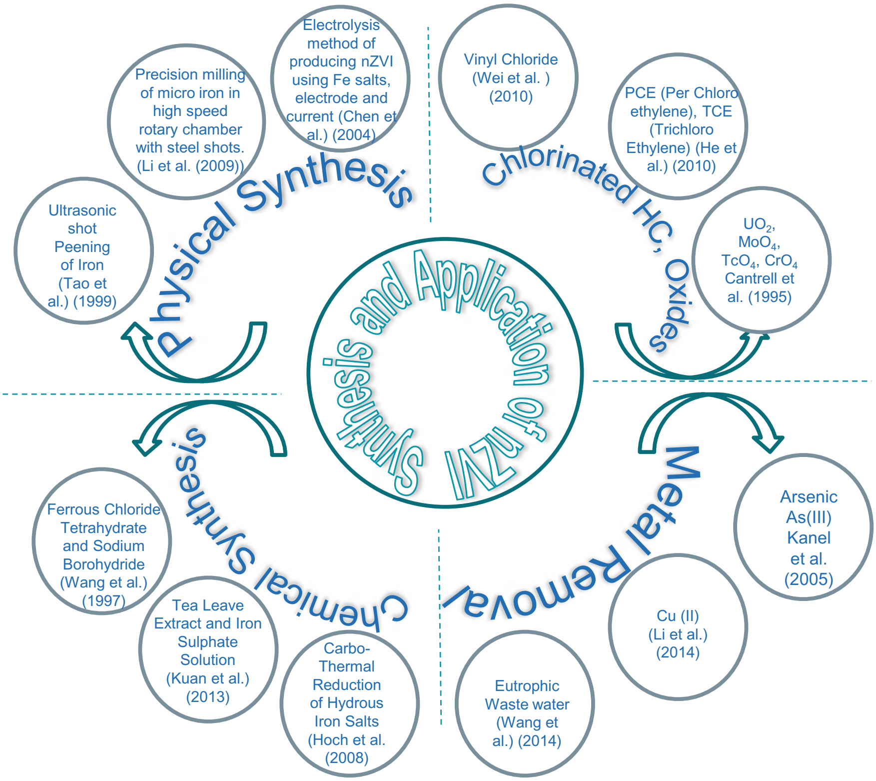

Fig. 8.8 Synthesis and application of nano-zero valent iron

perfect reactive barrier material, has problems of metal leaching through it Morar et al. (2012). Two major affecting the metal leaching was found to be (i) fly ash content and (ii) pH. Fly ash is a good adsorbent, but due to its alkaline nature, pH is increased from 5 to 10 in metal removal solution due to the leaching of calcium from fly ash into the aqueous solution. This in turns induces the formation of metal hydroxides which reduces the reactivity thereon Wantanaphong et al. (2005).

Activated Charcoals and Biochars: Huang et al. (2015) used activated charcoal as the reactive material alongside electrokinetic remediation for the removal of Pb, Cd, Cu, Zn. The maximum removal was of Zn, i.e., 78% under condition (2 V/cm, 15 days, 0.1 mol/l of oxalic acid), for Pb it was 69% under condition (1.5 V/cm, 10 days and 0.2 mol/L of oxalic acid), for Cu it was 84% under condition (2 V/cm, 15 days and 0.1 mol/L of oxalic acid), and for Cd it was 49% by (2 V/cm, 10 days, 0.05 mol/L). Hu et al. (2019) studied the effect of peanut shell biochar used along with slowly released nutrients (SRN), *Morganella Morgani* subspecies, which was found to be more effective in treating Cr(VI) than the traditional ZVI. The SRN was obtained by dissolving (40 g glucose, 80 g yeast extract and 30 g Agar) in 1 L water boiled for 10 min, after the mixture of immobilised biochars with SRM was used as PRB filler.

The development in the field of reactive materials synthesis is continuously taking path ahead. The reactive fillers are now composed of layers of different adsorbent materials, composites of multiple compounds and so on. There have been many new green materials and green technologies which are and will continue to remediate the contaminants from groundwater (Kumari et al. 2017). Several of these materials tested at batch scale are i) removal of Cr by Mn powder from battery waste solution (Kumari et al. 2018b) ii) remediation of E. Coli. by Ag nanoparticles by corn cob silica, and to name few technologies i) vermicomposting for Cu and Zn removal (Gogoi et al. 2015) ii) fouling control with the help of pre-oxidation combined with coagulation (Deka et al. 2020). The given Table (8.4) shows different PRB materials for different contaminants found in the groundwater, both geogenic and anthropogenic.

8.9 Case Studies and Economic Viability

The case studies are very limited in developing countries than the developed ones. McGovern et al. (2002) designed and built a funnel and gate PRB for remediating the petroleum hydrocarbon (toluene, ethylbenzene, xylene, alkanes) in southeastern Australia. After an operation period of ten months, ‘peat’ was proved to be effective reactive material with a removal efficiency of 72% overall. Germany was among the few countries which adopted PRBs without any further delay between years 1998–2001 (Birke et al. 2003) which also includes world’s largest funnel and gate system PRB installed at Edenkoben with six gates with the length being approximately 450 m. Wantanaphong et al. (2005) studied a wide range of reactive materials both natural and waste materials including (i) clinoptilolite (ii) calcified seaweed granules (iii) crushed cocoa shell iv) chitin shells (v) fly ash, and the surface area was found to be maximum in flash powder. The order of the efficiency of these materials in removing the metals Pb, Cd, Zn and Cu was fly ash > chitin > clinoptilolite > calcified seaweed > clay soil > cocoa shell. Several new materials are also making their way to reactive materials. Conca and Wright (2006) used a new material as a PRB filler called Apatite (II) $Ca_{10-x}Na_x(PO4)_{6-x}(CO_3)_x(OH)_2$ where $x < 1$, and this material is derived from fishbone waste and has been found to be better than the phosphate rocks, cow bones, various zeolites, ZVI filing, manures, etc. Conca (1997). The change in concentration in entering and exiting the PRB was quite noticeable, and the PRB has concealed over 45 kg of Cd, 91 kg of Pb, 4550 kg of Zn over five years. Indraratna et al. (2014) studied the remediation of acidic groundwater with the help of PRB in Shoalhaven floodplain at Sydney, Australia. Here, they used recycled concrete aggregates as PRB filler. This was the first study to the real-time monitoring and evaluation of PRB in the remediation of acidic groundwater. The governing equations used were encapsulated with the software like MODFLOW. Loss in hydraulic conductivity was observed at the entrance of the PRB due to the formation of metal precipitates. Twenty-two full-scale PRB projects were running

Table 8.4 PRB materials and their target contaminants

PRB material	Contaminant	Removal %	Source
Mulch (50%) + Gravel (50%)	Nitrate	66–99%	Gibert et al. (2018)
Sand (50%) + Sawdust (50%)	Nitrate	77%	Schmidt and Clark (2012)
Wood chips	Nitrate	>99%	Hiller et al. (2015)
Sediment wood particle	Nitrate	90%	Robertson et al. (2007)
Soil (70%) + Sawdust (30%)	Nitrate	70–95%	Schipper and Vujbodik-Vukovic (1998, 2000, 2001)
Soil (80%) + Sawdust (20%)	Nitrate	72–97%	Robertson et al. (2000, 2008)
Red mud	Fluoride	87.3%	Vinati et al. (2019)
Clay	Cs-137	NA	Source et al. (2015)
Natural pyrite (FeS_2)	Cr(VI)	27–100%	Liu et al. (2015)
Granular Iron	Chlorinated VOCs	No data	Vogan et al. (1999)
Bioaugumented Bio Barrier (*Mycobacterium* sp. and *Pseudomonas* bead) PRB	BTEX	84–97%	Xin et al. (2013)
ZVI + Polyhydroxybutyrate	1,2-dichloroethane	20–80%	Baric et al. (2014)
Wheat Straw + Coconut Shell BC	PAH	99%	Liu et al. (2019)
Clinoptilolite (01-29B)	Ammonium, Lead and Copper	>80%	Park et al. (2002)
Calcite	Nitrate	28–65%	Reddy et al. (2014)
	Phosphate	35–98%	
	Cadmium	88–96%	
	Copper	86–99%	
	Lead	98–99%	
	Nickel	0–14%	
	Chromium	15–60%	
	Zinc	4–99%	
Zeolite	Nitrate	35–75%	Reddy et al. (2014)
	Phosphate	70–73%	
	Cadmium	32–99%	
	Copper	95–98%	
	Lead	99–100%	
	Nickel	0–74%	
	Chromium	9–70%	
	Zinc	98–99%	

(continued)

Table 8.4 (continued)

PRB material	Contaminant	Removal %	Source
Iron fillings	Nitrate	91–100%	Reddy et al. (2014)
	Phosphate	88–94%	
	Cadmium	89–95%	
	Copper	80–100%	
	Lead	92–97%	
	Nickel	87–89%	
	Chromium	37–82%	
	Zinc	96–99%	
Sand	Nitrate	25–70%	Reddy et al. (2014)
	Phosphate	58–91%	
	Cadmium	3.5–9%	
	Copper	33–76%	
	Lead	11–100%	
	Nickel	0–3%	
	Chromium	9–49%	
	Zinc	0–49%	
Volcanic slag and Pumice	Copper	85%	Han et al. (2018)
Gillham and Hannes	Halogenated aliphatics (4 Halogenated methanes, 4 chlorinated ethanes, six chlorinated ethenes)	Up to 95% (slight increase in some aliphatics due to degradation of parent one was noticed for the little duration)	Gillham and Hannesin (1994)
Sediments containing SRBs, Silica Sand, Limestone, Municipal Compost	Sulfate (SO_4^{2-})	25–100%	Waybrant et al. (1998)
Sediments containing SRBs Wood Chips, Limestone, Urea, Chicken Manure, Composts	Sulfate (SO_4^{2-})	≥95%	Cocos et al. (2002)
Sheep Manure, Limestone, Oak Leaf, Composts	Sulfate (SO_4^{2-})	80–99%	Gibert et al. (2004)

with the context of treating chlorinated solvents, 14 pilot scales PRB projects for the same as per RTDF data (US EPA 2001). For the treatment of metals and inorganics, eight full scale and two pilot scales were under operations. Table (8.5) shows us the number of already set up PRBs in the USA and Europe, which are operating at a large scale and treating a wide range of contaminants from geogenic to anthropogenic.

In the Economic Analysis of PRB by (Robert Powell and Patricia Powell), they have compared the costs of construction and operation and maintenance for 1000

Table 8.5 Number of sites where PRBs are currently operational in full scale and the setup cost of these projects

Site name	Installation date	Contaminants (industries)	Configuration and reactive fillers	Cost (capital)
Sunnyvale, California, the USA	Jan 1995	TCE, DCE, VC, Freon (Earlier an Intersil Semiconductor Manufacturing Site)	Funnel and Gate; Fe^0	\$41,000,000
Southern Oregon, the US	Mar 1998	TCE (Aircraft Maintenance Hub)	Funnel and Gate, Fe^0	\$600,000
New Jersey (North), USA	Jan 1998	TCE (Municipal Site)	Hydraulic Fracturing, Permeation Infilling, Fe^0	\$1,120,000
Copenhagen, Denmark	1998	cis, trans, DCE, TCE, PCE, VC (Freight Yard)	Continuous Trench, Fe^0	\$235,000
Cheyenne, Wyoming	1999	TCE, cis-1,2-DCE, VC(Air Base)	Trench Box, Fe^0 and Sand	\$2,617,000
Lakewood, Colorado	Oct 1996	1,1,1-Trichloroethane, 1,1-DCE, TCE, cis-1,2-DCE (Highway Facility)	Funnel and Multiple Gate, Fe^0	\$1,000,000
Brunn am Gebirge, Austria	Oct 1999	Polycyclic Aromatic Hydrocarbons, Benzene, Toluene, Ethylene, Xylene (Industrial Site)	Adsorptive Reactors along with Hydraulic Barriers, Activated Carbon	\$750,000
Seattle, Washington, the USA	Oct 1999	TCE, PCE, cis-1,2-DCE, VC (Manufacturing Site)	Funnel and Gate	\$350,000
Fairfield, New Jersey, the USA	Sep 1998	PCE, TCE, 1,1,1-Trichloroethane (Manufacturing Site)	Continuous Trench, Fe^0	\$725,000
Kolding, Denmark	1999	TCE, Cr (Hardkrom Site)	Continuous Trench, Fe^0	\$358,000
Manning, South Carolina, the USA	Nov 1997	TCE, cis-1,2-DCE, VC (Industrial Site)	Continuous Site, Fe^0	\$350,000
Belfast, Ireland	Dec 1995	TCE, cis-1,2-DCE (Industrial Site)	Slurry Wall Funnel with In situ reaction vessels, Fe^0	\$375,000

(continued)

Table 8.5 (continued)

Site name	Installation date	Contaminants (industries)	Configuration and reactive fillers	Cost (capital)
Coffeyville, KS	Jan 1996	TCE, 1,1,1-Trichloroethane (Industrial Site)	Funnel and Gate, Fe^0	\$400,000
Watervliet, New York, the USA	1999	Halogenated VOCs (Manufacturing Site)	Continuous Trench, Fe^0 and Concrete Sand	\$391,000

gallons of water treatment by PRBS and pump & treat (P&T) System. At Watervliet location, the construction cost of PRB was \$528 per 1000 gallon of water, whereas for P&T, it was \$1608. At Somersworth landfill site, it was \$29 in comparison with \$357. At Intersil Site, the difference between O&M cost between P&T and PRB was \$40 per 1000 gallon of water, at USCG center, it was \$43, and at Fairfield New Jersey, it was \$21 for the same amount of water.

8.10 Conclusions

From its inception in the 90s, PRBs have come a long way in terms of its design, installation, fillers used. This groundwater remediation technology needs to be further researched. Though permeable reactive barrier has proved itself a much better alternative than the traditional pump and treat system. A problem like manganese precipitation when limestone is used as a reactive material should be looked after. The major advantages of PRB are its lower operational and maintenance cost, but the periodic removal of the precipitate formed around the reactive material and also the replacement of reactive material from the barriers in some cases may add to the costs, so close monitoring is required for the installed PRB. The study has noticed a few earlier problems associated with the PRBs which includes degradation of the reactive material. Column studies are required as much as batch studies so that the groundwater velocities and aquifer residence time can be simulated. There had been more focused nowadays on coupling systems, where the reactive barriers are coupled with the electrokinetic remediation. Researches are also needed in the field of how to enhance the longevity of the PRBs and how to cut the operational and maintenance cost. The capital cost of PRB is quite high then its counterparts, which solely depends on site characteristics (hydrology and geology), design of PRBs, method of installation and cost of generation of reactive materials which is being used. We can also look out for the synthesis of new cost-efficient reactive materials, which do not cause the formation of carbonates or hydroxides and end up clotting the pores of PRB. Nanomaterials will be playing an important role in terms of reactive barrier material. Very little pilot and full-scale projects are currently operational around the globe and that too in developed nations, and hence, the study is limited to only first world countries. Also, the study is limited only to ZVI when we talk about using it on tons basis as fillers. So, other options of fillers need to be determined as loss of reactivity is noticed in ZVI fillers after a certain period. The changes in the chemical composition and geochemical cycles should be regularly monitored inside the barrier and also in the downstream so that any kind of fouling. The more software-based analysis would be needed to do the real-time simulations of contaminant transport and groundwater flow to have a better understanding of PRBs.

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Chapter 9
An Insight into Microbial Remediation of Hexavalent Chromium from Contaminated Water

Aliya Naz, Abhiroop Chowdhury, and Brijesh Kumar Mishra

9.1 Introduction

Chromium is a transition metal, with varied applicability in tannery, electroplating, pulp and paper, dye and paint, textile and steel and chemical industries (Verger et al. 2018; Guertin et al. 2016). For this wide usage, the production of Cr from mines have increased drastically within last two decades (IBM 2013; USGS Mineral Yearbook 2015). Chromium exists in various oxidation states, out of which trivalent (Cr^{3+}) and hexavalent chromium (Cr^{6+}) are generally found in aqueous medium. Hexavalent chromium is mutagenic and carcinogenic as it can cause cancer on long-term exposure to human (Naz et al. 2016a, b; 2018). Chromium pollution through improper waste disposal and effluent influx from Cr-utilizing industries like ferrochrome, electroplating, tanning units as well as mining regions are the major contributors to this metal in the natural environment. Recent researches are focused on the exclusion processes of Cr^{6+} from the contaminated effluents foremost of which are chemical, electrochemical, adsorption, ion exchange filtration, and microbial reduction of Cr^{6+}. Conventionally, chemical and electrochemical reduction is the most common method used to treat contaminated water (Barrera-Díaz et al. 2012). This method has few major disadvantages like the requirement of high energy and generation of large volume of sludge, which increases the disposal problems rather than solving (Owlad et al. 2009; Jin et al. 2016).

The selection or innovation of economically efficient Cr^{6+} removal technique from contaminated wastewater is essential for the developing countries that try to balance

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their environmental expenditure with minimum financial footprint. The most effective technique explored at the tropical countries like India is the microbe mediated removal/reduction of Cr^{6+} as the optimum temperature in these regions is suitable for natural microbial growth, and external energy is not required for maintaining the growth rate of the organisms. The uses of pure and mixed culture for the Cr^{6+} remediation are a topic of debate between researchers working in this topic across the globe (Sugiyama et al. 2012; Doganli and Dogan 2013).

Recent developments of microbial techniques like aerobic and anaerobic suspended sludge bioreactor system, activated sludge system, upflow sludge anaerobic bioreactor (USAB), microbial fuel cell are widely used for bioremediation of trace metal contaminated effluents (Venkata Nancharaiah et al. 2012; Naz and Gupta 2013; Lytras et al. 2017; Kumari et al. 2017). Several microorganisms including aerobic and anaerobic have been identified which can be utilized for the chemical transformation of toxic chromium (Cr^{6+}) into non-toxic form (Cr^{3+}). Thus, the treatment of wastewater can be done by the semi-conventional microbial treatment systems, and the microbial fuel cell can be utilized to remediate the Cr^{6+}-contaminated vadose zone and aquifer water table (Molokwane 2010; Hsu 2011; Kumar et al. 2009). Thus, we can achieve a full-fledged Cr^{6+} remediation process to decontaminate effluent, surface water, and groundwater. Though microbial remediation technique is efficient for the chromium contaminated wastewater, the commercial use of this technology is still large-scale application trials. The main reason behind the limited application of microbial remediation is lack of knowledge, less popularity, and low demand.

Thus, this knowledge gap in identifying microbial strains with Cr− remediation potential and their possible utilization in wastewater treatment is the focus of this chapter. Thus, the chapter deals with the widely used microbial strain for the removal of Cr^{6+} from the contaminated water, their removal mechanism, microbial tolerance for Cr^{6+}, and the application of mixed microbial culture for the removal of Cr^{6+} from contaminated wastewater and utility of hybrid microbial bioremediation systems like microbial fuel cell to make this green process more applicable for commercial and industrial use.

9.2 Hexavalent Chromium Reducing Microbes

There is a wide variety of microbial species isolated from the different sources, which are not only adaptable in the metal-rich condition, but can also transform the toxic Cr− species to its less or non-toxic forms (Kasan and Baccker 1989). Microorganisms such as *Pseudomonas fluorescens* have genetic characteristics to tolerate metal stress because of their inherent characteristics in their nuclear and extranuclear plasmids. The microbial species found in heavy metal contaminated sites have plasmid or chromosomal-borne resistance to metal toxicity, and they are generally mutants among the natural population. Some of the microorganisms do not have any plasmid-borne characteristics to reduce metals, yet they can address this problem through certain inherent or spontaneous chromosomal mutations, e.g.

E. cloacae HO1 strain and *Bacillus* sp. QC1-2 (Campos et al. 1995; Thatoi and Pradhan 2017). However, their metal-reducing potential depends on many factors such as their own genetic configuration in addition to various environmental factors where they grow.

It is a topic of debate among researchers that microbes belong to the same species may not give same Cr^{6+} reduction efficiency or have similar Cr^{6+} tolerance, and the nature of growth medium can play a vital role in this differentiation. Mergeay (1995), Gogoi et al. (2015) reported that, the metal resistant capacity of microbes depends on providing nutrient medium. *Bacillus sphaericus* was isolated, investigated by many researchers and different reducing potential of the same species under different environmental conditions have been reported. These studies reveal that reducing efficiencies of microbes not only depend on the microbial species, but also the factors like source site of isolation, nutrient medium, initial Cr^{6+} concentration, contact/reaction time, and similar other environmental factors. The summary of the microbial species studied by many researchers has been classified depending upon the environmental conditions (aerobic, anaerobic, or both), where they have grown their tolerance level, contact time (HRT) and provided nutrient medium, along with their respective Cr^{6+} reduction efficiencies are categorized and described in Table 9.1.

Studies show that, maximum numbers of microbes that have a high tolerance level are mainly aerobic and belong to *Bacillus* sp. (Table 9.1). However, the tolerance level varied from 49,650–500 mgL^{-1} that may be due to various environmental conditions used in the studies. Sau et al. (2008) reported that among all the Cr^{6+}-resistant microbes, *Bacillus firmus* demonstrated maximum tolerance (49,650 mgL^{-1}) to Cr^{6+} and it is reduced to 104 mgL^{-1} of Cr^{6+} within 144 h of incubation time.

Hexavalent chromium tolerance and reduction have been observed by different microbial genus of aerobic and anaerobic group, for example, *Bacillus, Pseudomonas*, *Nesterenkonia, Cellulosimicrobium, Staphylococcus, Alcaligenes, Burkholderia, Arthrobacter*, *Acinetobacter, Desulfovibrio, Pantoea, Methanothermobacter, Desulfovibrio,* and *Desulfotomaculum*. But if reduction efficiency and utility of microbes for the reduction of Cr^{6+} to Cr^{3+} are considered, aerobic and facultative microbes are shown better efficacy (Narayani and Shetty 2013; Kumar et al. 2009).

9.3 Cellular Mechanism of Chromium Reduction

Scientific literatures elaborated on the microbial transformation mechanism for the reduction of Cr^{6+}, which suggests that the hydrogenase, nitroreductase, quinine reductase, ChrR, YieF, membrane associate reductase (MR), soluble associate reductase (SR) enzymes are responsible for catalyzing electron transfer process in the transformation of Cr^{6+} to Cr^{3+} (Park et al. 2000; Kwak et al. 2003; Ackerley et al. 2004; Thatoi et al. 2014). Electron donating species like NAD(P)H mediates the enzymatic transformation of hexa (+6) to tri (+3) species of chromium but generates Reactive Oxygen Species (ROS) in the process (Park et al. 2001; Chardin et al.

Table 9.1 Source and performance of microbial strains for the removal of Cr^{6+} from contaminated water

Microbial species	Source	Substrate/Medium	Tolerance Cr (mgL^{-1})	Initial Cr^{6+} (mgL^{-1})	Cr^{6+} removal (%)	Reaction Time/HRT (h)	References
Bacillus firmus	Electroplating effluents polluted soil	PYGA	49,650	104	100	144	Sau et al. (2008)
Bacillus sp.Ev3	Industrial wastewater	LB	4800	100	91	96	Rehman et al. (2008)
Bacillus sp. JDM-2-1	Industrial wastewater	LB	4800	100	85	96	Zahoor and Rehman (2009)
Bacillus maroccanus	Tannery waste contaminated soil	TMM+0.2%gluconate	2080	10.4	56-69	96	Viti et al. (2003)
Bacillus maroccanus ChrC22	Tannery waste contaminated soil	TMM+0.2% gluconate	1456	10.4	56-69	96	Viti et al. (2003)
Bacillus amyloliquefaciens	Sukinda chromite mine soil	NA	900	100	100	144	Das et al. (2014)
Bacillus subtilis	Tannery waste contaminated soil	Ca-M9 MM	800	50	100	65	Mangaiyarkarasi et al. (2011)
Bacillus sphaericus	Serpentine soil	PYG	800	20	62	48	Pal and Paul (2004)

(continued)

Table 9.1 (continued)

Microbial species	Source	Substrate/Medium	Tolerance Cr (mgL^{-1})	Initial Cr^{6+} (mgL^{-1})	Cr^{6+} removal (%)	Reaction Time/HRT (h)	References
Bacillus sphaericus	Tannery waste contaminated soil	NA	500	500	91.7	78	Kathiravan et al. (2010a)
Pseudomonas viridiflava	Cr(VI) contaminated Soil	TMM	1560	10.4	43	24	Viti et al. (2006)
Staphylococcus gallinarum W-61	Tannery effluents	LB	644.8	26	100	56	Alam and Ahmad (2011)
Arthrobacter aurescens	Cr(VI) contaminated aquifer soil (core)	VB	1000	60	100	408	Horton et al. (2006)

HRT Hydraulic retention time, *NA* Nutrient agar, *PYGA* Potato yeast glucose agar, *NB* Nutrient broth, *LB* Lysogeny broth, *PYG* Peptone yeast extract glucose, *MM* iThayer-Martin agar, *ZMA* Zobell Marine agar

2003; Gonzalez et al. 2005). Reactive oxygen species are known to exert harmful effects on the cellular protein and Deoxyribonucleic acid (DNA) and maybe one of the main causes for the development of cellular-level genetic mutation that can eventually lead to malignancy or cancer (Cheung and Gua 2007).

Microorganisms can adapt to metal-polluted environments by transforming their cellular metabolic processes via adsorption uptake, metal efflux, metal biotransformation or DNA methylation to avoid metal toxicity. Generally, these processes operate either by direct enzymatic reduction of Cr^{6+} to less toxic forms Cr^{3+} or indirectly by making metabolic complexes (Camargo et al. 2003; Pei et al. 2009). Microorganisms naturally growing in metal-contaminated environment are hence resistant to heavy metal toxicity. Works on chromite mine also suggest that microbes isolated from mine spoils, and effluents are resistant toward Cr-induced toxicity (Das et al. 2013). It is observed that during the biotransformation of Cr^{6+} to Cr^{3+}, bacterial proteins are generated that protect the cells from oxidative stress due to the production of ROS. Cellular reduction of hexavalent chromium is an active process that produces redox intermediate Cr species with (+5) or (+6) oxidation states along with stable (+3) state, that forms Cr− DNA ducts and is the major cause of toxicity-induced mutation and chromosomal breaks (Zhitkovich 2011).

According to advances in molecular biology, several chromosomal genes impart resistance to the toxicity of Cr^{6+} in bacteria, and due to this reason, microbial species are able to proliferate in Cr^{6+} contaminated environment showing Cr− resistance (Thatoi et al. 2014). For example, ChrR chromosomal gene conferred Cr resistance to *Pseudomonas aeruginosa* (Aguilar-Barajas et al. 2008; Thatoi et al. 2014). Bacterial species and Archean are known to evolve various metabolic biochemical processes for tolerating toxic compounds in both aerobic and anaerobic systems. However, the biochemical mechanism of the transformation of Cr^{6+} differs between aerobic and anaerobic microorganisms.

9.3.1 Aerobic Microbial Reduction

Aerobic microbes detoxify Cr^{6+} by oxygen-dependent processes in which carbon-rich substrate acts as electron donor while O^{-} is the electron acceptor. Cheung et al. (2006) reviewed that, aerobic microbes reduce Cr^{6+} in two or three steps; the first step is being Cr^{6+} to Cr^{5+} followed by Cr^{4+} and then finally Cr^{3+}. In this way, microbial cells release ChrR and SR enzymes which catalyze electron transfer to reduce Cr^{6+} and the formation of intermediate Cr^{5+}, which is again reduced to Cr^{3+}. The formation of Cr^{4+} intermediate in this process is still mysterious (Fig. 9.1).

Codd et al. (2001) investigated the formation of Cr^{4+} during the reduction of Cr^{4+} to Cr^{3+} and opined that the study of Cr^{4+} formation is very difficult because of its instability may be because of the absence of suitable detecting method (Lay and Levina 1998). Further, Chirwa and Molokwane (2011), reported that the presence of NADH, NADPH, and endogenous electrons in the microbial cell serves as electron donors which provide electrons for the reduction of Cr^{6+}.

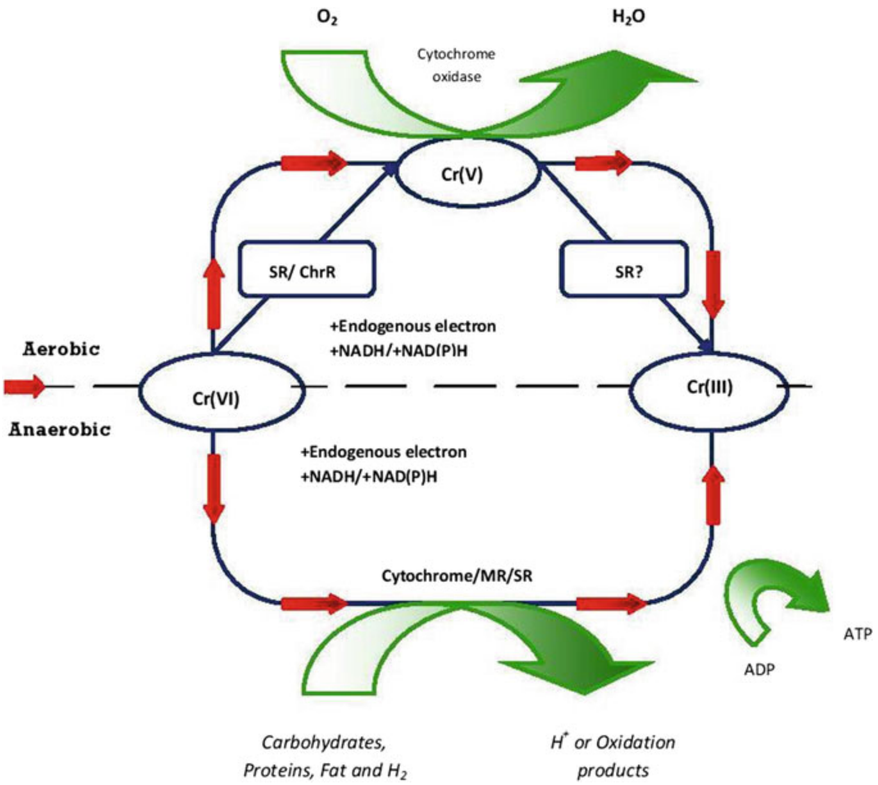

Fig. 9.1 Possible Cr^{6+} reduction mechanism in the microbial cell (modified from Wang and Shen 1995). The aerobic microbes reduce Cr^{6+} with help of soluble reductase enzymes (SR) using NADH (or by reserved electron donor) in two steps: First it reduced in unstable Cr^{5+} and then in stable Cr^{3+}. The anaerobes directly reduced Cr^{6+} to Cr^{3+} with help of either SR or membrane-bound reductase (MR) or both

9.3.2 Anaerobic Microbial Reduction

Anaerobic microbes also use NADH, NADPH, or endogenous electron to reduce Cr^{6+} as aerobes, but in most of the cases, anaerobic microbes are mainly associated with SR/MR or cytochromes reducing enzymes (Wang and Shen 1995). These enzymes share two electron pairs for reducing Cr^{6+} directly to Cr^{3+} (Fig. 9.1). Czako-Ver et al. (1999) stated that it is unclear that the reduction of Cr^{6+} to its intermediate [i.e., Cr^{5+} and Cr^{4+}], and the formation of Cr^{3+} is enzyme-mediated or spontaneous. On the contrary, other researchers reported that microbial transformation of Cr^{6+} is mainly based on the enzymatic reactions (Ishibashi et al. 1990; Park et al. 2000; Kwak et al. 2003; Cheung et al. 2006).

9.4 Microbial Growth Inhibition

Wong and Trevors (1988) reviewed the effects of chromium compounds on the microorganisms including bacteria and algae. *Scenedesmus acutus* algae stop its growth at >15 mgL^{-1} of Cr^{6+} (Travieso et al. 1999), while a mixture of *Scenedesmus, Selenastrum, and Chlorella algae is* grown at 100 mgL^{-1} of Cr^{3+} but could not tolerate Cr^{6+} of same concentration (Brady et al. 1994). Two strains of bacterial cell *Arthrobacter* sp. *and Bacillus* sp. were isolated from contaminated soil with tannery effluents, and both the bacteria can tolerate 100 mgL^{-1} of Cr^{6+} in agar medium, but only *Arthrobacter* grows in liquid medium. *Arthrobacter* sp. reduces up to 50 mgL^{-1} of Cr^{6+}, while Cr^{6+} reduction efficiency of *Bacillus* sp. is only 20 mgL^{-1}. *Arthrobacter* sp. proven superior to the *Bacillus* sp. in the ability to reduce and tolerate toxic Cr^{6+} (Megharaj et al. 2003). *Staphylococcus epidermidis* L-02 isolated from chromate contaminated anthropogenic wetland reduced Cr^{6+} under anaerobic condition. Researcher also observed that, the cell number and specific Cr^{6+} reduction rate decreases proportionally with the increase of Cr^{6+} dose. Due to Cr^{6+} toxicity, the microbial cell wall decreases from 50–100 nm as compared to control, i.e., 100–300 nm (Zakaria et al. 2007), which may have been a reason behind the reduced hexavalent Cr removal efficiency of certain bacterial species as it limits the adsorption surface area of the membrane.

Studies have been done on the effect of Cr^{6+} on the microorganisms present in the aerobic mixed cultures present in activated sludge process (ASP) (Gokcay and Yetis 1991). Few researches indicate that even small concentrations (1–5 mgL^{-1}) of Cr^{6+} can have a toxic influence on beneficial microbes' growth (Gokcay and Yetis 1991). Some studies also refer that after an optimum concentration of Cr^{6+} concentration, there is a gradual decrease in bio-reduction rate as microbes' lose their tolerance to Cr- toxicity (Chirwa and Wang 2000). This Cr^{6+} dose that affects the Cr-tolerance of microbes differs from species to species and is an important point of scientific debate.

Very few works have been done on the remediation of Cr^{6+} through anaerobic microbes. Aerobic condition is proved to be the most favorable for the reduction of Cr^{6+} through aerobic microbes. Cr^{6+} reducing dominant genera are *Bacillus* and *Pseudomonas*. Species of *Bacillus* (*B. fusiform* NTR9, *B.*ES29, *B.* sp. ev3, *B.* JDM-2-1, *B.* sp. CSB-8, *B.* QC1) and species of *Pseudomonas* (*P. fluorescens*, *P. fluorescens* LB300, *P.* Sp. C-171) has been proven to be effective in reducing up to 100 mgL^{-1} of Cr^{6+}.

Other microbial genera like *Arthrobacter, Ochrobactrum, Cellulosimicrobium, Staphylococcus, Alcaligenes*, *Streptomyces* also found effective to reduce different concentrations of Cr^{6+}. Although few studies have done on Cr^{6+} reduction in the anaerobic condition. *Desulfovibrio vulgaris* is able to reduce 100% Cr^{6+} at the initial concentration of 20.8 mgL^{-1} (Lovley and Phillips 1994), while *Achromobacter* sp. Ch-1 and *Pannonibacter phragmitetus* can able to tolerate high range of Cr^{6+} concentration and can reduce Cr^{6+} concentration in the range from 250 to 500 mgL^{-1} in the both aerobic and anaerobic environmental conditions (Ma et al. 2007; Chai et al. 2009). It is also reported that most of the microbial cultures are very much suitable for the removal of lower concentration (1–100 mgL^{-1}) of Cr^{6+}, while high Cr^{6+} concentration inhibits the microbial growth rate, disrupts the cell structure, and ultimately reduces the biomass of microbial culture (Stasinakis et al. 2004; Narayani and Shetty 2013).

9.5 Application of Mixed Cultured Bioreactors

Though Cr^{6+} is very toxic, it inhibits the growth of microbial cells, damages the cells, and affects the metabolic activities of microbes, and studies revealed that, there are both living and dead cells able to adsorb Cr^{6+} ions (Gokcay and Yetis 1991). It is difficult to maintain laboratory conditions for the pure culture so the biological treatment of Cr^{6+} using single microbial species is not feasible at large scale (Narayani and Shetty 2013). Dermou et al. (2005) used a pilot-scale biological reactor inoculated with indigenous microbial consortia. They operated bioreactors in three-mode; batch, continuous and sequencing batch reactor (SBR) with recirculation while the SBR-recirculation process was found to be more efficient in Cr^{6+} removal than the former.

According to Katiyar and Katiyar (1997), cell immobilizations are much-advanced method to reduce/biosorb Cr^{6+} as compared to free cell culture. Immobilized cells are more stable, high biomass loaded and can be regenerated easily, reusable, and they do not require a continuous nutrient supply for growth. It can be easily separable from water and does not cause clogging problems in a continuous flow system. Because of the above reasons, the bed and mixed bed cultured bioreactors are proven to be more effectice and widely advocated by scientific academia. Thus, bioreactors consisting Cr^{6+} reducing bacteria are cost-effective, easy, secure, and techno-feasible process for Cr^{6+} removal from water (Ganguli and Tripathi 2002).

Immobilized materials like alginate-carboxymethyl cellulose, rubber wood sawdust, calcium alginate, bed of PVC, granular activated carbon, agar layer on the surface of the synthetic membrane, gravel, elemental sulfur, glass beads, wood husk, and activated carbon have been used to support biofilms of chromium reducing bacteria (Xu et al. 2011; Kathiravan et al. 2010b; Benazir et al. 2010; Yang et al. 2009). Farag and Zaki (2010) supported that, immobilized and mixed cultured cells can be reused at least three times, without losing their Cr^{6+} reducing efficiency. The concept of reusing depends on the microbial species. Some microbial species cannot reused as they are prone to cell lysis. The neverending academic search for more and more effective and reusable microbial species is a scientific enigma and has spiked the interest of researchers worldwide.

Figure 9.2 shows the suppose process for microbial remediation of Cr^{6+} contaminated water. It is clear from the schematic diagram, prior to installation in industries, laboratory trials are very much important to understand the applicability of microbes toward Cr6+ removal from contaminated water. Isolations of microbial cells from the Cr^{6+} contaminated waste would save the acclimatization time and also may prove more efficient than the same microbial strain isolated from non-contaminated sites.

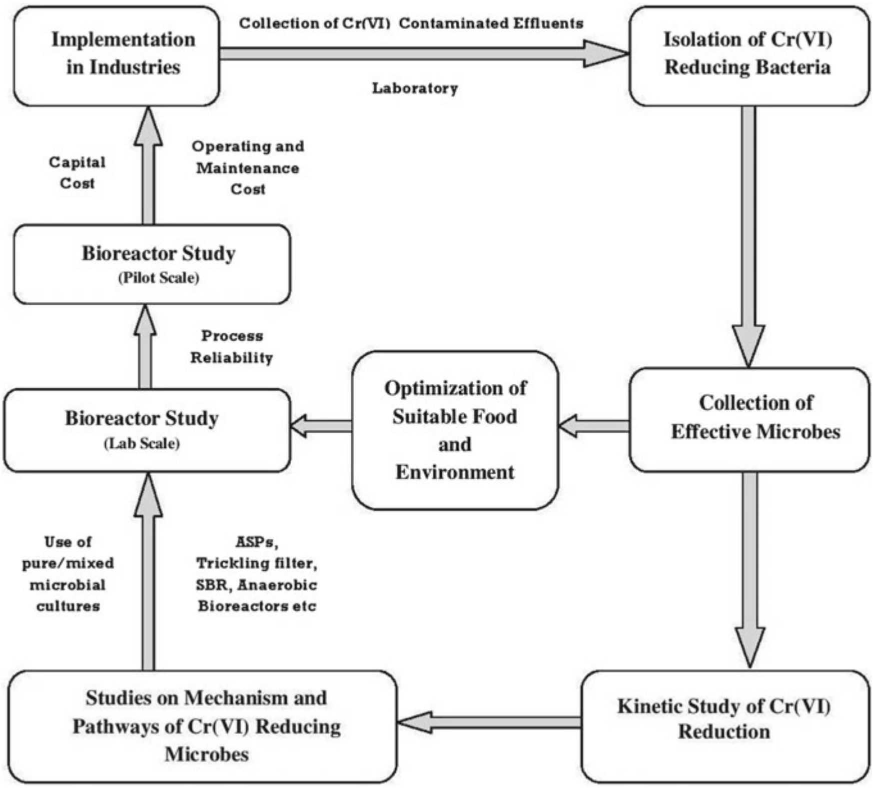

Fig. 9.2 Application of microbial bioreactors for Cr^{6+} removal

The packed bed microbial culture, immobilized cells, trickling filters, activated sludge process, biofilm bed reactor, and sequencing batch reactor (SBR) all can be effective to remove Cr^{6+} from water (Molokwane et al. 2008; Dey and Paul 2014; Field et al. 2013). In mixed aerobic cultures or activated sludge process (ASP), Cr^{6+} directly reduced to Cr^{3+} by chromium reducing microbes. The reduced chromium remains in the microbial cell, and after the death of cells, they finally get precipitated as sludge. Precipitated dead cells contain reduced metals, and they may be removed either by independent settling or by physical trapping in the sludge floc matrix. A study by Stasinakis et al. (2004) indicated a removal of 40% of the total Cr^{6+} during activated sludge process while the rest of the Cr^{6+} was sorbed by the sludge flocs in Cr^{3+} chemical form. According to Chen and Gu (2005), an acclimated activated sludge showed 100% efficiency in the removal of Cr^{6+} and approximately 98.56% of total chromium at influent level of 20 mgd^{-1}. However, at higher concentration (60 mgd^{-1}) of Cr^{6+}, the removal efficiency of microbes decreases.

9.6 Case Studies

The utility of microbial species isolated from chrome liquor, tannery waste, effluent treatment plant, and serpentine soil is studied by many researchers for the removal of Cr^{6+} (Table 9.1). These species found suitable not only to remove toxic chromium from water but also to reduce chemical and biological oxygen demands.

- Verma et al. (2009) isolated different species of *Bacillus* like *B. brevis, and B subtilis* to ascertain their comparative effectiveness to reduce Cr^{6+} in the concentration range of 160–180 mgL^{-1}. And, *B. coagulans* was not found effective to reduce Cr^{6+} in that range in comparoson with the other two strains.
- Ahmad et al. (2010) constructed a pilot-scale bioreactor (Chrom-BacTM) inoculated with *Acinetobacter haemolyticus* microbial strain and found a complete reduction of 17–81 mgL^{-1} of Cr^{6+} from electroplating water. They stated that, the performance of Chrom-BacTM was not affected by different factors like in the fluctuation of pH (6.2–8.4) and nutrient temperature (30–38 °C). The technical feasibility of a Chrom-BacTM system was demonstrated at 200 L pilot scale.
- According to Wani et al. (2019), *Pseudomonas entomophila MAI4* bacterial strain was isolated from industrial effluent, showed significant removal of Cr^{6+} at the controlled laboratory environmental condition and concentration dose of 100 ppm, and showed 80% Cr^{6+} reduction efficiency in the original industrial wastewater.

9.7 Conclusion

The chapter sheds light on the applicability of microbes toward reducing Cr^{6+} from water in both aerobic and anaerobic conditions. The reduction of Cr^{6+} can be achieved effectively by microbial systems for the water containing Cr^{6+} in appropriate amounts. As described in the chapter, the metal tolerance and resistant potential in microbes not only depend on that particular microbial species, but also on the environmental conditions and provided nutrient medium.

There are numbers of aerobic and facultative microbes that found suitable for Cr^{6+} reduction; but in the economical point of view, aeration at field level is not cost-effective. Microbial reduction of Cr^{6+} can be improved by prior acclimitization of aerobic and anaerobic Cr^{6+} tolerating microbes before their application in batch or continuous or hybrid bioreactor system. As only few works have done on the anaerobic microbial remediation of Cr^{6+}, there exist a research gap that need to be addressed. Further, studies should be done on recovering Cr from Cr^{6+} reducing sludge/microbial biomass in a economic, feasible process with least environmental footprint.

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Chapter 10
Review on Trends in the Removal of Pharmaceuticals and Personal Care Products (PPCPs) from Water and Wastewater

Suvendu Manna, Uttariya Roy, Anirban Biswas, Shubhalakshmi Sengupta, Piyali Basak, and Papita Das

10.1 Introduction

Residual personal care product and pharmaceuticals are becoming one of the most emerging threats to human civilizations. These types of pollutants slowly change the ecological balance of environment. In addition, excessive pharmaceuticals in the environment could change the antibiotic sensitivity of microbes. It is reported that more than 3000 types of compounds and their derivatives are being used in the preparation of drugs that include antibiotics, analgesics, beta-blockers, contraceptives, tranquilizers, lipid regulators, and medicines for impotence (Siegrist and Joss 2004). Simultaneously, thousand different types of chemical agents are being used to prepare personal care products for skin, hair, and teeth (Daughton and Ternes 1999). It has been reported that currently over 6 million of PPCPs are commercially available worldwide. In addition, pharmaceutical use is raising 3–4% by weight in every year (Daughton 2004). In an investigation undertaken in North America, it was found that 80% of river in the USA are contaminated with PPCPs (Onesios et al. 2009). Moreover, this study pointed that drinking water in cities also found to be

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contaminated with PPCPs. This study also suggested that these types of pollutants causing ecological imbalance in the region (USEPA 2014).

PPCPs are comprised of an extremely varied set of compounds to be used in agricultural practice, veterinary medicine, human health, and cosmetic care. This group of pollutants is considered as pseudo-persistent pollutants, although their polar nature, short half-lifetime, and trace concentrations in water (Petrovic et al. 2009). This is because a multitude of individuals frequently used these types of chemicals and eventually discharged into the environment. Subsequently, either due to non-treated or insufficient wastewater treatment they come into the drinking water resources. PPCPs contain a diverse set of functional groups such as hydroxyl, carboxyl, ketone, and amine which make them more complex in nature. It should be noted that pharmaceuticals classified as per their active substances within subgroups of a pharmaceuticals does not signify that they always follow certain chemical behaviors. Small changes in the chemical structure often significantly changes solubility, polarity, and other properties of these pollutants. Distribution of these types of pollutants in air, water, sediments, soils, and animals is largely dependent on these types of changes (Kummerer 2009).

Several European and American countries have classified pharmaceuticals and personal care products which includes antibiotics, bacteriostatics, analgesics, and anti-inflammatory drugs, anti-epileptics, β-blockers, cytostatics, blood lipid regulators, hormones, musk fragrances, antidepressants, disinfectants, and antiseptics. Detail chemical properties and corresponding toxicity data of those PPCPs have been reported with Tables 10.1 and 10.2.

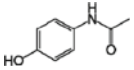
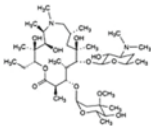
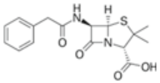
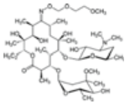
In this chapter, toxicity and fate of PPCPs have been discussed. Also, the removal processes of PPCPs are discussed critically to understand their pros and cons.

10.2 Types of Personal Care Products and Pharmaceuticals Found in Water

10.2.1 Personal Care Products

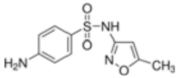
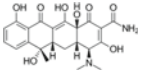
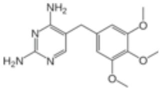
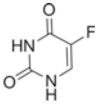
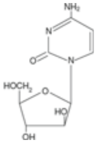
Among the chemicals used in the preparation of personal care products, diethyl phthalate (DEP) is a decent example as it is used widely in cosmetic fragrance mixtures. A list of such chemicals with their health effects has been shown in Table 10.3. It is often suspected that phthalates can disrupt the endocrine functionality by reducing the sperm count in men. Also, it is often linked with the reproductive defects in the developing male fetus. Moreover, metabolites of phthalate often associated with insulin resistance and obesity in men (Stahlhut et al. 2007). Report indicated that exposure to phthalate can cause liver and kidney failure in children. Thus, the Health Canada banned six types of phthalates in children's toys. Manufacturers are not bound to write itemized individual components on the product label. Rather they listed generic term representative of a furtive combination of dozens of substances.

Table 10.1 Chemical properties of pharmaceuticals

Compound	Structure	Molecular weight (g mol^{-1})	LogK$_{Ow}$	pK$_a$	LD$_{50}$	LC$_{50}$
Analgesic						
Acetaminophen		151.163	0.46	9.38	>2250	>5900
Antibiotic						
Azithromycin		749	4.02	8.74	>2000	–
Benzylpenicillin		334.4	1.83	2.74	8900	–
Roxithromycin		837.047	–	1.7	–	–

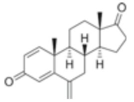
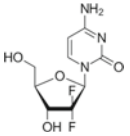
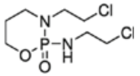
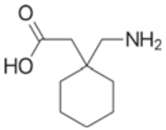
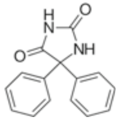
(continued)

Table 10.1 (continued)

Compound	Structure	Molecular weight (g mol^{-1})	$LogK_{Ow}$	pK_a	LD_{50}	LC_{50}
Sulfamethoxazole		253.28	0.89	1.6; 5.7	>2300	–
Tetracycline		444.4	−1.37	3.3	808	–
Trimethoprim		290.32	0.91	7.12	4850	–
Anticancer						
5-Fluorouracil		130.08	−0.89	8.02	230	>1.8
Cytarabine		243.22	−2.46	4.22	>3150	–

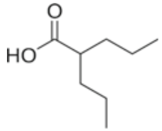
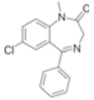
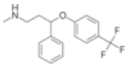
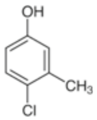
(continued)

Table 10.1 (continued)

Compound	Structure	Molecular weight (g mol^{-1})	LogK$_{Ow}$	pK$_a$	LD$_{50}$	LC$_{50}$
Exemestane		296.4	3.1	–	–	–
Gemcitabine		263.2	−2.01	3.6	500	–
Ifosfamide		261.08	0.86	14.59	>150	–
Anticonvulsant						
Gabapentin		171.24	−1.1	3.68; 10.70	500	–
Phenytoin		252.27	2.47	8.33	150	–

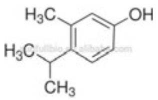
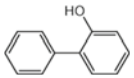
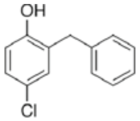
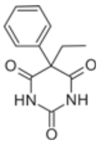
(continued)

Table 10.1 (continued)

Compound	Structure	Molecular weight (g mol^{-1})	LogK$_{Ow}$	pK$_a$	LD$_{50}$	LC$_{50}$
Valproic acid		144.21	2.75	4.8	>28	1098
Antidepressant						
Diazepam		284.74	2.82	3.4	>9	>12
Fluoxetine		309.33	9.8	1.25-4.3	284	–
Antiseptic						
4-Chloro-m-cresol		142.58	3.1	9.55	500	0.583

(continued)

Table 10.1 (continued)

Compound	Structure	Molecular weight (g mol^{-1})	LogK$_{Ow}$	pK$_a$	LD$_{50}$	LC$_{50}$
Biosol		150.22	–	–	–	–
Biphenylol		170.21	3.09	9.55	1400	5
Chlorophene		218.68	3.6	–	2510	5620
Barbituate						
Phenobarbital		232.23	1.47	7.3	150	1460

(continued)

Table 10.1 (continued)

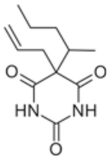
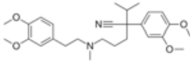
Compound	Structure	Molecular weight (g mol^{-1})	$LogK_{Ow}$	pK_a	LD_{50}	LC_{50}
Secobarbital		238.28	1.97	7.8	65	–
Calcium channel antagonist						
Verapamil		454.6	3.79; 2.15	8.92	8	0.6

Table 10.2 Chemical properties of personal care product

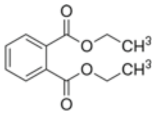
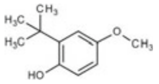
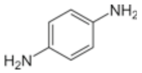
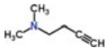
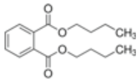
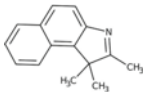
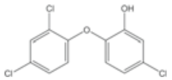
Compound	Structure	Molecular weight (g mol^{-1})	LogK$_{Ow}$	pK$_a$	LD$_{50}$	LC$_{50}$
Diethyl phthalate (DEP)		222.24	2.47	–	>1000	4.64
BHA		180.24	–	–	4000	–
P-phenylenediamine		108.14	−0.25	6.2	17	5.75
DEA		125.21	–	–	–	–
Dibutyl phthalate		278.34	4.5	–	>4	>25
Petrolatum		209.29	–	–	–	–
Triclosan		289.51	4.76	7.9	3700	825

Table 10.3 Types of personal care product and their health effects

Name	Applications	Health effects
Diethyl phthalate (DEP)	Used in cosmetic fragrance mixtures	Endocrine disruptors, reduced sperm count, defects in the developing male fetus, obesity and insulin resistance, liver and kidney failure in young children
BHA	Used in moisturizers and makeup as preservatives	Endocrine disruptors and may cause cancer
P-phenylenediamine	Used in hair dyes, cosmetics	Cause cancer, toxic to the brain
DEA	Used in some creamy and foaming products, such as moisturizers and shampoos	Cause cancer
Dibutyl phthalate	Used as a plasticizer in some nail care products	Endocrine disruptor and reproductive toxicant
Parfum	Used in a variety of cosmetics	Can trigger allergies and asthma, cause cancer and neurotoxicity
Petrolatum	Used in some hair products for shine and as a moisture barrier in some lip balms, lipsticks, and moisturizers	Cause cancer
Triclosan	Used in some antibacterial cosmetics, such as toothpastes, cleansers, and antiperspirants	Cause hormonal disorders

Thus, in this report focus has been given to only those compounds that are commonly found in a wide range of personal care products. Butylated hydroxyanisole (BHA) is an antioxidant used mainly in conditioners and makeup. This chemical is doubted to be a cancer-causing and endocrine disruptive agent. *P*-phenylenediamine is another chemical mainly used for hair dyes and cosmetics. This chemical has potential to cause cancer and brain damage. Diethanolamine (DEA) is mainly used in creamy and foaming products like conditioners and shampoos. DEA often transforms into nitrosamines, which known to be carcinogenic. Dibutyl phthalate is a plasticizer mainly used in nail care products. This is another chemical suspected to be endocrine disruptor and reproductive toxicant. Mixture of different chemical ingredients is used as fragrance in a variety of cosmetics. Some of these ingredients trigger allergies and asthma, and some linked to cancer and neurotoxicity. Some of these ingredients are known to be very harmful to aquatic and other wildlife. Often, petrolatum is used in hair products for shining and moisture barrier in lip balms, lipsticks, and moisturizers. Triclosan and petroleum product might be contaminated with polycyclic aromatic hydrocarbons, which is often used in toothpastes, cleansers, and antiperspirants as antibacterial agent. Structural, chemical, and toxicity details of the personal care products have been shown in Table 10.2.

10.2.2 Pharmaceuticals

Recent discovery of pharmaceutical resides in groundwater, agricultural feedstock, even in packaged drinking water triggered serious concern as pharmaceutical is known to cause serious health issues to human and aquatic animals. With time pharmaceutical use is increasing. Also, in developing countries like India, people take medicine without proper prescription. This releases an untold amount of different pharmaceuticals in the surface and groundwater resources. Thus, it can be said that these types of pollutants would be the most common pollutants in water resources. Currently, pharmaceuticals are also used for farming and aquaculture. The pharmaceuticals used for farming and aquaculture are used for initiating specific biological action. Consequently, its release into the environment could pose potential health hazards to aquatic life.

Most of the PPCPs are produced such a way that it becomes biologically active and hydrophilic. Due to these properties, PPCPs are readily absorbed within the tissues of human and other living being. Often these PPCPs are found to be persistent for avoiding degradation before they start to work (Radjenovic et al. 2007). Depending on the compound and its properties, parent compounds of PPCPs and/or their metabolites are often excreted through urine. A literature review performed by Alcock et al. (1999) gave an excellent indication of fate of pharmaceuticals (Alcock et al. 1999). They indicated that 30–90% of an administered dose of most antibiotics is excreted via urine. More importantly, the antibiotics excreted were found to be active (Alcock et al. 1999). Similarly, Calamari et al. (2003) pointed that more than 90% of administered dose of some antibiotic was found to be excreted as the parent compound (Calamari et al. 2003). Though PPCPs are known to be released in very low concentration (mostly in the ng/L to μg/L range), they could initiate potential health impact, especially when accumulated within human tissue. PPCPs such as steroids and estrogens are being used in oral contraceptives and have high potency. Upon release to the environment, these PPCPs could cause biological effects even at very low concentrations (Calamari et al. 2003). Different types of pharmaceuticals and their corresponding health effects have been listed in Table 10.4. Structural, chemical, and toxicity details of different pharmaceuticals have been shown in Table 10.1.

10.3 Fate of Pharmaceuticals and Personal Care Products

There are many reviews where exposure routes of different PPCPs into the aquatic and soil environment had been discussed widely (Halling-Sorensen et al. 1998; Kummerer 2001; Heberer 2002; Jorgensen and Halling-Sorensen 2000). The environmental risk assessment strategy for PPCPs exposure had also been reviewed and discussed previously (Daughton and Ternes 1999; Jones et al. 2004; Hernando et al. 2005; Fent and Weston 2006; Zuccato et al. 2006). Some authors listed the annual quantities of PPCPs prescribed for different countries (Halling-Sorensen et al. 1998; Jorgensen

Table 10.4 Types of pharmaceuticals and their health effects

Name	Applications	Health effects
Steroids and estrogens	Used in oral contraceptives	Cause many biological disorders
Ibuprofen	Relief from pain, rheumatoid arthritis, osteoarthritis	Cause cardiovascular disease, hypertension, risk of ulceration, bleeding, advance renal disease, skin reaction
Carbamazepine	Used for seizure disorder, neuropathic pain	Cause skin rash, short breath, sore throat, bleeding gums, dark urine, and loss of appetite
Sulfamethoxazole	Used for treatment of various infections caused by bacteria	Cause diarrhea, irritation eyes, chest pain, cough, weakness
Acetaminophen	Used to treat headache, muscle aches, arthritis, colds, fever	Nausea, upper stomach pain, itching, loss of appetite, clay-colored stools
Fluoxetine	Used to treat the major depressive disorder, obsessive-compulsive disorder, panic disorder	Hives, itching, inability to sit still, restlessness, joint or muscle pain

and Halling-Sorensen 2000; Fent and Weston 2006). Many reviewers also indicated the effects of PPCPs in humans and mammals (Fent and Weston 2006) including its metabolization in humans (Richardson and Bowron 1985). In addition, the effects of PPCPs in aquatic vertebrates and invertebrates were also reviewed and reported by many researchers (Daughton and Ternes 1999; Halling-Sorensen et al. 1998; Jones et al. 2004; Fent and Weston 2006). Many researchers also reviewed and compared different PPCPs elimination processes used in wastewater treatment plants currently (Janex-Habibi et al. 2004; Larsen et al. 2004) including the pretreatment processes of highly contaminated wastewater feed sources like urinals and hospitals.

Wastewater treatment facilities used to treat municipal spent reduce the organic load in the discharged effluent. This reduces the loss of oxygen in receiving waters. Unfortunately, those facilities are not precisely designed to eliminate PPCPs. Also, the ability of biologically activated sludge-based secondary treatment process for PPCP removal has been poorly understood till date. Loftus et al. (2015) studied the fate and transport of pharmaceuticals present in lagoon-treated wastewater effluent applied as cropland irrigation in Illinois, USA. They found six priority PPCPs in lagoon-treated wastewater effluent. However, the study indicated that the concentration of the six PPCPs in the treated wastewater effluent was lower than the untreated influent. The study pointing out that lagoon treatment is not sufficient for removal of PPCPs from wastewater.

In another study, 13 PPCPs were used to investigate their degradation profile in anaerobic sludge degradation process (Carballa et al. 2007). Mixture of PPCPs was added to the raw sludge before feeding the anaerobic digesters.

The results indicated that degradation efficacy was not same for all the 13 PPCPs used in this study. The removal efficacy varies in the range between 0 and 60%. This study also indicating that anaerobic sludge digestion is also not sufficient to eradicate PPCPs from the wastewater completely.

10.4 Toxicity and Regulations

Personal care products, the largest class of unavoidable category of threats to our health, are being used widely throughout the world. These types of toxic cosmetics have ingredients that initiate health hazards. Bisphenol A (BPA) is a classic example of this type of ingredients. BPA is largely used in pipes, interior of food cans, steel drums, sealing teeth, and plastic water bottles. It is reported that BPA exposed to human rapidly. The study undertaken by NHANES III pointed that around 93% of urine samples from humans between 6 years and older were found to have the unacceptable amount of BPA. This study also indicated that the formula-fed infants with plastic bottles have 10 times more BPA in their urine than that for the breast-fed infants. As per the Endocrine Society, BPA interferes with the normal functioning of male and female reproduction systems and breast development. It also initiates prostate cancer, thyroid metabolism disorder, obesity, and cardiovascular diseases. Low doses of BPA often correlated with impaired immune function, early onset of puberty, obesity, diabetes, and hyperactivity.

Hydroquinone is an active ingredient of skin lighteners. It inhibits tyrosinase, the key enzyme for melanin synthesis. It is also known to be carcinogenic, genotoxic, and mutagenic (McGregor 2007; NTP 1989). Parabens are used in cosmetics and personal care products as preservatives, such as deodorant, shampoo, conditioner, and moisturizers. These chemicals also have health issues like carcinogenicity and genotoxicity (Darbre et al. 2004; Darbre and Harvey 2008; Miller et al. 2001).

Use of plant-derived biochemicals often believed to be better than their synthetic alternatives. In recent years, plant derived bio-chemicals are being used drastically in the cosmetic and personal care products. However, these bio-chemicals should also be tested for their health hazards. It is known that these bio-chemical could initiate adverse dermal effects including irritation, sensitization, phototoxicity, and immediate-type allergy. It is a well-known fact that taking plant derived chemicals as dietary supplements and/or herbal medicines might be natural but not always equivalent to being safe. Realistic approaches are needed to establish the quality and safety standards of botanical ingredients for consumer safety.

Due to its rapid use, PPCPs also mix into the air, water, and soil and start to destroy the ecological imbalance. Aquatic systems often are the final repository of pollutants like PPCPs which could pose severe toxicity to the aquatic biota. In a recent study, toxic effect of four PPCPs on benthic invertebrates was investigated. The report indicated that all the four PPCPs were very toxic to the studied benthic invertebrates.

Recently, more than 100 different PPCPs were found in environmental and drinking water samples. Toxicity of few of those PPCPs was discussed here. 1,4-Dioxane is a by-product of ethoxylation process of some cleansing and moisturizing product. It often found as contaminant in cosmetics and personal care products like shampoos, deodorants, mouthwashes, and toothpastes. This chemical is known to be carcinogenic, nephrotoxic, neurotoxic, and toxic to respiratory.

2-bromo-2-nitropropane-1,3-diol is an antimicrobial agent and used as preservative for shampoos and cosmetics. It often breaks down into nitrosamines which is toxic in nature. This chemical is toxic to gastro-intestine, immune system, skin, and liver.

Acrylamide is an impurity of polyacrylamide which is used as binding, thickening, or flocculating agents in cosmetics. It causes cancer to kidneys, liver, testes, and spleen.

Aluminum salts are used as antiperspirants in deodorant which is known to be linked with Alzheimer's and breast cancer.

Benzyl alcohol is being used as precursor for various esters used in the making of soap, perfume, and flavoring agents. It is often used in e-liquid of e-cigarettes as a flavoring agent. It may cause allergy upon contact to skin. It causes gasping syndrome to neonatal and produce necrosis. Butylated hydroxytoluene is used as food additive, antioxidants, and in fragrance. It often causes skin, eye, and lung irritation and toxic to immune system.

10.5 Removal Strategies for Personal Care Products and Pharmaceuticals

In recent years, different types of processes are being tried for removal of PPCPs from wastewater. All the processes used till date for PPCPs removal are discussed in the following subsections.

10.5.1 Flocculation and Coagulation

Flocculation and coagulation are very simple and popular methods for the separation of many pollutants from wastewater by using flocculants or coagulants. In their study, Ternes et al. (2002) had tried to remove diclofenac, carbamazepine, clofibric acid, bezafibrate, and primidone from wastewater by precipitating with ferric chloride. However, they fund that removal efficiency for all the five pollutants were less than 10%. They also found that other process like degradation with ozone and adsorption by charcoal is much better option for PPCPs removal than coagulation. In a similar study, Carballa et al. (2007) used ferric chloride, aluminum sulfate, and aluminum polychloride for removal of seven different types of PPCPs which include galaxolide, tonalide, diazepam, carbamazepine, ibuprofen, naproxen, and diclofenac from water. Their report indicated that only galaxolide and tonalide had the highest removal efficiency between 50 and 70% during the flocculation test. The other pollutants showed removal efficiency less than 25%. Also, carbamazepine and ibuprofen were not removed from water.

10.5.2 Activated Sludge Process

Activated sludge process is a biological treatment widely used in conventional wastewater treatment plants (WWTPs). Though volatilization, adsorption, and biodegradation are important steps of activated sludge process, reports indicated that volatilization and adsorption have least contributions for PPCPs removal (Gobel et al. 2005; Suarez et al. 2010; Li et al. 2015). Biodegradation is the main mechanisms for the activated sludge-based process. However, many factors like pH, effectiveness of the degraders, and retention time affect the PPCPs removal efficiency in this process. Ternes et al. (2007) tried to remove diclofenac, clofibrate acid, ibuprofen, ifosfamide, and cyclophosphamide using activated sludge process and found very low removal efficiency. Song et al. (2009) on the other hand found that for efficient PPCPs degradation sufficient retention time. They also pointed out that existing sewage treatment plants have very short retention time which is not sufficient for the degradation of PPCPs at the operational process. On the other hand, Wang et al. (2002) indicated that low abundance of degraders and the lack of degraders in the environment could also lower the efficiency of activated sludge process. They prescribed biological acclimation and bio-augmentation to tackle these issues.

10.5.3 Advanced Oxidation Technology

10.5.3.1 Ozonation

Oxidation of organic pollutants with ozone is one of the most studied processes. Ozone has been widely used for the removal of PPCPs. The rate of ozonation mainly depends on the formation of hydroxyl radicals. Thus, to enhance the oxidation efficacy H_2O_2 is being used with ozone very frequently for eliminating PPCPs from water (Bai et al. 2016). The reviews of Esplugas et al. (2007) and Wang and Chu (2016) indicated that ozone has very high PPCPs oxidizing abilities. However, these reviews also pointed out that ozonation rate could be declined dramatically if hydroxyl radical scavengers are present in the mixture. Also, wastewater is a complex system with different types of pollutants; thus, detail study is needed to investigate the effect of wastewater composition on the hydroxyl radical formation.

Ternes et al.(2007) used ozone in their study to remove carbamazepine, diclofenac, solid alkyd resin, and oxcarbazepine from raw water. They found that addition of ozone in the range of 0.5 mg/L could remove almost 97% of carbamazepine and diclofenac from water. O_3/H_2O_2 was also used for PPCPs oxidation (Zwiener and

Frimmel 2000). On the other hand, Rosal et al. (2009) used a catalyst along with ozone to remove solid alkyd resin. They reported that the addition of TiO_2 as catalyst with ozone at pH 5 can remove PPCPs completely in less than 10 min. However, further detail study is needed to establish the superiority of the ozone-based processes as total organic carbon removal efficiency is not sufficient for these processes. Also, the more studies should be done to confirm that the intermediate by-products not harmful.

10.5.3.2 UV Irradiation

Use of ultraviolet (UV) radiation for water treatment is very popular. It usually used as disinfecting agent for drinking water. Due to its photolysis activity, UV light is also being used to remove PPCPs from water (Kim et al. 2009). However, UV photolysis is reported to be not effective ways for all types of PPCPs (Vogna et al. 2004). Recently, PPCPs degradation potential of UV light is enhanced by combining them with a catalyst. Yuan et al. (2011) have used hydrogen peroxide in combination with UV radiation for the removal of antibiotics from water. The mechanisms of UV/H_2O_2 system are generation of oxide radicals in the presence of UV and oxidation of PPCPs. Till now many researchers had attempted to use UV/H_2O_2 combination for the removal of PPCPs from water (Kim et al. 2009; Rosenfeldt and Linden 2004; De la Cruz et al. 2012; Keen and Linden 2013; Ma et al. 2015). The studies showed that the UV/hydrogen peroxide system was very efficient for many types of PPCPs. However, it showed less promising for many other PPCPs. This pointing out that more studies in detail is necessary to establish the applicability of the UV/H_2O_2-based process in PPCPs removal. Also, their effect in the presence of organic matters, metallic ions, and suspended particles should also be monitored in detail.

10.5.3.3 Fenton Oxidation

PPCPs removal through Fenton oxidation is another very popular oxidation technique. Similar to the other oxidation techniques, Fenton process also depends on the generation and activity of hydroxyl radicals. Different types of Fenton processes and their mechanisms are discussed in detail by Feng et al. (2013) and (Bokare and Choi 2014). Till now, Fenton process has utilized widely to remove PPCPs from wastewater (Feng et al. 2005; Bautitz and Nogueira 2007; Veloutsou et al. 2014; Boaventura 2014; Annabi et al. 2016; Wan and Wang 2016; Polo et al. 2016; Trovó et al. 2008; Goi et al. 2008; Kaczmarek and Lis 2009; Ay and Kargi 2010; Michael et al. 2010; Dirany et al. 2011; Li et al. 2012; Chen et al. 2013). The literature presented above indicated that almost all the PPCPs could be degraded by Fenton oxidation. However, these processes also produce toxic secondary by-products. Thus, more detail studies on the toxicity analysis of PPCPs by-products are needed before the implementation of this process in the wastewater treatment.

10.5.3.4 Ionizing Irradiation

Recently, gamma irradiation-based advanced oxidation processes have become very popular for degradation of PPCPs from wastewater. Many reports have pointed out that gamma irradiation is very promising for the removal of PPCPs (Wang and Chu 2016; Hu and Wang 2007; Xue and Wang 2008; Yu et al. 2010; He et al. 2014; Liu et al. 2014a, b). In a recent report, it has been found that biodegradability of lincomycin, sulfamethoxazole, and tetracycline could be improved by irradiating with gamma rays (Kim et al. 2015). Degradation and decomposition of different types of PPCPs using gamma rays have been studied by many researchers (Sanchez-Polo et al. 2099; Zheng et al. 2011; Shah et al. 2014; Kimura et al. 2012; Liu and Wang 2013). It is reported that during gamma irradiation different types of intermediates products could be generated from the original pollutants (Nielsen et al. 2014; Zhang et al. 2016). The toxicity of these intermediate products should be investigated.

10.5.4 Adsorption

Adsorption is the simple, easy to use, and relatively economic process than the other types of pollutant separation processes. Till date, different types of adsorbents are used for the removal of all major types of pollutants present in wastewater. Different types of adsorbents used in PPCPs removal have been discussed in the following subsections.

10.5.4.1 Activated Carbon

Activated charcoal is one of the most widely used adsorbents for the removal of almost all types of pollutants from wastewater. Its versatility, large specific surface area, and porous structure made it an unavoidable choice for water purification. Even this has been used to separate traces amount of emergent contaminants from water. Obviously, it was also used to remove PPCPs from wastewater (Ho 2006; Nowotny et al. 2007; Plazinski 2010). Powdered activated charcoal (PAC) was also used for removal of many PPCPs from sewage. Recently, trace amount of almost 20 different types of PPCPs has been separate by Nowotny et al. (2007) from municipal sewage using PAC. This study pointed out that except few almost all the used PPCPs were separated with high efficiency. In another study, very common diclofenac, carbamazepine, clofibric acid, bezafibrate, and primidone were removed from water using PAC efficiently (Zhang et al. 2016). All these studies are pointing toward the promising nature of activated charcoal for PPCPs removal. However, it also has drawbacks like poor removal efficiency in lower pH, energy intensive charcoal preparation, and poor recyclability. Thus, before its application in large-scale PPCPs removal from industrial and municipal wastewater, more detail studies are needed.

10.5.4.2 Metal-organic Framework

Metal-organic framework containing a metal ion and organic species is an interesting synthetic material, promising for wastewater treatment for its porous structure in micro-porous or mesoporous range (Vogna et al. 2004; Barea et al. 2014; DeCoste and Peterson 2014; Furukawa et al. 2013; Jhung et al. 2012; Wu et al. 2012; Yang et al. 2013). Also, it can be modified easily with desired functional groups (Hwang et al. 2008; Khan et al. 2013). Still now, many virgin and functionalized metal-organic framework had been used for the separation of various hazardous chemicals (Barea et al. 2014; DeCoste and Peterson 2014; Jhung et al. 2012; Khan et al. 2013; Ahmed and Jhung 2016; Hasan and Jhung 2015; Jiang et al. 2013). For use in water purification, this type of materials should be functionalized with specific groups (Bhadra et al. 2015). Recently, two metal-organic framework had been functionalized in their acid and basic sites and used to remove PPCPs from water (Hasan et al. 2013; Hasan et al. 2012). The study indicated that the removal efficiencies of the functionalized materials were enough. However, much more study in detail is needed to establish the efficacy of these types of materials in PPCPs removal.

10.5.4.3 Nanomaterials

In recent times, nanomaterial-based processes gained more attraction for wastewater treatment. Graphene and related derivatives are being used rapidly for removal of different types of pollutants from water. Graphene is a two-dimensional single layer carbon sheets with a honeycomb-like structure. Graphene and its derivatives like graphene oxide have very high specific surface area and photoelectrical properties. These types of nanomaterials have been used for PPCPs removal. The studies indicated that these materials are promising in PPCPs removal (Zhang et al. 2016). However, it was noticed that the efficiency of these nanomaterials depends on types of PPCPs and their physiochemical properties. Also, the influence of pH and contact time has significant effects on the removal efficacy of the nano-adsorbents. Though these types of nanomaterial are found to be promising, till date only laboratory-scale batch studies with synthetic wastewater has been investigated. Detail investigation including column and pilot scale studies with PPCPS containing real wastewater is needed for understanding the suitability of these materials in water management.

Carbon nanotubes (CNT) have also been used for PPCPs removal from water. Like graphene, CNTs also have very high surface area and excellent electrical properties. Different types of PPCPs like ketoprofen, carbamazepine, sulfamethoxazole, and triclosan have been removed from water using CNT (Zhang et al. 2016). Also, triclosan, ibuprofen, acetaminophen, carbamazepine, caffeine, prometryn, carbendazim, and 4-acetylamino-antipyrine could be removed from water using multi-walled CNT (Wang and Wang 2016). All the above studies indicated that CNT has very high PPCPs serration capacity from water. However, the separation efficacy of CNT was found to be depended of the surface chemistry and physiochemical properties of CNT and the PPCPs.

10.5.5 Membrane Technology

Membrane-based pollutant serration is one of the most trusted methods and currently is being used globally. High separation efficiencies for almost all types of pollutants make them the near perfect solution to solve water-related issues. However, due to high cost of membranes, extensive energy requirement for maintaining pressure and fouling is very common issues for membrane-based water treatment processes. Researchers are still trying to find the satisfactory solutions to these issues. Along with other types of pollutants, this type of separation techniques has also been used for PPCPs removal as well. Nanofiltration (NF) and ultrafiltration (UF) types of membrane separation techniques have been used to compare their separation efficiencies of 27 different PPCPs. They reported that NF was more effective than UF for the removal of almost all of the 27 PPCPs. In another study, 31 different PPCPs containing well water and drinking water were purified using NF and reverse osmosis (RO)-based water treatment plants (Radjenović et al. 2008). The study indicated that the separation efficiency of the process was more than 85% for all types of PPCPs. A municipal sewage treatment plant in Germany (Röhricht et al. 2010) used polyethersulfone membranes to separate PPCPs from the municipal sewage and found that the removal rate of PPCPs like carbamazepine, dichlorobenzene, and sulfonamide was around 65%. With late beginning in our area, a lot of water environment workers have also achieved some encouraging results after hard efforts, such as NF removal of carbamazepine, and antibiotics. In recent times, NF membrane-based process has been tried for separation of different types of PPCPs till date (Cheng et al. 2008).

10.5.6 Biodegradation

Effluents generated in the wastewater treatment plants are extensively been used worldwide for various purposes. It is estimated that around 7–8% of the total generated treated municipal wastewater was reused in the USA to satisfy the water demand for irrigation (Miller et al. 2001). Though it is a wise practice, people have to face the adverse consequences caused due to effluent-derived organic contaminants. Emerging organic pollutants like PPCPs are present in the effluents (Loraine and Pettigrove 2006). PPCPs even at trace levels could be accumulated in the soils resulting in environmental problems like contamination to groundwater (Ternes et al. 2007; Kinney et al. 2006; Xu et al. 2009).

Apart from the processes described in the above section, biodegradation of PPCPs is one of the best techniques to remove these types of contaminates from effluents. Many researchers have removed PPCP by biodegradation in sequencing batch reactors (SBRs), wastewater treatment plants (WWTPs), membrane bioreactors (MBRs), constructed wetlands, and sand columns. Table 10.5 has summarized all the processes with their removal efficiency. From Table 10.5, it is evident that for same individual

Table 10.5 Pharmaceuticals removal efficiencies specifically attributed to biodegradation (Wang and Wang 2016)

Compound	Removal efficiency (%)	System studied
Analgesic		
Acetaminophen	99	Batch
Antibiotic		
Azithromycin	50	Batch
Benzylpenicillin	25	WWTP, laboratory scale
Roxithromycin	85–95	Anaerobic digester, pilot scale
Sulfamethoxazole	99	Anaerobic digester, pilot scale
Tetracycline	ND	Batch
Trimethoprim	70	Batch
Anticancer		
5-Fluorouracil	ND	Batch
Cytarabine	80–95	Batch
Exemestane	20–86	Batch
Gemcitabine	42–50	Batch
Ifosfamide	ND	Batch
Anticonvulsant		
Gabapentin	90	Batch
Phenytoin	50	Batch
Valproic acid	99	Batch
Antidepressant		
Diazepam	38–60	Anaerobic digester, pilot scale
Fluoxetine	ND	Batch
Antiseptic		
4-Chloro-m-cresol	99	Batch
Biosol	80	Batch
Biphenylol	99	Batch
Chlorophene	99	Batch
p-chloro-m-xylenol	80	Batch
Triclocarban	21–97	WWTP, full scale
Triclosan	38–99	Batch, Continuous flow aerobic reactors, laboratory scale, Soil batch
Barbituate		
Phenobarbital	80	Batch
Secobarbital	70	Batch
Calcium channel antagonist		
Verapamil	ND	Batch

compounds the removal efficiencies vary with therapeutic classes and treatment processes for separate studies. Also, Tables 10.4 indicates that no compound is entirely removed even after application of various removal processes.

Table 10.5 indicates that biodegradability of individual pharmaceuticals and or the systems studied cannot be generalized or predicted. Further, research in this area is needed to elucidate the reasons of variations in PPCP biodegradation. Biodegradation pathways should be investigated to understand the byproducts and its effects on ecology and human health compared to the parent PPCPs. Ternes et al. cautioned that in some cases the parent compound might not be detected but the transformation products might initiate potential health hazards (Ternes et al. 2007). Biodegradation studies measuring only mineralization and/or measuring separation of parent compounds also needed to examine the metabolic pathways and breakdown products. The microbes degrading PPCPs should also be investigated further. This is needed to understand if biodegradation of a compound is done by a single microbes or a group of microbes. This will improve the knowledge of efficient PPCP biodegradation.

10.6 Conclusions

The review presented in this paper included general idea about different PPCPs, their regulation law, and removal processes. This review indicates that more strict law and regulations are needed to minimize PPCPs pollution in the environment. The review also discussed different removal techniques for PPCPs removal from water and wastewater. Also, it is pointed that though the knowledge of occurrence and fate of PPCPs in the environment have increased, there are still scopes for further research. As pointed in the paper, biodegradation is one of many removal processes. Other mechanisms should also be explored to understand the mechanisms controlling PPCPs removal. Synergistic interaction among multiple chemicals and multiple types of process should also be addressed. PPCPs are not the only chemicals, and biodegradation is not the only process; further, studies in this regards are needed urgently. This will increase the understanding of PPCPs behavior in the environment. Also, it will help to understand how biodegradation can be better utilized to prevent or reduce PPCPs contamination of the environment.

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Conflict of Interest Authors declare no conflict of interest for this work.

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Chapter 11
Nanotechnology: An Efficient Technique of Contaminated Water Treatment

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11.1 Introduction

For the existence of life and good health, water is an ultimate need. The whole planet is suffering from water scarcity, and this issue grieved more due to the alarming pollution. From the data of world health organization, it is suggested due to the microbial contamination and lots of health issues are arising worldwide (Heymann 2007). Every year around two million people lose life due to infections originated from infected water. Although many techniques are used for treating water like disinfection and radiation, the water contamination is not fully cured. The heavy metals like zinc, cadmium, lead and mercury contaminate the water bodies, thereby releasing toxic substances in the water which is fatal for the living environment (Verma and Dwivedi 2013; Baby et al. 2010). The advanced industrialization and growing urbanization are burdened the natural sanity with harmful chemicals and wide range of pollution. Water pollution is one of the alarming issues that the world is facing. The rapid population outbreak in the coming year needs a massive supply of clean drinking water, domestic purpose, commercial, agricultural, etc., demand to support the growing human race as reported by Pendergast and Hoek (2011). In the year 2014, the World Health Organization reported that by the year 2025, fifty per cent of world's population will face the problem of water scarcity (Guarino 2017). In developing countries, more than half of the industrial wastewater is released to the environment without proper treatment. The available technology for wastewater treatment and the production of pristine and safe water is not sufficient to meet pace with a rapid increase of water pollution and demand for pure water supply in

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developed as developing countries. Hence, it is needed to adopt such water treatment technology which is equally economical and highly efficient. Nanotechnology is one such technique which has attracted researchers in the last decades due to better performance in water treatment in comparison with existing conventional methods (Qu et al. 2013). The materials having dimension lesser than hundred nanometre are defined as nanomaterials as reported by Tesh and Scott (2014). This range of materials has extraordinary chemical and physical characteristics in comparison with their bulkier structure. The property of large surface area of nanomaterials generally has allowed larger density of active centres per unit mass. Additionally, nanomaterial displays higher surface free energy which results in upgradation in the reactivity of the surface. Till now, from the literature survey it is evident that nanomaterial is capable enough to treat wastewater particularly in the field of sensing, disinfection, catalytic oxidation, adsorption, etc., as reported by Das et al. (2015), Ayati et al. (2014) and Ali 2012). In Tesh and Scott (2014), Karn et al. (2011) reported that zero-valent iron nanoparticles by injection are one of the most frequently applied nanotechnologies for groundwater treatment in America. Initially, nanoparticles tend to accumulate on the water system causing reduction in the pressure and severe activity as reported by Lofrano et al. (2016). Further, the most difficult tasks remain the separation of the degraded or exhausted nanoparticles from the treated water for further use. Moreover, the nature and behaviour of nanomaterials during the treatment of wastewater are yet to be understood clearly. The consequences of the remaining nanomaterials after the treatment of wastewater are the topic of concern for the environment and human health which can act as an obstacle in the application of this technique as reported by Dale et al. (2015). In order to fill up this loophole to bring out the desirable impact of this technique, it is necessary to find a better material which can reduce the release of nanomaterial in treated water while retaining its reactivity. In these contexts, nanocomposites have been identified as potential candidate for the desired approach. It is designed by using different support materials like membranes or polymers on which desired nanomaterials are loaded. The nanocomposites can be defined as material having multiphase where the dimension of the constituent is one hundred nanometre as reported by Tesh and Scott (2014). This chapter throws light on the advanced applications of nanotechnology in wastewater treatment. The various types of nanomaterials like carbon nanotubes, graphene-based, metal and metal oxide-based, zeolites, nanocomposites, metal–organic frameworks are discussed focussing on their structures and performances in the removal of water contaminants. Moreover, few bioremediation techniques for purification of water are also discussed. The toxicity of the nanomaterial after treatment of wastewater on the environment also needs to be tackled carefully to ensure the safety of the environment which is also mentioned in this chapter.

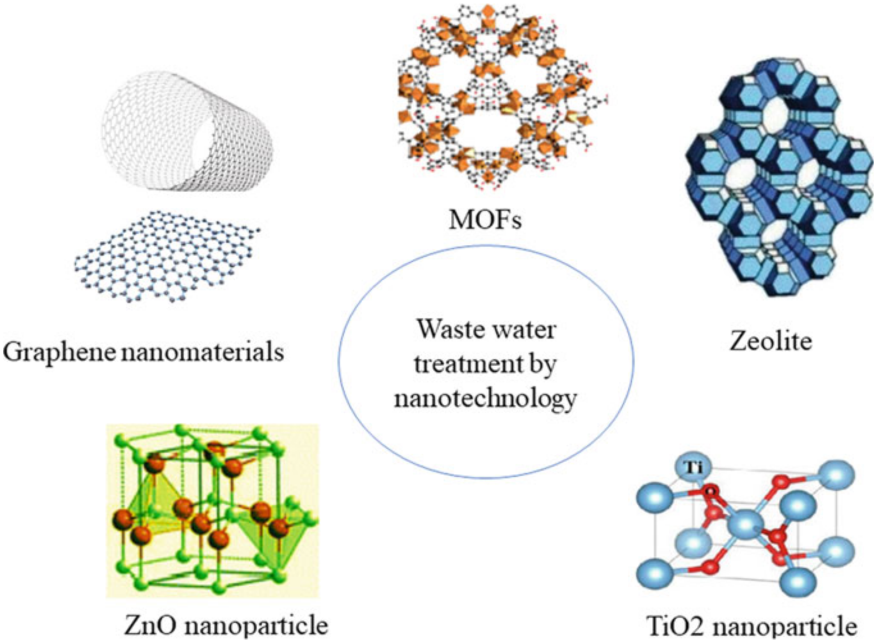

Fig. 11.1 Nanomaterials used for wastewater remediation

11.1.1 Water Nanotechnology

With the advancement of nanotechnology, its utilization has gained attraction in the field of wastewater treatment. In this part, a brief summarization of the various techniques of nanotechnology for treating wastewater is discussed like adsorption, oxidation and sensing. In Fig. 11.1, nanomaterials used for wastewater treatment are displayed.

11.1.2 Adsorption

Separation procedure based on membranes or adsorbents is the most frequently used technique for wastewater polishing. Traditional adsorbents generally face difficulties like low selectivity and loading capacity. Adsorbents based on nanomaterials such as carbon nanotubes, metal or metal oxide have the property of high surface areas, reactivity and special affinity towards different contaminants. In Ali (2012) and Khajeh et al. (2013) respectively, reported regarding the adsorption performance of nanomaterial-based adsorbents that their rate of adsorption for specific contaminants is higher in magnitude in comparison with the traditional adsorbents.

11.1.3 Catalysis

Photocatalytic or catalytic oxidation refers to the method in which microbial pathogens and trace contaminants are removed from the water in the advanced manner. Reddy et al. (2016) reported that this method is significant for pre-treatment as it enhances the rate of biodegradation of non-biodegradable and hazardous contaminants (Reddy et al. 2016). The high ratio of surface to volume of the nanocatalysts noticeably display upgraded the performance of catalysis in comparison with the corresponding bulkier counterparts. In addition, the crystal structure and the bandgap of the nano-semiconductors displayed size dependency. Moreover by immobilizing the nanomaterial over different supporting groups, there was an enhancement in the stability of the nanocatalyst and the resulting nanocomposite was found to be consistent with the photoreactors, according to Petronella et al. (2017).

11.1.4 Disinfection

In order to minimize the growth of diseases caused due to water contamination, the process of disinfection is vital step. There are certain criteria for an idealized disinfectant like it should be able to deal with wide range of microbes within a short span of time, absence or minimum production of fatal by-products, minimum toxic impact on human health and environment, economical and easy to handle, oncorrosive and can be disposed safely. Higzay et al. (2010) reported many nanomaterials exhibiting antimicrobial characteristics like chitosan nanoparticles; Rai et al. 2009 reported, Hebeish et al. (2013) reported photocatalytic TiO_2; Martynková and Valášková (2014) reported carbon nanomaterials. The above-mentioned nanoparticles were capable of killing or destroying microbes by the toxic metal ions released from them and can also destroy cell membrane by coming in contact, etc. In contrast to traditional disinfectants, the nanomaterial-based disinfectants achieved the task with more sustainably which led to the release of lesser by-products as reported by Li et al. (2008).

11.2 Sensing

Traditional methods of monitoring and sensing face obstacles in the case of less concentration of pollutant at microlevel in complex cases of water pollution. Urgent and instant detection of desired harmful and toxic pathogenic substances especially during water-based accidents are the demand of the time. Some nanomaterials such as noble metals like silver or gold, quantum dots, carbon nanotubes have extraordinary magnetic, optical and electrochemical characteristics; hence, when they are combined with sensing devices, they can selectively assist in the detection of trace pollutants (Li et al. 2008).

11.2.1 Nanomaterials Applied in Water Treatment

11.2.1.1 Zeolites

These are defined as crystalline, inorganic porous material bearing highly ordered structure and generally comprises of oxygen, aluminium and silicon according to (Camblor et al. 1998). The unique characteristics of zeolites which make it suitable for various applications like ion exchange, separation and catalysis are high surface area, chemical and mechanical resistance as reported by Song et al. (2005). These characteristics are the reason behind its application in the treatment of wastewater. The traditional method of synthesis of zeolites of the range from 1 to 10 micrometre, while nanoscaled zeolites consist of five-to-hundred nanometre with uniform and discrete crystals as reported by Ding and Zheng (2007), Camblor et al. (1998), Xu et al. (2004).

11.2.2 Carbon-Based Nanomaterials

11.2.2.1 Graphene Nanomaterials

Graphene is defined as consisting of single layer of graphite structure having the structure similar to honeycomb. It has unique electrical and thermal conductivity. One of the oxidative forms of graphene which consists of oxygen-based functional moieties like epoxy, carbonyl, hydroxyl is graphene oxide. Its attractive properties have captured the attention for application related to various environmental problems. Graphene possesses excellent number of pi-bonds. Graphene and graphene oxide bear large surface area. According to Sun et al. (2010), generally in the adsorption process induced by graphene-based nanomaterials, there are five interactions which are possible and they are electrostatic and covalent interaction, hydrogen bonding, pi–pi interaction and hydrophilic effect. These materials are identified to be suitable for treatments of wastewater using adsorption process to eliminate the contaminants from the water. Graphene oxide and reduced graphene oxide, which is the modified form of graphene oxide, are reported to be capable of eliminating heavy metals from the contaminated water like arsenic (trivalent and pentavalent), mercury (divalent), cadmium (divalent), copper (divalent), lead (divalent). The graphene-based nanomaterial is also capable of adsorbing anionic contaminants. Li et al. (2011) reported that graphene is capable of adsorbing fluoride very efficiently with a load capacity of around thirty-five milligram per gram at 25 °C at pH seven (Li et al. 2011). In Vasudevan and Lakshmi (2012) reported their research on the adsorption of phosphate using graphene-based nanomaterials. Graphene oxide along with its composites also displayed the promising capacity of dye removal and for ionic dyes generally depends on covalent bonding and electrostatic interaction. Graphene oxide demonstrated better adsorption efficiency for cationic dyes in comparison with anionic dyes because of strong electrostatic repulsion. But graphene and their corresponding composites are reported by Luo et al. (2012) to be displaying better adsorption of anionic dyes due to their covalent bonding and ion exchange property. By the process of hybridization and modification of the surface, the efficiency of reusability, separation, and removal of graphene nanomaterials can be enhanced, thereby making it a better and significant candidate for application for the decontamination of polluted water. But, few challenges which stand as hurdle in their way are their high cost, safety and reusability.

11.2.3 Carbon Nanotubes

The carbon nanotubes display antimicrobial property, and this is exhibited by two pathways: physical and chemical (Lelimousin and Sansom 2013). In physical method, inhibition of the passage of microbes occurs by using filters, and in chemical method, its activity is performed via reaction with pathogenic substances (Upadhyayula et al. 2009). From the literature survey, it is reported that carbon nanotubes are capable of destroying cells of bacteria through interacting with them physically or by incurring stress by oxidation which results in the degradation of the cell (Kotchey et al. 2012). The chemical pathway of carbon nanotube antimicrobial action requires the contact of targeted pathogenic substances and carbon nanotubes. But, the chemical way of application is limited due to the issue of obtaining uniform dispersion and stable carbon nanotube in water. The physical approach is quite effective and efficient for microbe filtration like virus and bacteria. Single-walled carbon nanotubes are identified to be effective in filtering almost all the pathogenic substances. Their dimension ranges from two to five nanometres which is very small (Manshian et al. 2013).

11.3 Metal and Metal Oxide-Based Nanomaterials

Metal and metal oxide nanomaterials recently gained attraction due to their efficient performance in economical removal of contaminants. In Hua et al. (2012) reported that examples of metal and metal oxide are cerium oxides, magnesium oxides, titanium oxides, manganese oxides, aluminium oxides, ferric oxides, nano-sized zero-valent iron, etc.

From the literature survey, it is reported that these metal and metal oxide-based nanomaterials displayed significant performance in the sorption process of number of metallic contaminants like reported by Kanel et al. (2006), Cd reported by Boparai et al. (2011) and Engates and Shipley (2011), Cr reported by Hu et al. (2005) and Yu et al. (2014), U reported by Crane et al. (2011) with very high selectivity and capacity (Crane et al. 2011).

11.3.1 Zero-Valent Iron Nanomaterial

In Wang and Zhang (1997) reported that zero-valent iron nanomaterial is first-generation nanotechnology for environmental remediation especially for treatment if groundwater. From the laboratory results, it was reported that zero-valent iron nanomaterial is efficient in the transformation a wide range of contaminants such as heavy metal arsenic (trivalent), lead(divalent), copper(divalent), Nickel(divalent), chromium(hexavalent) as reported by Ponder et al. (2000), Kanel et al. (2006)) and Li and Zhang (2006), nitrate and perchlorate (inorganic ions) as reported by Choe et al. (2000) and Cao et al. (2005) and much more. Alternatively, these particles can also be attached on some supporting solid matrix like zeolite or activated carbon in order to upgrade its efficiency in its application for wastewater treatment as reported Zhang (2003). Choe et al. (2000) reported the use of zero-valent iron nanomaterial in the reduction of nitrate into nitrogen gas (Choe et al. 2000). The data and result discussed above confirm that nano-sized zero-valent material is a promising candidate for groundwater and industrial effluent remediation.

11.3.2 Iron Oxide Nanomaterial

Selecting a suitable technique and materials for treating and wastewater is a very crucial job and is achieved by considering many conditions. Some of these factors are economical, eco-friendly, efficiency and flexibility of the treatment technique; reusability was reported by Zhang and Fang (2010), Xu et al. (2012) and Oller et al. (2011). The property of magnetism is extraordinary which assists in purifying water by affecting the physical characteristics of contaminants present in wastewater. According to Ambashta and Sillanpää (2010) and Mahdavian and Mirrahimi (2010) reported that the integration of magnetic separation and adsorption has extensive application for cleaning environment and treatment of water. The nano-sized-based iron oxide material is identified as potential candidate wastewater treatment in industrial sector because of their cost-effectiveness, better stability, strong adsorption and ease of separation as reported as Hu et al. (2005), Carabante et al. (2009) and Fan et al. (2011). According to White et al. (2009), Girginova et al. (2010) and Girginova et al. (2010) reported that these iron oxide-based nanomaterials are utilized for the removal of contaminants in both field and laboratory-scale test. Currently, there are two categories of applying iron oxide nanomaterials for treating wastewater: one involves the utilization of these materials as a type of immobilizing carrier and nanosorbent for enhancing the efficiency of removal and other group includes using it as photocatalyst in order to degrade these contaminants into lesser toxic form.

11.3.3 Titanium Oxides Nanomaterial

Titanium dioxide displays photocatalysis when ultraviolet radiation is present. Titanium dioxide possesses antibacterial property because of the release of reduced oxygen species like peroxide and hydroxyl free radicals produced in the presence of ultraviolet radiation via the series of reduction and oxidation reaction occurring in a cell. The unique property of using titanium dioxide nanomaterial as disinfectant is their characteristic of displaying photocatalysis also in the presence of visible sunlight (Sakthivel and Kisch 2003). This nature can be upgraded by mixing titanium dioxide with different metals. It is a very efficient and perfect option for the treatment of water due to its stability in water, cost-effectiveness and non-toxicity while ingestion. It is used as thin-film coating on the surface of reactor and in UV reactor as slurry (Reddy et al. 2015).

11.4 Zinc Oxide Nanoparticles

Like titanium dioxide, zinc oxide nanoparticles demonstrate better ultraviolet absorption and also efficient photocatalysis. During photocatalysis, zinc oxide nanomaterial produces hydrogen peroxide in the cells as a result of which cell components are subjected to oxidation. Moreover, they are also capable of inhibiting the growth of bacteria by penetrating into the envelope of the cell, thereby disorganizing the membrane of bacteria. But, if zinc oxide nanomaterials enter the natural water sources, they can be dangerous for the aquatic organisms. These materials get dissolved easily, and this limits its use in drinking water Szabó et al. (2003).

11.4.1 Nanocomposites in Water Treatment

11.4.1.1 Nanocomposite Membrane

The membrane processes which are available commercially for the purification of water are ultrafiltration, nanofiltration, microfiltration, reverse osmosis, electrodeionization and electrodialysis (Frenkel 2008). Few other processes which are used in limited number include pervaporation, membrane distillation and forward osmosis. The membrane process of nano- and ultrafiltration is found to be efficiently separating emulsion and oil. But, the ultrafiltration technique fails in the removal of contaminants of large size because they do not contain any charge. As we know that seawater due to its salinity is very corrosive and hence requires the utilization of stainless steel and austenitic, and as a result, excessive energy consumption, high cost and maintenance are required. To ease this problem, various nanofiltration membranes are present as an alternative to ultrafiltration and osmosis. The advantage of using nanofiltration over existing conventional reverse osmosis processes is that there is less energy consumption and less pressure (Van der Bruggen and Vandecasteele 2003). There are wide range of application of nanofiltration membranes like the elimination of viruses, microbes, heavy metals and pesticides and also seawater desalination (Van der Bruggen et al. 2001). From the literature survey, it is reported that the technical of viral nanofiltration is very effective and efficient in separating all the biological contaminants. Nanomaterials like alumina fibres and nanotubes are used for building materials which possess controlled dimensions, density and shape in order to filter specific components (Mera et al. 2010). Ceramics and polymer are the main categories of membrane materials which exhibit unique benefits for the fabrication of membrane with multifunctionalities (Mera et al. 2009). The unique thermal and chemical stability of ceramic membranes adds extra benefits like enabling it to perform even in extreme condition of temperature and pH and also in the presence of oxidizing surrounding (Rossi et al. 2014). Ozone oxidizes carbon–carbon double bonds of organic molecules and electron-rich species. Some polymeric materials like sulfonated polyethersulfone, cross-linked poly(furfuryl alcohol), thin-film composite, cellulose acetates are reported to be used for desalination.

11.4.2 Magnetic Nanocomposites

Magnetic nanomaterial and nanocatalyst are capable of purifying different types of inorganic and organic contaminants dispersed in water (Shipley et al. 2009). In general, metals and enzymes are applied as catalyst but their catalytic performance enhances by modifying it into nanoscale. At nanoscale, the materials are longer lasting, more reactive and also display better selectivity. Investigation is performed on magnetic nanoparticles because of their application in the removal of many chemical owing to their high surface area and property of binding with chemical even in the absence of auxiliary adsorbent material. Magnetite (Fe_3O_4) nanoparticles displayed efficient adsorption behaviour for removing arsenic. These nanoparticles can be later easily being removed from treated water at lower magnetic field (Fuhrer et al. 2011). The smaller size of these nanoparticles causes enhancement in surface area, surface energy and fraction of atoms on the surface. By using microwave synthesis method using sodium hydroxide and ferrous sulphate in the presence of solvent mixture containing water and ethylene glycol, magnetite magnetic microsphere can be synthesized. Other iron-containing minerals which are applied in wastewater treatment by the adsorption process are maghemite, lepidocrocite, hematite, goethite, ferrihydrite, feroxyhyte and akaganeite. On surface modification, magnetic nanomaterials display selectivity towards different contaminants and effectively remove heavy metals like As and other pollutants from water.

11.4.3 Metal–Organic Framework for Heavy Metal Removal from Water

Rapid pollution of ground and surface water due to heavy metal contamination is a crucial issue worldwide. It not only affects the purity of the environment but also have adverse impact on human health. Excessive abundance of these harmful metals causes the risk to human life by initiating much dreadful disease like cancer and also affects other species by accumulating in the food chain. It is very essential to eliminate these elements from surrounding especially from water bodies up to permissible level. Metal–organic frameworks or MOFs are defined as category of porous adsorbent material made up of metal clusters and organic linkers. These frameworks are connected in 3D lattices. Metal–organic frameworks exhibit a number of benefits in the field of adsorption. The unique characteristics of porous structure and high surface area enabling it to be applied for many fields like drug delivery, catalysis, gas storage and separation (Kuppler et al. 2009). The property of porosity and large surface area supports the contaminants in accessing the adsorption site and gets diffused into the framework. The crystallinity aids MOF with highly ordered pores, and shape and size of these pores can be controlled by selecting suitable ligands and metal ions (Yaghi et al. 2003). MOFs can be effectively used in the removal of pollutants from water, and this is a very popular area of research nowadays. Table 11.1 displays some important MOFs and their role in heavy metal removal.

11.4.4 Removal of Nanoparticles After Water Treatment

Using nanoparticles for various environmental applications causes the release of these particles and accumulation in the environment. In order to assess the amount of risk that can be incurred on the environment, knowledge regarding its persistence, toxicity, bioavailability and mobility is required. The rapid utilization of nanoparticles for various industrial applications and the purification of water especially drinking water arise a threat that these nanomaterial will remain in the environment and will cause damage and hence needs to be eliminated by suitable pathways. Conventional pathways for the elimination of suspended matter in the wastewater popularly include filtration and sedimentation. But, the size of the nanoparticles is very small, and hence, the sedimentation technique is not suitable for removal unless they aggregate and form larger size. Techniques like flocculation can be also not suitable for eliminating nanoparticles from the water, and hence, some novel process is required. Techniques like reverse osmosis and nanofiltration which are also applied for removal of pathogenic substances from wastewater can be also applied for removing nanoparticles. These hindrances are based on the fact that these nanomaterials are mobile in the presence of porous medium due to their minute size, thereby they get dispersed over a large area and remain persistent in the environment for a longer time.

Table 11.1 Examples of metal–organic framework applied in heavy metal removal

S. No.	Heavy metal	Metal–organic framework	Method	References
1	Arsenic	ZIF-8	Adsorption	Bahrani et al. (2019)
		UiO-66	Adsorption	Audu et al. (2016)
		FE-BTC	Adsorption	Kobielska et al. (2018)
2	Cadmium	PCN-100	Adsorption	Saleem et al. (2016)
		HKUST-1	Ion exchange	Yang et al. (2016)
		AMOF-1	Adsorption	Fang et al. (2010)
3	Chromium	ZIF-67	Adsorption/ion exchange	Aboutorabi et al. (2016)
		Cu-BTC	Adsorption	Li et al. (2017)
		Chitosan-MOF	Adsorption	Maleki et al. (2015)
4	Lead	MOF-5	Adsorption	Rivera et al. (2016)
		TMU-5	Adsorption	Rahimi and Mohaghegh (2016)
		MnO_2-MOF	Adsorption	Qin et al. (2011)
5	Mercury	PCN-100	Adsorption	Saleem et al. (2016)
		Bio-MOF	Adsorption	Mon et al. (2016)
		LMOF-263	Adsorption	Rudd et al. (2016)
6	Nickel	Chitosan-MOF	Adsorption	Maleki et al. (2015)
7	Cobalt	TMU-5	Adsorption	Rahimi and Mohaghegh (2016)
8	Copper	ZIF-8	Adsorption/ion exchange	Zhang et al. (2016)
		MOF-5	Adsorption	Bakhtiari and Azizian (2015)
		TMU-5	Adsorption	Rahimi and Mohaghegh (2016)

(continued)

Table 11.1 (continued)

S. No.	Heavy metal	Metal–organic framework	Method	References
9	Zinc	Cu-terephthalate-MOF	Adsorption/ion exchange	Zou et al. (2013)
10	Iron	Cu-terephthalate-MOF	Adsorption/ion exchange	Zou et al. (2013)

According to Wiesner et al. 2006, it was assumed that due to the smaller size nanoparticles should not be so much mobile because their higher diffusion will cause more number of contacts with the porous media surface like sand filters or groundwater aquifers used in water treatment (Auffan et al. 2009). Even though nanotechnology has positive impact on health due to its application on the purification of water but also has adverse impact on human health and environment if they remain suspended in the treated water as reported by Bergamaschi et al. (2006), Elder et al. (2007), Aschberger et al. (2011), Fratoddi et al. (2015), Sharifi et al. (2012), Bystrzejewska-Piotrowska et al. (2009), Baun et al. (2008), Farré et al. (2009) and (Aschberger et al. 2011). Waste produced during the synthesis and use of these nanoparticles will cause harmful effects on the environment, and hence, there are chances that human beings can be affected by ingestion, inhalation, skin contact and absorption in the digestive tract. Recently, there are no sufficient data available regarding that all the nanomaterials have a toxic effect on organism or environment or all the nanomaterials have antimicrobial activity, as reported by (Elder et al. 2007). Hence, more research and development are needed to find out facts regarding toxicity of nanomaterials. In Table 11.2, some of the examples of toxicity of nanomaterials are displayed.

11.5 Bioremediation Methods of Water Contaminants

Bioremediation refers to the utilization of microorganisms for degradation or reduction of the quantity of poisonous waste in a contaminated system. The various treatment techniques in this context include clean-up of contaminated system like stream, sludge, soil and water. Due to the extensive urbanization, industrialization and farming as well as various other activities of human have caused the degradation of land leading to pollution and decrease in the productivity of the crops. The technique of bioremediation is an efficient method for treating and recovering the ecosystem in a greener manner (Divya et al. 2015).

Table 11.2 Examples of the toxic effects of nanomaterials

Nanomaterial	Dose and exposure route	Species	Effects	References
TiO_2 particles, nanoscale rods or dots	1 or 5 mg; Intratracheal instillation	Rats	TiO_2 rods or dots produced transient inflammatory and cell injury effects and were not different from the effects of larger-sized TiO_2 particles	Warheit et al. (2006)
SWCNT	2-mg implant; Subcutaneous implantation	Mice	Activation of the histocompatibility complex in CD4*/CD8 + T-cells.	Koyama et al. (2006)
Ultrafine TiO_2	0.5, 2 or 10 mg/ml; Aerosol inhalation	Mice, rats, hamsters	Pulmonary particles overload and inflammation in rats and mice exposed to 10 mg/ml. Inflammation included an increased number of macrophages and neutrophils, progressive fibrosis in rats, elevated protein and lactate dehydrogenase levels	Bermudez et al. (2004)
SWCNT	0.1 or 0.5 mg; Intratracheal instillation	Mice	56% mortality in 0.5 mg dose, weight loss, kung lesions in 0.5 mg group, necrosis, macrophages and granulomas, interstitial and peribronchial inflammation	Lam et al. (2004)

(continued)

Table 11.2 (continued)

Nanomaterial	Dose and exposure route	Species	Effects	References
Intact or ground MWCNT	0.5, 2 or 5 mg; Intratracheal instillation	Rats	Intact MWCNT-induced collagen-rich granulomas and surrounding alveolitis	Muller et al. (2005)
MWCNT	12.5 mg; Intratracheal instillation	Guinea pigs	Pneumonitis and pulmonary lesions	Grubek-Jaworska et al. (2006)

SWCNT Single-walled carbon nanotubes; *MWCNT* Multi-walled carbon nanotube

11.5.1 Bioremediation of Industrial Effluents

In this twenty-first century, the effluents releasing from industries are the principal source of toxic and poisonous contaminants in our surrounding as reported by Mohana et al. (2008) and Gowri et al. (2014). Worldwide outburst of urbanization and industrialization has caused extreme increase in the level of organic contaminants in the ecosystem as reported by Chaudhari et al. (2009). Cyanobacteria displayed promising efficiency in the treatment of wastewater and industrial discharge treatment, detoxification of effluents of fuel, feed, food, fertilizer and chemical industries, bioremediation of terrestrial and aquatic habitats. In Dubey et al. (2011) reported some of the species of cyanobacteria like *cyanothece* sp., *Nodularia* sp., *Synechococcus* sp., which displayed efficient biosorption and biodegradation efficiency for effluents released from industries. Microbes used in municipal sewage activated sludge treatment include Pseudomonas, *Zooglea* sp. *Acinebacter*, *Alcaligenes* and *Flavobacterium* as reported by Adamse et al. (1984). According to Mahmood et al. (2013) it was reported that most suitable microbes responsible for textile effluent bioremediation includes *Micrococcus* sp., *Pseudomonas* sp., *Bacillus mycoides*, *Bacillus cereus* and *Bacillus subtilis* Mahmood et al. (2013). In Kamika and Momba (2012) reported bacteria like *Bacillus licheniformis* and *Pseudomonas putida* for the domestic water as well as moderately heavy metal concentrated water bioremediation Bahrani et al. (2019) Audu et al. (2016), Kobielska et al. (2018) and Saleem et al. (2016).

11.6 Conclusion

Nanotechnology has gained attention recently from researcher community. Apart from water treatment, nanomaterial has other application in the field of environment.

Most of the nanotechnology for the wastewater treatment is performed only at laboratory scale, and most of the technique is not possible to establish in comparison with the traditional technique because of high cost. As a result, it is not easy to predict the future scenario of this technology. Another challenge remains in incorporating the nanotechnology in the already prevailing water purification system. Reverse osmosis and nanofiltration (membrane processes) have gained attraction for the purification of water for public consumption and also in industries due to their flexibility, and easy maintenance and operation. Moreover, the toxicity of the nanomaterial on the environment is a matter of concern and hence needs care in the selection of material and designing for purification of water. There is not much information regarding the toxicity of this material on the environment. Hence, it can be concluded that, nanotechnology has both sides of a coin, i.e. positive in the direction of effective water purification and negative in the direction of imparting risk to the environment, when it remains persistent for a longer time. On a final note, it can be assumed that nanoparticles are ideal and promising candidates for the purification of water, and hence, there is a future scope if sufficient research and development will be done to eliminate the negative face of this technology.

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Chapter 12
Chlorophenols Dechlorination Water Treatment Using Ni-Iron Bimetallic Systems: Implications of the Degree of Chlorination, Nickel Coating, and Iron Oxide Phases

Buddhika Gunawardana, Naresh Singhal, and Peter J. Swedlund

12.1 Introduction

Chlorophenols (CPs) are manufactured organochlorine compounds and contain phenol (an aromatic compound) with chlorines (between one and five). Phenol is manufactured with the addition of a hydroxy group to a carbon in benzene replacing a hydrogen. The group of CPs includes mono-CPs, di-CPs, tri-CPs, tetra-CPs, and pentachlorophenol and altogether 19 different chlorophenol isomers (ATSDR 1999).

CPs are often used as chemicals for wood preservation, disinfectants, pesticides, and herbicides (ATSDR 1999). Use of CPs is causing extensive groundwater and drinking water contamination because of improper disposal of CP containing waste, leaching from landfills containing CP-treated waste, evaporation from treated wood products, waste generated during paper production and bleaching of wood pulp with chlorine, and burning of wastes with CPs (ATSDR 1999). In addition, CPs can be dissolved in drinking water because of the chlorination of trace levels of phenolic compounds present in water, if any, during the disinfection process, as complex compounds formed if hypochlorite acid reacts with phenolic acids and phenoxy herbicides degradation products (WHO 2003).

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The United States Environment Protection Agency has listed some of the CPs as priority toxic pollutants (USEPA 2019, 2018a, b). Toxicity of CPs increases with increasing degree of chlorination (Czaplicka 2004). Among all CPs, pentachlorophenol (PCP), a wood preservative and biocide (UNEP 2014), is reported as the most toxic CP (Tanjore and Viraraghavan 1994). Further, PCP is listed as a human carcinogen (IARC 2019; USEPA 2010), priority pollutant (USEPA 2019, 2018a, b; EC 2016), and toxic to aquatic organisms (UNEP 2014). The maximum contaminant level of PCP in drinking water has been imposed as 1 ppb (USEPA 2018a, b). Increased awareness about the toxicity and environmental impacts of CPs has led to banning or restricting the use of PCP worldwide (UNEP 2014). However, persistence of CPs leads to the continued ubiquitous presence of CP compounds as contaminants in surface water, groundwater, soil, and sediments. Dechlorination and removal of PCP have gained attention in contaminated groundwater treatment. However, degradation/removal of tetrachlorophenol (TeCP), trichlorophenol (TCP), and dichlorophenol (DCP) have received only little attention. Treatment and removal of CPs has become a difficult task due to their inherent characteristics such as hydrophobic nature and aromaticity linked stability.

Degradation of various CPs has been reported using different technologies in the literature. Reductive dechlorination of CPs with zero-valent iron (ZVI) has been reported by Gunawardana et al. (2018) and Kim and Carraway (2000); photocatalysis process has been tested by Lan et al. (2011), Li et al. (2011) and Ma et al. (2019); microbial degradation-assisted dechlorination was reported by Xu et al. (2018), Yang and Chen (2016); use of membrane biofilm reactors was reported by Long et al. (2018). Among the various treatment techniques available, ZVI is popular as a reactive medium for dechlorination of chlorinated contaminants because of the aspects such as economical, relatively highly reactive, and pose minimal environmental impact (Choi et al. 2008; Gunawardana et al. 2011; Kim and Carraway 2000). Use of permeable reactive barriers (PRBs) is a passive treatment and a financially feasible method for the treatment of contaminated groundwater (Henderson and Demond 2007; Fu et al. 2014; Furukawa et al. 2002). ZVI with a variety of particle sizes can be used as the reactive medium in PRB applications. However, microscale ZVI has been commonly tested and popular for dechlorination of chlorinated organic contaminants (Cheng et al. 2007; Choi et al. 2008; Chun et al. 2010; Gillham and Ohannesin 1994; Feng and Lim 2005; Kim and Carraway 2000; Klausen et al. 2003; Matheson and Tratnyek 1994; Nardo et al. 2010; Patterson et al. 2016; Phillips et al. 2010).

The reductive dechlorination process of chlorinated organics by ZVI is dependent on a number of variables. The contaminant transformation when in contact with ZVI in the aqueous medium is led by various species which act as reducing agents that are simultaneously present in the aqueous system and lead to, (1) direct contaminant reduction by the electrons released from Fe^0 (primary reductant), and (2) indirect contaminant reduction by other reductants such as electrons released by adsorbed/structural Fe^{II} (secondary reductants), H/H_2 and Fe_3O_4 and green rust (tertiary/quaternary reductants) (Hu et al. 2018). Previous studies have reported various factors that influence the reactivity, longevity, and dechlorination potential of ZVI

(Gunawardana et al. 2018, 2019; Henderson and Demond 2007, 2011; Jeen 2005; Jin suk et al. 2009; Li and Benson 2010). Among the many factors, the inherent characteristics of the iron oxide phases cause a major influence on the reactivity of ZVI and dechlorination potential (Gunawardana et al. 2018, 2019). Such iron oxide phases can be the oxides initially present on the ZVI surface before reaction with CPs as well as the oxides continuously evolving during the reaction of CPs in the CP-ZVI system. In general, different iron oxide phases are present as a combination on an as-received unmodified ZVI particle surface that is formed because of the exposure of ZVI to atmospheric O_2 during many stages of ZVI processing such as the production process and storage conditions (Cornell and Schwertmann 2003). In addition, when ZVI is introduced to an aqueous medium, various iron oxides and/or oxyhydroxide precipitates continuously evolve and accumulate on the ZVI surface because of Fe^0 oxidation and ZVI corrosion occurring in the ZVI/H_2O environment (Matheson and Tratnyek 1994). The iron oxides initially present or form during the reactions can also affect the ZVI performance over time. There are several competing mechanisms by which the iron oxides formed on ZVI can either enhance or inhibit ZVI reactivity. These oxides can act as (1) reactive or non-reactive sorption sites for contaminant molecules, (2) incorporate the contaminants and entrap within an oxide film during its formation, (3) affect the number of effective reactive sites and surface area available on ZVI for dechlorination, and (4) impede the electron transfer process, especially when these oxide phases formed on the ZVI are non-conducting passive oxide layers (Davenport et al. 2000; Gotpagar et al. 1999; Noubactep 2007; 2013; Ritter et al. 2002; Scherer et al. 1999).

The characteristics of different iron oxide phases on the ZVI surfaces (initially present and that are formed while reacting with the CPs) play a significant role on the ZVI reactivity for dechlorination (Gunawardana et al. 2018). Magnetite is known to comprise a high electrical conductivity with a low bandgap between its valence and conduction bands (0.1 eV;) Cornell and Schwertmann (2003) and lead to an enhancement in the electron transfer (Liu et al. 2006). In contrast, some Fe^{III} oxides and oxyhydroxides claim for a higher bandgap between the valence and conduction bands (e.g. lepidocrocite 2.06 eV; goethite 2.10 eV; maghemite 2.03 eV; and wustite 2.30 eV) (Cornell and Schwertmann 2003). These oxides result in ZVI surface passivation and hinder the ability of electrons and contaminant molecules transfer process through the interfaces of solid and liquid (Farrell et al. 2000). ZVI surface passivation has been observed when non-conducting oxides (haematite, 2.20 eV; lepidocrocite, wusite) form on the ZVI surface which seems to hinder the electron transfer process from the Fe^0 to CP molecules (Gunawardana et al. 2019). Therefore, the application of ZVI in PRBs for CP dechlorination is limited by various factors such as (1) decrease in degradation rates during the reaction period because of reduction in ZVI surface reactivity as a result of passive oxide phases formation, and (2) build up of degradation products during the reaction which may be competitors simultaneously present in the aqueous medium competing as co-contaminants for the same reactive sites and electrons for dechlorination (Gunawardana et al. 2018).

The application of bimetals synthesized with the combination of another secondary metal such as Ni, Pd, or Pt [comprise of a high reduction potential than ZVI; ZVI, −0.44 V; Ni, −0.257 V; Pd, 0.915 V; or Pt, 1.188 V; Arning and Minteer (2007)] on the ZVI surface has been tested to mitigate the limitations to the use of ZVI to remove chlorinated organic compounds (Choi et al. 2008; Gunawardana et al. 2019; Kim and Carraway 2000; Ko et al. 2007; Shih et al. 2011; Wang et al. 2008; Zhang et al. 2006). Enhanced hydrodechlorination of chlorinated phenols was reported by bimetals (Choi et al. 2008; Ko et al. 2007; Liu et al. 2001; Xu et al. 2012; Zhou et al. 2010) and aliphatic compounds (Feng and Lim 2005; Schrick et al. 2002). On the other hand, some studies did not observe any PCP degradation when using unmodified ZVI (Hou et al. 2009; Morales et al. 2002), while Pd/Fe, Pd/Mg (Morales et al. 2002), and Ni/Fe (Cheng et al. 2010; Zhang et al. 2006) partially dechlorinated PCP with build up of lower degree CPs and phenol. The nanoscale bimetals (e.g. Pd/Fe) showed high reactivity and transformed 4-CP, 24-DCP, and 246-TCP to phenol (Zhou et al. 2010). In contrast, Kim and Carraway (2000) reported a significant reduction in PCP dechlorination when using bimetals such as Pd/Fe, Pt/Fe, Ni/Fe, Cu/Fe compared to unmodified ZVI. The increased reactivity of bimetals could be attributed to the (1) secondary metal acting as a catalyst and enhancing the CP hydrogenation reaction and (2) formation of galvanic cells and enhances the electron transfer process (Tian et al. 2009). The cost of Pd or Pt is high, thus limiting the field application potential. Hence, Ni as an effective and economical alternative secondary metal is preferable for actual field application of bimetals as the reactive medium in PRB systems (Kim and Carraway 2000).

During the reactions, dechlorination is the preferred mechanism. However, other than the dechlorination process, incorporation of CP molecules with the oxides during their evolution throughout the reaction claims a crucial role in the CPs removal from water by bimetal/water systems (Gunawardana et al. 2018, 2019; Noubactep 2008). Interestingly, CPs incorporation, that is sorption, co-precipitation, and/or physical entrapment, with the iron oxide phases occurs concurrently with the dechlorination (Gunawardana et al. 2019). The incorporated CP molecules with the oxide layers limit the availability of CPs in the aqueous phase in direct contact with the bimetals for dechlorination, thus such incorporated CPs cannot be further degraded. Further, the incorporation process could be influenced by the physical–chemical properties of CPs and affect the efficiency of bimetals for the CPs dechlorination process. Increased amounts of ligand sorption on to iron oxides have been observed with the increase in pKa values of the ligand compounds (Song et al. 2008). Thus, it can be hypothesized that the affinity for incorporation of CPs with the oxide phases will increase with the decrease in the degree of chlorination of CPs; pKa of 2,4-DCP, 2,4,6-TCP, 2,3,4,6 TeCP, and PCP are 7.68, 5.97–7.42, 5.22–5.62, 4.60–5.25, respectively (Olaniran and Igbinosa 2011; Shiu et al. 1994). In addition, the changes in the morphology of the ZVI or bimetal surface due to the formation of various iron oxide phases over time under different conditions can change the surface properties/reactivity of iron and dramatically affect the CP removal processes from solution (Gunawardana et al. 2018, 2019).

The degradation of CPs using ZVI, other metals or bimetals and a comparison between CP degradation efficiencies have been studied by previous researchers (Choi et al. 2008; Kim and Carraway 2000; Ko et al. 2007; Liu et al. 2001; Xu et al. 2012). Previous studies have concentrated on comparing the reactivity of different metals or bimetals (with Pd, Ni as the catalyst) for CP degradation. Although these studies had reported that the ZVI materials used were obtained from different suppliers, comprehensive studies have not been carried out to identify the potential role of ZVI surface characteristics (e.g. oxide phases) on the reactivity for CP dechlorination.

Further, PCP sorption using one type of ZVI has been quantified (Kim and Carraway 2000) as well as sorption with bimetals (Ni/Fe, Pd/Fe, Pt/Fe, Cu/Fe, Mg/Ag, Pd/Mg) (Kim and Carraway 2000; Patel and Suresh 2006; 2007). Nonetheless, there are no comprehensive studies reported in the literature which uses ZVI-based bimetals to investigate incorporation levels of different CPs with different degree of chlorination. The sorption onto iron oxides could be influenced by the physical–chemical properties of CPs, which could lead to concerns with CPs dechlorination efficiency by ZVI and bimetals. Previous research also provides evidence that ligands with a greater pKa value resulted in increased sorption onto iron oxides such as ferrihydrite (Song et al. 2008). Based on this concept, it may be expected that the tendency for incorporation will increase as the degree of chlorination decreases, given that the pKa of 2,4-DCP, 2,4,6-TCP, 2,3,4,6 TeCP and PCP are 7.68, 5.97–7.42, 5.22–5.62, 4.60–5.25, respectively. Consequently, the possible relationship between iron oxide formation, CP dechlorination and/or incorporation as well as the effect of degree of chlorination on CPs incorporation/dechlorination processes when using bimetals remains uncertain and requires proper studies to understand the underlying mechanisms.

Therefore, in view of the gaps in the literature, this study aimed at investigating the effectiveness and efficiency of bimetallic particles for CP dechlorination and the effect of degree of chlorination and iron oxide phases on CPs incorporation and dechlorination when using Ni/Fe bimetallic system. Four model contaminants (PCP, 2,3,4,6-TeCP, 2,4,6-TCP, 2,4-DCP) were chosen for the study. These CPs were selected as they are common degradation products of PCP dechlorination and due to the toxic concerns of these CPs in the environment (ATSDR 1999; Tanjore and Viraraghavan 1994). Both dechlorination and incorporation processes of selected CPs were examined using Ni/Fe bimetal. The present study also focused on the distinct role CP removal mechanisms (dechlorination and incorporation) in removing CPs from the aqueous phase as a function of the different variables considered during the present study.

12.2 Materials and Methods

12.2.1 Materials

High purity chemicals such as PCP powder (ACS grade, 98%), 2,3,4,6-tetrachlorophenol (2,3,4,6-TeCP, Supelco, 98%), 2,4,6-trichlorophenol (2,4,6-TCP, Aldrich, 98%), 2,4-dichlorophenol (2,4-DCP, Aldrich, 99%), analytical standards of PCP, phenol, chlorophenol isomers in methanol and nickel sulphate ($NiSO_4.6H_2O$, >98%) were purchased from Sigma-Aldrich. Analytical grade solvents (ethyl acetate, acetone), sulphuric acid (H_2SO_4), and hydrochloric acid (HCl) were obtained from Ajax Finechem. A stock solution (5000 mg/L) of individual CPs, i.e. PCP, 2,3,4,6-TeCP, 2,4,6-TCP, and 2,4-DCP was prepared with the use of ethyl acetate as the solvent. Deionized (DI) water with resistivity of 18.20 MΩcm was prepared using a Millipore-Q system and used for all the experiments. For the preparation of deoxygenated DI water (DW), the DI water was first degassed at 80 °C and 100 kPa for one hour using a vacuum pump and then sparged with O_2-free N_2 gas for half an hour (dissolved oxygen level <0.2 mg/L).

The bimetal particles, i.e. nickel-coated ZVI (Ni/Fe) were synthesized as explained by.Kim and Carraway (2000) The ZVI used for the preparation of Ni/Fe particles was electrolytic iron powder (<100 mesh, North American Höganäs). Before using for Ni/Fe synthesis, the ZVI particles were pre-treated with H_2SO_4 (Liu et al. 2006). For the acid pre-treatment, as-received ZVI particles (500 g) were added to 1 N H_2SO_4 solution (1.5 L), the mixture was agitated for 30 minutes at 100 rpm and room temperature using a rotary shaker, and rinsed with DW. Post-rinsing of the particles with DW, they were dried under continuous purging of N_2 gas for 4 hours at 100 °C and then stored under N_2 gas environments until use for the synthesis of Ni/Fe bimetals. The Ni/Fe particles were prepared using a reductive adsorption method (Kim and Carraway 2000). A reaction solution with Ni was prepared by adding a known volume of a Ni stock solution (2 ml of 2.4% Ni solution prepared with $NiSO_4.6H_2O$ and 10% H_2SO_4) to 200 ml of DW water (pH of the prepared solution = 1.60). Then, 100.0 ($\pm$0.01) g of acid pre-treated ZVI was added to the solution (Kim and Carraway 2000). The mixture containing the Ni and ZVI was placed on a rotary shaker and agitated for one hour at 100 rpm and followed by rinsing with DW and acetone, air-dried at room temperature, and stored under O_2-free N_2 gas to use for the experiments. The Ni^{2+} solution was analysed for total Ni concentration pre- and post-exposure to acid-washed ZVI using the atomic absorption spectroscopy (AAS). The AAS results showed 92% Ni removal from the solution after Ni/Fe synthesis. Hence, based on the AAS analysis, the content of Ni deposited on the Ni/Fe bimetallic particles was calculated to be 442 ppm (mg of Ni per kg of Fe).

12.2.2 Experimental Procedure

Batch experiments were performed using Wheaton amber vials (30 ml) under identical experimental settings and anoxic conditions over the 25 day reaction period. Individual stock solution of PCP, 2,3,4,6-TeCP, 2,4,6-TCP, and 2,4-DCP (5000 mg/L) was prepared using ethyl acetate. Each CP was added and tested as a single compound in each vial. The initial concentration of each CP introduced to the batch reactors was 5 mg/L. This was equivalent to 19 μM of PCP, 22 μM of 2,3,4,6-TeCP, 25 μM of 2,4,6-TCP, and 31 μM of 2,4-DCP being initially introduced and available in each system before reaction with Ni/Fe bimetal. In each batch reactor, 1.00 (±0. 01) g of Ni/Fe and 10 ml DW were added and 10 μl of the respective CP stock solution was spiked. The high purity O_2-free N_2 gas was used as the headspace gas and the batch reactors were continuously purged with high purity O_2-free N_2 gas during the addition of deoxygenated water, CP stock solution, and during setting up the batch experiments to keep the reactors under anoxic conditions. The batch reactors were immediately sealed with aluminium caps with PTFE/silicone septa after the addition of respective CP solution and continuously agitated at 100 rpm on a rotary shaker at 23 (±1) °C until each sampling time. The control vials were prepared in a similar procedure without the addition of Ni/Fe bimetal particles. Duplicate experiments were conducted. At every sampling time over 25 days reaction duration, the pH of the reaction solution was monitored. At each sampling time, four reactors with Ni/Fe and two control vials without Ni/Fe were used for analyses.

The remaining concentration of parent CPs and the corresponding degradation products (Total CP concentration) as well as the aqueous concentrations of the parent CPs (dissolved CP concentration) in each reactor was determined at each sampling time using separate vials. A liquid–liquid extraction method with acid modification was used to extract the CPs from the Ni/Fe solids and the reaction solutions (Gunawardana et al. 2018; Kim and Carraway 2000). The total concentrations, which is the dissolved plus incorporated concentration of parent CPs and its degradation products, were determined after extracting the Ni/Fe bimetal/water mixture with ethyl acetate and concentrated HCl. In order to measure the concentration of total CP and degradation products, ethyl acetate (5 ml) was added to each batch reactor (containing the reaction solution and Ni/Fe particles). The mixture was continuously agitated for 30 minutes on a rotary shaker at 100 rpm, and then 1 ml concentrated HCl was added and the mixture was agitated for another ten minutes (Kim and Carraway 2000). The aqueous concentration (i.e. dissolved) of the parent CPs was determined after extracting the filtered reaction solutions with ethyl acetate and concentrated HCl. For the quantification of dissolved CPs in the solution, aqueous solution (9 ml) filtered by 0.2 μm regenerated cellulose (RC) membrane filters was used to along with the liquid–liquid extraction procedure using ethyl acetate/HCl as explained above for the quantification of total CP concentrations. After the liquid–liquid extraction procedure, 1.5 ml of the ethyl acetate layer was extracted, filtered (0.2 μm RC) and then stored in GC/MS autosampler vials for CPs and degradation product analysis. The solid contents (Ni/Fe particles) from the batch reactors sacrificed for quantification of the dissolved CP concentration were kept and utilized for the characterization of the iron oxide phases formed and present during the reaction period using Raman analysis.

12.2.3 Analysis

Quantification of CPs and its degradation products was carried out using the gas chromatography–mass spectrometer (Shimadzu model GCMS-QP2010S, Japan) (Gunawardana et al. 2018, 2019). A capillary column (ZEBRON ZB5-msi) with the dimensions of 30 m L × 0.25 mm ID × 0.25 μm thickness was used for the analysis. Selected ion monitoring (SIM) method was used with split mode injection of two μl of the sample at a ratio of 80:1 for separation and quantification of parent CP and degradation products. The carrier gas was high purity helium (1 ml/min), injection temperature 250 °C, column temperature program: 70 °C for 2 minutes, ramped at 5 °C minute^{-1} to 200 °C and held for 2 minutes, and ramped at 10 °C min^{-1} to 300 °C, and held for 5 minutes. A gas chromatograph (GC—SRI 8610C) with a column (HayeSep Q 80/100, Alltech, 6′ × 1/8″ × 0.085″ SS) coupled with a thermal conductivity detector (TCD) was used for quantification of the amount of hydrogen gas accumulated in the headspace of batch reactors during the reaction period. The operating conditions of the GC/TCD were: column temperature—24 °C; carrier gas—N_2 with a 10 ml/min flow rate.

12.2.4 Solid-Phase Characterization

The specific surface area of the unmodified ZVI, acid-washed ZVI, and Ni/Fe bimetallic particles were determined using the Brunauer–Emmett–Teller (BET) N_2 method and a Micromeritic Tristar 3000 (USA). The morphology, characteristics, and elemental information on selected regions of the ZVI and Ni/Fe surfaces and the presence of Ni on the Ni/Fe particle surface were obtained using FEI Quanta 200 F environmental scanning electron microscope (ESEM) coupled with a SiLi (lithium drifted) energy dispersive spectroscopy (EDS) (USA). A back-scattered detector was used with a 20 kV beam potential to collect the images.

Raman spectroscopy (Renishaw Raman system 1000 spectrometer, Australia) was used to identify (1) the specific iron oxides present on the Ni/Fe particles prior to exposure to CP solutions and (2) the specific iron oxides formed on the Ni/Fe particles post-exposure to CP solutions. Eight oxide phases typically present on iron surfaces (akaganeite, maghemite, haematite, magnetite, lepidocrocite, goethite, feroxyhyte, ferrihydrite) were considered, synthesized as the reference iron oxides (Cornell and Schwertmann 2003), and characterized using Raman spectroscopy (Gunawardana et al. 2018). A natural wustite mineral specimen was characterized by EDS and Raman analysis and confirmed with the literature (Nadoll and Mauk 2011). During the Raman analysis, of all Ni/Fe samples reacted with CPs, it was observed that the spectra of different iron oxides present overlapped extensively, which indicated the presence of a mixture of oxide phases. The presence of a mixture of oxide phases made it complex for clear identification of individual oxide phases in the observed spectra. Therefore, multivariate curve resolution with alternating least squares (MCR-ALS) within MATLAB (Mathworks®) was used for quantification of specific iron oxides (Jaumot et al. 2005). The green rust oxides were excluded and not considered for the group of reference spectra, as they are reported as unstable and subject to transformation to other oxides under the conditions used in the present study.

The effect of Ni/Fe treatment on the concentration of different CPs degraded after 25 days reaction period was compared using statistical analysis (one-way and two-way analysis of variance) and SPSS statistical software (IBM SPSS Statistics version 20.0.0 [SPSS Inc., USA]). The effect of Ni/Fe treatment on the amount of CP degraded, levels of extractable CPs incorporated as well as H_2 gas accumulated after 25 days reaction were compared. The differences were considered as significant at 95% confidence level.

12.3 Results and Discussion

12.3.1 Dechlorination of Chlorophenols Using Ni/Fe

The degradation of four CPs (PCP, 2,3,4,6-TeCP, 2,4,6-TCP, 2,4-DCP) using Ni/Fe and the subsequent formation of daughter compounds is presented in Fig. 12.1. After 25-day reaction period, the CPs reactivity with Ni/Fe in the order of highest to lowest was: PCP > 2,3,4,6-TeCP > 2,4,6-TCP ≈ 2,4-DCP (Fig. 12.1). After 25 days reaction, approximately 55% of PCP, 46% of 2,3,4,6-TeCP, 34% of 2,4,6-TCP, and 30% of 2,4-DCP, which was initially introduced to each system, were removed from the aqueous phase (Fig. 12.1). Among the four CPs tested, PCP showed a significantly higher amount of dechlorination ($p < 0.05$), whereas 2,4,6-TCP showed a significantly lower amount of dechlorination ($p < 0.05$) after 25 days of reaction with Ni/Fe.

Dechlorination of PCP and 2,3,4,6-TeCP using Ni/Fe resulted in accumulation of CPs with a lower degree of chlorination, with trace amounts of phenol being detected (Fig. 12.1b, c).

The CPs with a lower degree of chlorination continuously forming and accumulating in the system during the reaction of PCP or TeCP with Ni/Fe bimetal (Fig. 12.1b, c) can create a competition for the same electrons and reactive sites on the Ni/Fe and ZVI surfaces for dechlorination. Hence, the formation and gradual accumulation of CPs with a lower degree of chlorination may create adverse impacts on the rate of dechlorination of PCP or TeCP by Ni/Fe. Such a competitive effect between the parent CP and daughter CPs (with a lower degree of chlorination) can lead to partial dechlorination of PCP or TeCP. On the other hand, when 2,4,6-TCP was reacted with Ni/Fe, small concentrations of DCPs and monochlorophenols (MCPs) were observed

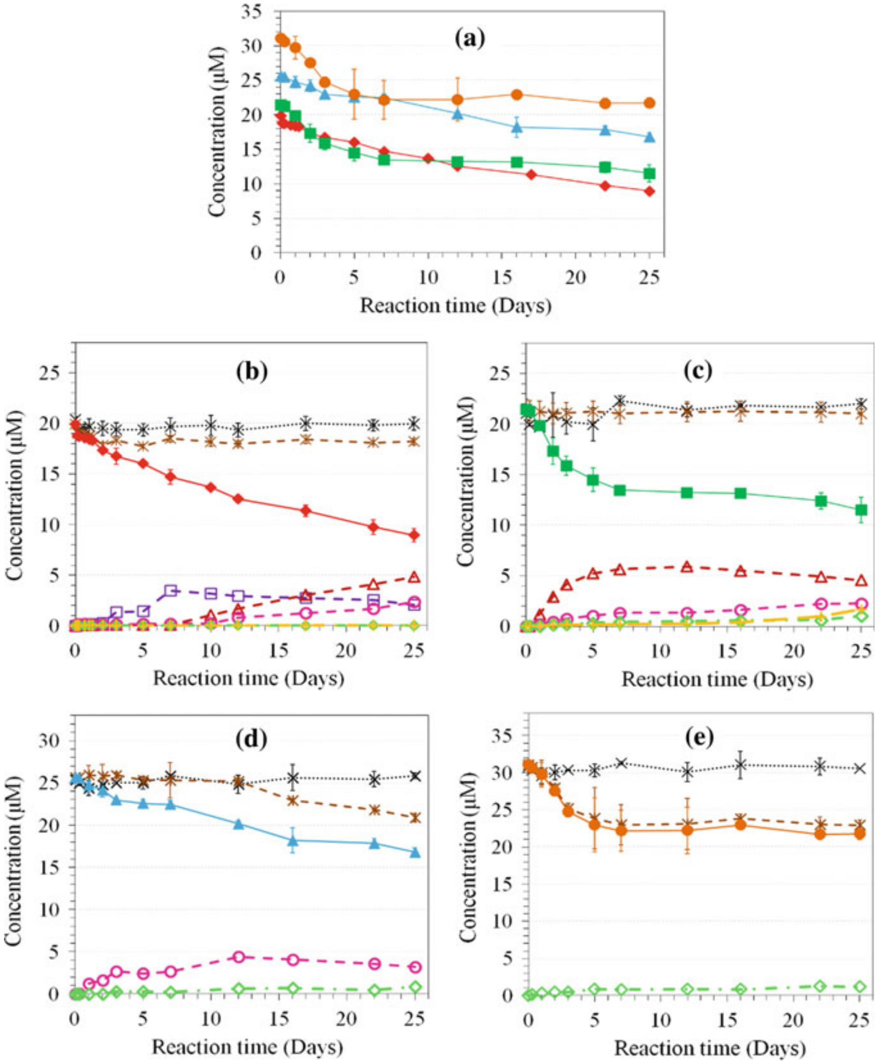


Fig. 12.1 **a** Ni/Fe bimetal degradation of Pentachlorophenol (◆), 2,3,4,6-tetrachlorophenol (■), 2,4,6-trichlorophenol (▲)and 2,4-dichlorophenol (●); **b** Ni/Fe bimetal degradation of pentachlorophenol (◆)and formation of TeCPs (□), TCPs (Δ), DCPs (○), MCPs (◇), and phenol (+); **c** Ni/Fe bimetal degradation of 2,3,4,6-tetrachlorophenol (■)and formation of TCPs (Δ), DCPs (○), MCPs (◇), and phenol (+); **d** Ni/Fe bimetal degradation of 2,4,6-trichlorophenol (▲)and formation of DCPs (○)and MCPs (◇), and **e** Ni/Fe bimetal degradation of 2,4-dichlorophenol (●)and formation of MCPs (◇); control (✕); mass balance (✱). Error bars indicate ± one standard deviation. *Total TeCPs were the sum of all the TeCPs measured, total TCPs were the sum of all the TCPs measured, total DCPs were the sum of all the DCPs measured and total MCPs were the sum of all the MCPs measured*

as the main degradation products (Fig. 12.1d). Degradation of 2,4-DCP using Ni/Fe resulted in the accumulation of minute concentrations of MCPs as the end product (Fig. 12.1e).

The mass balance recoveries obtained for PCP and 2,3,4,6-TeCP with Ni/Fe bimetallic system were within 93–96% of the amount of respective CP initially added to the solution (Fig. 12.1). The remaining two CPs (2,4,6-TCP and 2,4-DCP) demonstrated high mass balance recoveries (91–97%) during the initial reaction period (Fig. 12.1). The 2,4,6-TCP and 2,4-DCP concentrations decreased over the reaction time, and however, a noticeable increase in the corresponding dechlorination products was not observed resulting in a gradual decrease of mass balance of these two CPs over time (Fig. 12.1). Despite the greater mass balance recoveries demonstrated by 2,4,6-TCP and 2,4-DCP at the beginning of the reaction period, these mass recoveries decreased considerably to between 70 and 80% during the later stages of the reaction period (Fig. 12.1d, e). As such, it could be suggested that CPs incorporation must have been a significant process of removal of 2,4,6-TCP and 2,4-DCP from solution when using Ni/Fe. The incomplete recovery of the parent CPs with a lower degree of chlorination and/or their degradation products could possibly be attributed to the formation of iron oxides with different characteristics, strong incorporation of CP molecules with the oxides formed during the reaction and lack of extraction/recovery of CPs and the degradation products during the extraction process (these aspects are elaborated in the subsequent sections).

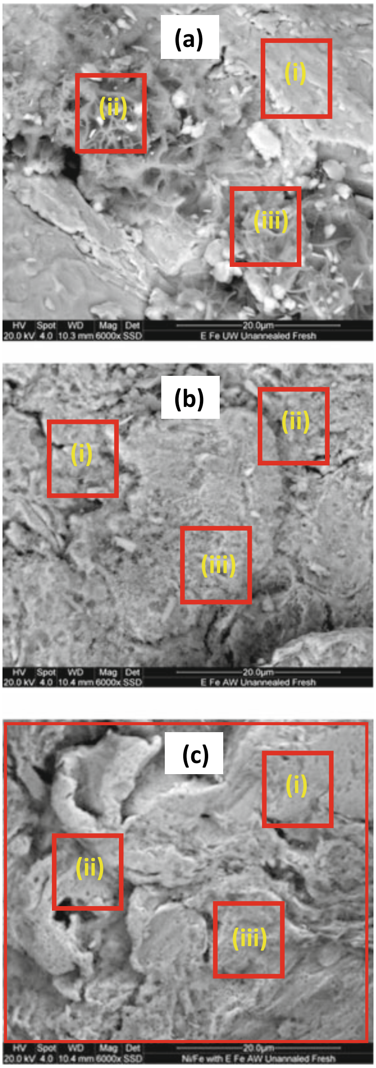
The CPs dechlorination reaction with Ni/Fe bimetal demonstrated pseudo-first-order behaviour with $C_t = C_0 e^{-kt}$, where C_0 is the initial CP concentration (μM), C_t is the CP concentrations at reaction time t (μM), and k is the first-order observed reaction rate constant (day^{-1}). The observed reaction rate constants were 0.0594 day^{-1}, 0.0275 day^{-1}, 0.0180 day^{-1}, and 0.0170 day^{-1} for PCP, 2,3,4,6-TeCP, 2,4,6-TCP and 2,4-DCP, respectively. The trend of the observed rate constants (highest to lowest) further supports the observed reactivity of the CPs with Ni/Fe (PCP > 2,3,4,6-TeCP > 2,4,6-TCP > ≈ 2,4-DCP). The behaviour and observed rate constants are consistent with previous research reports where the batch experiment results proved first-order behaviour when chlorinated phenols were degraded with bimetallic systems (Choi et al. 2008; Kim and Carraway 2000; Ko et al. 2007; Liu et al. 2001). The general trend of CP reaction rates with Ni/Fe bimetal (1) did not comply with the data presented by Ko et al. (2007) who reported increased reaction rates using Ni/Fe with the decreased degree of chlorination and (2) agree with Patel and Suresh (2006) findings, who reported a decrease in reaction rates with the decreased degree of chlorination using Mg/Ag bimetal. This discrepancy between the reaction rates of this study and previous studies could be due to the differences in, (1) experimental conditions, (2) ZVI characteristics, (3) type/quantity of catalyst used, and (4) method of reaction rates estimation. The surface area normalized dechlorination reaction rate constants (K_{SA}) of CPs in water-Ni/Fe bimetal system was calculated based on the BET specific surface area of Ni/Fe and found to be 0.02×10^{-2} Lm^{-2} day^{-1} for PCP and 0.01×10^{-2} Lm^{-2} day^{-1} for 2,3,4,6-TeCP, 2,4,6-TCP and 2,4-DCP. It was not possible to estimate the area of only the reactive sites on the Ni/Fe surface; the measured BET specific surface area of Ni/Fe metal surface is an absolute measurement representing the total area of Ni/Fe metal surface. Hence, the reactivity of Ni/Fe bimetal for CP dechlorination could be assessed only based on the observed dechlorination reaction rates.

It was anticipated that the use of Ni as a catalyst would result in enhanced CPs dechlorination by Ni/Fe bimetal. However, the use of Ni/Fe bimetal resulted in only partial dechlorination of CPs tested. Partial dechlorination of CPs observed with Ni/Fe could be a result of the formation of a permanent Ni coating as a thin film on the ZVI surface during Ni/Fe preparation, which could cover the ZVI reactive sites thus restricting the electron and CP molecules transfer process for effective dechlorination. These aspects are discussed under Sect. 12.3.2-Ni/Fe characterization.

12.3.2 Characterization of ZVI and Ni/Fe Material

The analysis of specific surface area of various materials showed that the specific surface area of unmodified ZVI, acid pre-treated ZVI, and Ni/Fe were 0.212 ± 0.002, 0.910 ± 0.003, 2.696 ± 0.011 m^2/g, respectively. An increase in the ZVI surface area after each modification indicates the possibility of variations and changes of the composition or morphology between the materials after respective modifications, which could have influenced the CP dechlorination potential (Cwiertny et al. 2007).

The surface morphology and elemental distribution on the ZVI, Ni/Fe surfaces and the presence and distribution of Ni on the bimetal particles were obtained using the ESEM-EDS analysis (Fig. 12.2). The EDS analysis showed Fe, O, and C as the main elements on the unmodified and acid pre-treated ZVI surfaces (Fig. 12.2a, b). The EDS scans done in many small regions on the surface of the Ni/Fe bimetallic particles did not show any evidence of scattered deposition of Ni over the ZVI surfaces. An example of an EDS scans done on small areas on the Ni/Fe particles are shown in Fig. 12.2c [Fig. 12.2c; (i), (ii), and (iii) areas marked in red)]. However, the EDS scans done on a wide area on the Ni/Fe surface demonstrated the presence of deposited Ni [Fig. 12.2c (iv) area marked in red]. Prior to using for the preparation of Ni/Fe bimetallic particles, the acid-washed ZVI surface was initially mainly covered with magnetite. Due to magnetite's high conductivity, Ni^0 could be rapidly deposited as a thin layer on the surface of the acid pre-treated ZVI particles during the synthesis of Ni/Fe. The assumption underlying this hypothesis is that due to the high conductivity of magnetite, the reduction of Ni^{2+} to Ni^0 occurs instantaneously and rapidly on a magnetite surface. Accordingly, based on the observations of this study, we hypothesize that during the Ni/Fe synthesis and reductive Ni deposition process ($Fe^0 + Ni^{2+} \rightarrow Ni^0 + Fe^{2+}$), Ni has deposited on the ZVI, not as clusters/scattered deposition of Ni particles scattered/dispersed in parts of the ZVI surface but as a thin Ni film over the ZVI surface. A schematic diagram illustrating the behaviour of the ZVI and oxide phases during the acid washing and Ni/Fe preparation is presented as Fig. 12.3.



Elemental analysis on as received ZVI surface using ESEM/EDS

Location	Elemental weight (%)		
	Fe	O	C
(i)	94.1	3.3	2.6
(ii)	93.3	3.9	2.8
(iii)	94.5	3.6	1.9

Elemental analysis on acid washed ZVI surface using ESEM/EDS

Location	Elemental weight (%)		
	Fe	O	C
(i)	85.5	10.8	3.7
(ii)	86.3	9.8	3.9
(iii)	88.0	9.5	3.5

Elemental analysis on Ni/Fe bimetallic surface using ESEM/EDS

Location	Elemental weight (%)			
	Fe	O	C	Ni
(i)	83.3	12.8	3.9	-
(ii)	84.3	12.2	3.5	-
(iii)	85.0	11.5	3.5	-
(iv)*	83.9	11.7	4.2	0.2

Fig. 12.2 Environmental scanning electron microscopy (ESEM) images and EDS analysis, **a** as-received ZVI, **b** acid-washed ZVI, **c** Ni/Fe. *The areas marked in red squares were randomly selected and scanned using the EDS for elemental analysis*

The oxides present on the Ni/Fe bimetallic surfaces pre- and post-reaction with CPs were determined by Raman spectroscopy and MCR-ALS analysis. Typical Raman patterns of the reference oxide phases considered during the study are shown in Fig. 12.4. The typical Raman spectra of unmodified ZVI, acid pre-treated ZVI, unreacted Ni/Fe bimetal, and Ni/Fe bimetal after 25 days reaction with the four CPs are shown in Fig. 12.5.

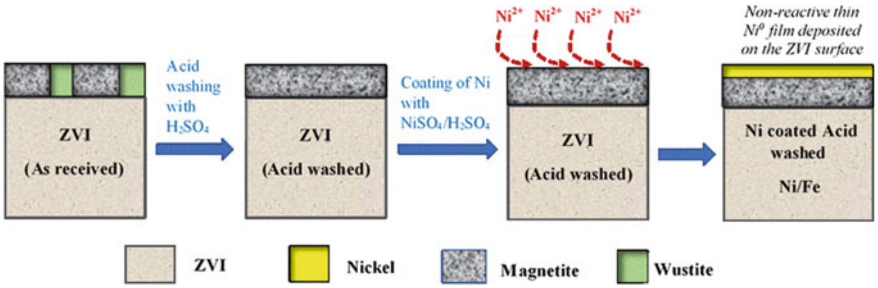


Fig. 12.3 Possible behaviour of the ZVI and respective oxide phases during acid washing process and Ni/Fe bimetal preparation

The relative amounts of oxides present on the Ni/Fe (estimated by MCR-ALS analysis) before and after reaction with CPs are presented in Table 12.1. Prior to reaction with CPs, only magnetite was present on the Ni/Fe surface. However, during the reaction of each CP with Ni/Fe, a decrease in the relative amount of magnetite was observed (Table 12.1). In contrast, while magnetite amount was decreasing, several other iron oxides (akaganeite, haematite, lepidocrocite, wustite, goethite, ferrihydrite) were detected on the Ni/Fe surface during the 25 days reaction period with each CP tested (Table 12.1).

The changes in the iron surface morphology due to the formation of various iron oxide phases over time under different conditions can change the surface properties/reactivity of iron and dramatically affect the CP removal processes from solution (Gunawardana et al. 2011, 2018). In addition, the reactivity of the Ni/Fe bimetallic iron surfaces could be affected by the electric conductivity of oxide phases present and formed on the Ni/Fe and iron surfaces.

Findings showed that the dechlorination of CPs could be limited by the formation of akaganeite, haematite, goethite, lepidocrocite, and wustite (Table 12.1) as they have low conductivities at room temperature compared to magnetite (Cornell and Schwertmann 2003). The passive oxides formed seemed to decrease the number of redox reactive sites on the Ni/Fe surface and impede the electron transfer and transport of CP molecules. Such phenomenon could hinder the CP dechlorination leading to partial dechlorination and accumulation of lower degree CPs (Fig. 12.1), and possibly increased the CPs incorporation process (especially, 2,4,6-TCP and 2,4-DCP) with the iron oxides.

The relative amounts of passive oxide phases detected on the Ni/Fe surface showed a progressive growth over the reaction duration, especially when 2,4,6-TCP or 2,4-DCP was introduced as the testing CP in the reactors (Table 12.1). This progressive growth of passive oxides as well as their ageing could lead to further entrapment of the adsorbed CPs in the oxides/oxyhydroxides structures and reduce desorption of such CP molecules to the aqueous phase. Lack of availability of CPs in the aqueous phase could further limit the dechlorination of CPs by Ni/Fe.

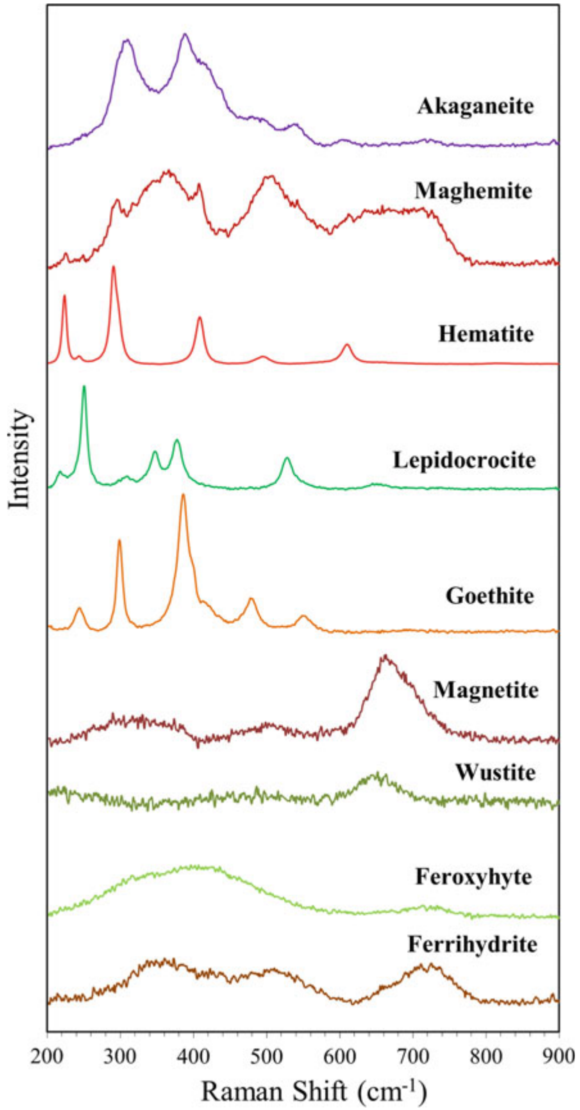
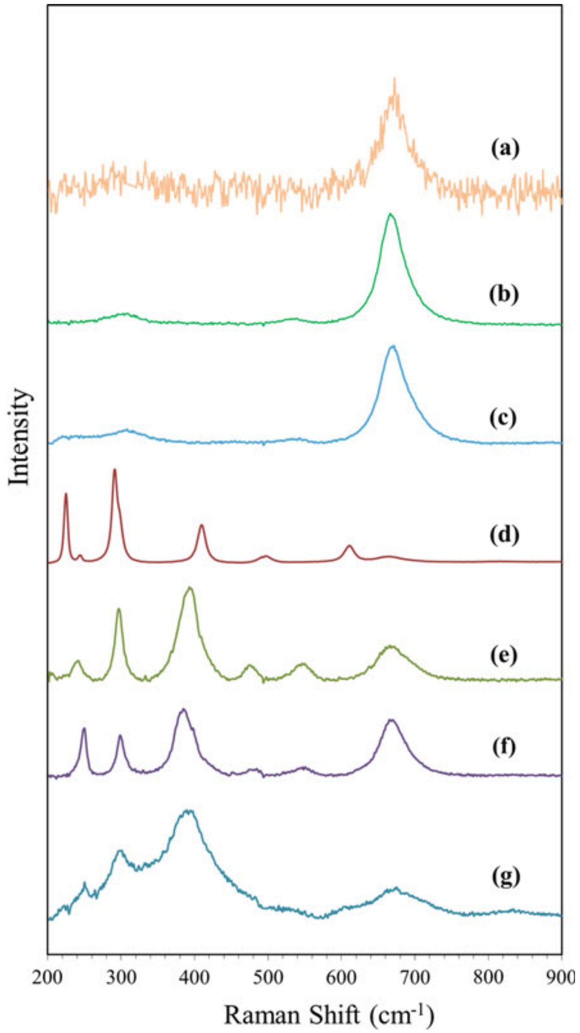


Fig. 12.4 Raman spectra of reference iron oxides used

CPs with higher pKa values (2,4-DCP: pKa of 7.68 and 2,4,6-TCP: pKa of 5.97–7.42) seemed to have a higher tendency for incorporation with the oxides hindering the dechlorination process. Furthermore, when 2,4,6-TCP and 2,4-DCP were reacting with Ni/Fe, detection of lower amounts of magnetite and greater amounts of passive oxides (akaganeite, haematite, lepidocrocite, wustite, goethite, ferrihydrite), compared to the amounts of respective oxides detected with PCP and 2,3,4,6-TeCP, provides evidence of decreased reactivity of 2,4,6-TCP and 2,4-DCP observed with

Fig. 12.5 Raman spectra of samples that was unreacted: **a** ZVI (as-received) **b** ZVI (acid-washed) **c** Ni/Fe bimetal, and typical sample spectra after 25 days reaction of Ni/Fe with **d** PCP **e** TeCP **f** TCP **g** DCP



the Ni/Fe bimetal. During the reaction of 2,4,6-TCP and 2,4-DCP with Ni/Fe, various passivating oxides started accumulating on the ZVI surface immediately during the initial reaction period of 1 day when in contact with Ni/Fe. Furthermore, Raman analysis showed continuous accumulation of such passivating oxides on the Ni/Fe surface throughout the 25-day reaction period of 2,4,6-TCP and 2,4-DCP with Ni/Fe. This progressive growth of passive oxides as well as their ageing could lead to strong entrapment of the adsorbed CP molecules with the oxides/oxyhydroxides structures and reduce the extraction/desorption potential of such CPs during the chemical extraction process resulting in poor mass balance recoveries. Based on the literature, Fe^{II} oxides have a greater solubility compared to that of Fe^{III} oxides and

Table 12.1 Percentages of iron oxides present on the iron surface at the start, after 1 day, 12 days, and end of experiments (estimated by MCR-ALS analysis)

Treatment	Type of CP	Type of iron oxide						
		Akgt	Hemt	Magnt	Lepidt	Goeth	Wus	Ferrih
ZVI (as-received)[a]		–	–	74	–	–	24	<5
ZVI (acid-washed)[b]		–	–	100	–	–	–	–
Ni/Fe[c]		–	–	100	–	–	–	–
Ni/Fe[d]	PCP	–	<5	95	–	–	<5	–
	2,3,4,6-TeCP	–	<5	90	–	7	–	–
	2,4,6-TCP	–	5	86	5	<5	<5	–
	2,4-DCP	<5	–	82	<5	<5	<5	<5
Ni/Fe[e]	PCP	–	5	88	–	–	7	–
	2,3,4,6-TeCP	–	<5	84	–	12	–	–
	2,4,6-TCP	<5	6	74	7	<5	7	–
	2,4-DCP	5	–	75	10	<5	<5	<5
Ni/Fe[f]	PCP	–	10	71	–	–	13	6
	2,3,4,6-TeCP	–	<5	75	–	23	–	–
	2,4,6-TCP	<5	14	61	8	5	12	–
	2,4-DCP	9	–	65	15	<5	<5	6

Akgt Akaganeite, *Hemt* Haematite, *Magnt* Magnetite, *Lepidt* Lepidocrocite, *Goeth* Goethite, *Wus* Wustite, *Ferrih* Ferrihydrite

[a] The ZVI (as-received) surface at the start of the experiment

[b] The ZVI (acid-washed) surface at the start of the experiment

[c] The Ni/Fe bimetal surface at the start of the experiment

[d] The Ni/Fe surface after 1 day of reaction

[e] The Ni/Fe surface after 12 days of reaction

[f] The Ni/Fe surface after 25 days of reaction

"–" Respective iron oxide(s) were not detected on the metal surface(s)

"<5" Percentage amount of respective iron oxide(s) detected on the metal surface(s) was less than 5%

magnetite has a greater solubility compared to $Fe(OH)_2$ (Cornell and Schwertmann 2003). Thus, the incorporated CP and/or degradation products with the passive iron oxides seemed to be difficult to extract using HCl and ethyl acetate leading to poor CP mass balance (Fig. 12.1).

On the other hand, during the reaction of PCP and 2,3,4,6-TeCP with Ni/Fe bimetal, magnetite was the dominant oxide phase at the beginning and throughout the reaction period although some passive oxides started accumulating on the Ni/Fe towards the later part of the 25 days reaction period (Table 12.1). Presence of low levels of passivating oxides on the Ni/Fe surface during the reaction of PCP and 2,3,4,6-TeCP could potentially result in (1) lower levels of incorporation of the degradation products (i.e. CPs with lower degree of chlorination) with such oxide phases and (2) greater desorption and extraction efficiency of such lower degree CP degradation products (2,4,6-TCP and 2,4-DCP) and higher mass balance.

Nonetheless, the exact reasons for the variations observed in the formation/accumulation of different oxide phases during the reaction of Ni/Fe with various CPs of different degree of chlorination (i.e. PCP, 2,3,4,6-TeCP, 2,4,6-TCP, and 2,4-DCP) could not be explained by the findings of the present study. Therefore, specific studies need to be conducted to understand the behaviour and surface chemistry of ZVI and Ni/Fe bimetallic reactions when reacting with the CPs with different degree of chlorination.

12.3.3 Accumulation of Hydrogen Gas in Batch Reactors

Hydrogen gas accumulated in batch reactors was measured at each sampling time. The data of hydrogen gas formed during the reaction of the four CPs (PCP, 2,3,4,6-TeCP, 2,4,6-TCP, and 2,4-DCP) with Ni/Fe bimetal is presented in Fig. 12.6a. The hydrogen gas formation was observed with all the treatments, although the total hydrogen pressure remained <0.5 atm even after 25 days of reaction.

In a Ni/Fe bimetal system, Ni can perform as a catalyst to enhance the formation of atomic hydrogen or a metal hydride phase on the iron surface. Hence, Ni can potentially enhance the CP degradation via hydrodechlorination (Ko et al. 2007; Tian et al. 2009). Also, the catalytic activity of Ni is known to enhance the H_2 gas production as a result of enhanced ZVI corrosion and encourage H_2 to react as a reductant (Feng and Lim 2005; Matheson and Tratnyek 1994). However, in this study, low hydrogen gas accumulation (Fig. 12.6a) and partial CP dechlorination were observed (Fig. 12.1). The lower hydrogen gas formation with Ni/Fe is indicative of (1) lower reactivity of Ni/Fe, (2) inhibition of production of H_2 gas due to the deposition of Ni possibly as a thin layer concealing the reactive sites on the ZVI

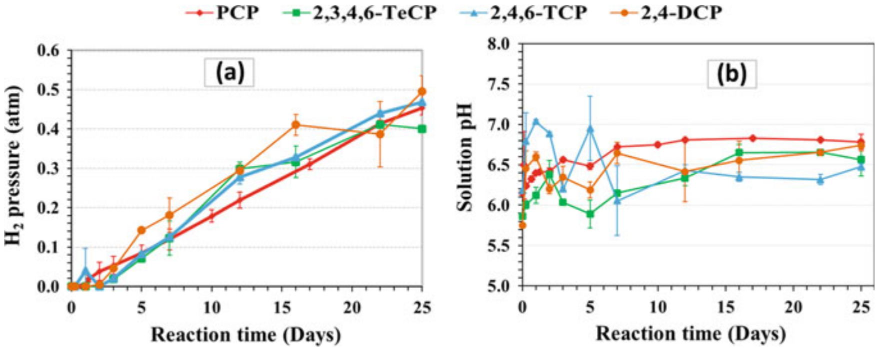


Fig. 12.6 **a** Hydrogen gas accumulated in the batch reactors **b** variation in solution pH for 25 days reaction of CPs with Ni/Fe. *Error bars represent ± one standard deviation*

surface, or (3) formation of passive oxides blocking the ZVI reactive surfaces. Less hydrogen gas formation with the Ni/Fe (Fig. 12.6) is consistent with the lower/partial CP degradation observed using this system (Fig. 12.1).

The rate of hydrogen gas formation may vary depending on the characteristics of the ZVI surface as well as the electron acceptors present in the systems. However, the results showed that the rate of hydrogen gas accumulation with each CP was approximately the same with some fluctuations observed with 2,4-DCP and seems to be independent of the type of CP present in the system (Fig. 12.6).

The solution pH was measured at each sampling time with Ni/Fe and each CPs and the data is presented in Fig. 12.6b. In general, an increase in the solution pH was observed over the reaction duration. An increase in pH from 5.6 or 6.1 to 6.1 or 7.1 was noted during the initial reaction period (1–2 days) followed by a pH decrease over the remaining duration of the experiment. After 25 days of reaction, the pH levels between 6.3 and 6.9 were observed with all treatments (Fig. 12.6b). An increase in solution pH occurs due to a consumption of protons during CP dechlorination and production of hydroxide ions during metal corrosion. In addition, some studies attributed the change in solution pH to the accumulation of daughter compounds with different acid dissociation constants during the degradation of parent CP compound using zero-valent metals (Kim 1999; Liu et al. 2001). Previous studies also have reported an increase in solution pH during interaction of CPs with ZVI and/or ZVI-based bimetals (Choi et al. 2008; Kim and Carraway 2000; Liu et al. 2001; Wei et al. 2006).

12.3.4 Incorporation of Chlorophenols onto Ni/Fe Solid Phase and Iron Oxides

Removal of the tested CPs from solution with Ni/Fe occurred due to concurrent dechlorination and incorporation. The amount of extractable CP incorporated per unit mass of Ni/Fe (C_s, μmole CP/g of Ni/Fe) was calculated in each system as follows: $C_S = [(C_T - C_W) * V_W)]/M_{Ni/Fe}$, where C_T = total system CP concentration [μmole/l]; C_W = aqueous phase CP concentration [μmole/l]; V_W = volume of aqueous solution [l]; and $M_{Ni/Fe}$ = initial amount of Ni/Fe used in the batch reactor [g]. The amounts of extractable CP incorporated in the Ni/Fe solid phase are presented in Fig. 12.7.

A rapid increment in the amount of incorporated CPs was observed during the initial reaction period up to 5 days (Fig. 12.7), which could be due to sorption of CPs on to the reactive and/or non-reactive sites of Ni/Fe particles and/or physical entrapment/co-precipitation of CPs with the iron oxides (Noubactep 2009; Noubactep 2008). In addition, the compounds present in the Ni/Fe bimetallic-water system as well as the iron oxide phases forming on the Ni/Fe surface subject to continuous change, thus could affect the amount of CPs incorporated with the oxide phases during the reaction period. Approximately constant levels of incorporated and extracted CP concentration demonstrated by some CPs at the later stages of the

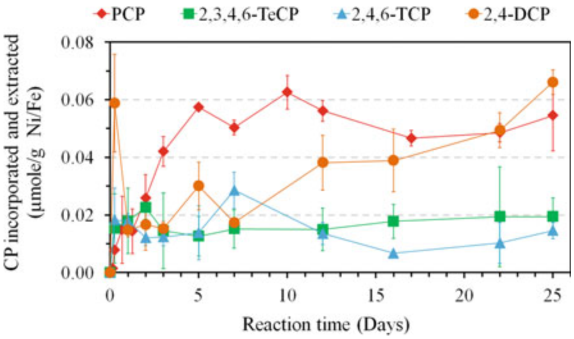


Fig. 12.7 Incorporated and extracted CP concentrations on Ni/Fe when reacted with Ni/Fe. *Error bars represent* ± *one standard deviation. Initial amount of PCP* (0.19 μmole/g Ni/Fe), 2,3,4,6-*TeCP* (0.22 μmole/g Ni/Fe), 2,4,6-TCP (0.25 μmole/g Ni/Fe) *and* 2,4-DCP (0.31 μmole/g Ni/Fe) *were available in each system*

reaction (Fig. 12.7) could be attributed to strong incorporation of such CPs with the oxide phases formed during the reaction and lack of recovery of these incorporated CP molecules.

Noticeable amounts of lower degree CPs and/or phenol would be expected to be detected in the Ni/Fe systems as end products when dechlorination is the principal process. However, as illustrated in Fig. 12.1, when 2,4,6-TCP and 2,4-DCP reacted with Ni/Fe, only minute levels of CPs were detected as end products in the respective systems. Consequently, incorporation must have been a significant removal process of 2,4,6-TCP and 2,4-DCP by Ni/Fe from solution. Nevertheless, the detected minute levels of CPs as end products in these systems provide evidence of dechlorination; however, a majority of these end products may have also been incorporated with the iron oxides during the reaction.

This study does not facilitate the identification of the specific incorporation process such as sorption, co-precipitation, or physical entrapment with the oxide phases. However, the findings of this research provide evidence of a decrease in the mass recovery with the decrease in the degree of chlorination of CPs (Fig. 12.1). This is expected based on the theory of decrease in sorption affinity of CPs for an iron oxide with the degree of chlorination increases (as illustrated in Fig. 12.1). The fact that the lower degree CPs had the lowest recovery during extraction supports the possibility that oxide phases remaining after extraction strongly retain some of the CPs.

12.4 Conclusions

The effect of degree of chlorination on dechlorination and incorporation of four CPs (PCP, 2,3,4,6-TeCP, 2,4,6-TCP, and 2,4-DCP) was investigated using Ni/Fe bimetallic iron particles. Ni/Fe treatment resulted in partial CPs dechlorination and accumulation of lower CPs. In general, CPs with a higher degree of chlorination demonstrated greater CP dechlorination. The reactivity of CPs with Ni/Fe bimetallic system followed the sequence of PCP > 2,3,4,6-TeCP > 2,4,6-TCP $\approx$ 2,4-DCP over the 25 days reaction. As the degree of chlorination of the CPs decreased, the CPs showed an increased affinity for incorporation (sorption, co-precipitation and/or physical entrapment of CP and/or degradation products) with the iron oxides, incomplete mass recovery of CPs, and decreased dechlorination. In particular, 2,4,6-TCP and 2,4-DCP demonstrated a greater tendency for incorporation with the iron oxides. This effect of 2,4,6-TCP and 2,4-DCP may be attributed to the higher pKa values of these two CPs leading to a greater affinity for incorporation with the oxides thus lack of availability of these two CPs in the aqueous phase hindering the dechlorination. Furthermore, relatively high amounts of passive oxides (akaganeite, haematite, lepidocrocite, wustite, goethite, ferrihydrite) along with relatively low amounts of magnetite (compared to that with PCP and 2,3,4,6-TeCP) was detected during the reaction of 2,4,6-TCP and 2,4-DCP with Ni/Fe bimetal. The passive oxides seemed to hinder the dechlorination of 2,4,6-TCP and 2,4-DCP, but possibly increased CPs incorporation with the oxides.

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Chapter 13
Reigning Technologies and Their Challenges for Antibiotics Removal

Chandrashekhar Bhagat, Manish Kumar, and Pranab Kumar Mohapatra

13.1 Introduction

Pharmaceuticals like antibiotics, hormones, anesthetics, and anti-inflammatories are the new class of emerging contaminants found in the environment (Sarmah et al. 2006; Kumar et al. 2019a, b; Gogoi et al. 2018). Considering their basic function, these compounds are inherently bioactive and bio-available in the ambient environment and it leads to the ambiguous post-therapeutic consequence on the non-targeted organisms (Southgate et al. 2000; Mohapatra et al. 2016; Leung et al. 2012). Among all, pharmaceuticals antibiotics are competent antimicrobial agents and have been extensively used in human medicine for infection and various diseases control (Mahmood et al. 2019; Diwan et al. 2009, 2010; Cao et al. 2016), agriculture, aquaculture, animal husbandry, and live storage stoke (Kolpin et al. 2002, 2004; Kirst 2001; Kang et al. 2018). As emerging contaminants in the environment, there has been increasing concern about pharmaceutical products like antibiotics (Gothwal and Shashidhar 2015; Goel et al. 2015; Berglund et al. 2014) because tons of antibiotics are used in the year for various purposes. Hence, this increased antibiotics thread in the various environmental compartments leads a serious concerned about the elimination of antibiotics from wastewater (Mutiyar and Mittal 2013, 2014).

Elimination means the removal of the parental compound and its by-product from the concern environmental compartment, especially from aquatic matrices (Watkinson et al. 2007, 2009). The treatment which is employed for the removal of only

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parental compounds is known as primary elimination process/treatment (Karthikeyan and Meyer 2006). Primary treatments are generally stated when analytical approaches like liquid chromatography–mass spectrometry (LC-MS) (Batt and Aga 2005) or high-performance liquid chromatography (HPLC) are used in antibiotics removal studies. Some chemicals or biological indicators like BOD, COD, DOC loss, ORP, and the concentration of effluent give the idea about the effectiveness of the treatment. Quantification of single parameter like CO_2 generation in the removal process is able to provide an efficiency of mineralization that leads to the complete degradation of a molecule through owned metabolites and convert that mineralization output into CO_2, water, and inorganic salts like sulfate, sulfide, nitrite, etc. The need for removal of unwanted (organic/inorganic) substances from the environment system is the consequence of the evolution of several removal techniques (Kümmerer K. 2009a, b).

The removal processes can be biotic and non-biotic, the biotic means biodegradation by biological means and non-biotic means removals by employing the physical or chemical processes or a combination of both processes. The non-biotic processes are sorption, hydrolysis, photolysis, oxidation, reduction, liquid extraction, and membrane techniques (Singh et al. 2019; Singh et al. 2020; Kumar et al. 2016). Most of the removal techniques performance is dependent on condition such as the composition of matrix, temperature, pH of the system, and centration of contaminant. The techniques which are used to remove the antibiotics contaminants from the wastewater are conventional treatment processes (filtration, coagulation, flocculation, sedimentation and activated sludge process, trickling filters, etc.), ecological treatments (constructed wetlands), adsorption techniques, advance oxidation techniques, and physical processes, etc. (Das et al. 2015; Kumar et al. 2010). This chapter gives an overview of different removal techniques used and associated challenges for the elimination of antibiotics.

13.2 What Is Antibiotic and Antibiotics Contaminant

A chemical compound that used to prevent/killed/destroyed the growth of microorganism is known as antibiotics (Homem and Santos 2011), for examples, penicillin, amoxicillin, tetracycline, Ciprofloxacin, etc. Sometimes antibiotics are also expanded into antibacterial, antifungal, antimicrobial, and antitumor compounds. Many of them are from a microbial source, but some of them may be semi- or completely fabricated. These substances are enduring and having high resistance to decomposition and persistence is high, and hence accumulation in the different environmental matrices increases day by day (Larsson et al. 2007). The antibiotics residue found in various environmental matrices, i.e., river water (Xu et al. 2009), wastewater (Mutiyar and Mittal 2014), lake water, groundwater (Sacher et al. 2001), soil sediments, etc., and their concentration above the detection limit is known as antibiotics contaminant (Fig. 13.1).

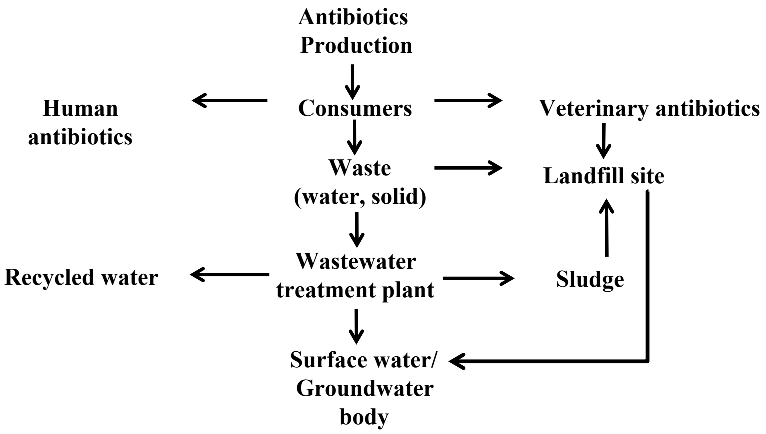

Fig. 13.1 General pathways of antibiotics contaminants in the environment

13.3 Effects of Antibiotics Contamination

The presence of antibiotics at its detection limits in various environmental matrices has recently been reported as a serious threat to the environment and human health, due to causing antibiotic resistance (Kakavandi et al. 2019). Subsequent existence of antibiotics residues in the environment matrix could affect aquatic and terrestrial organisms (Costanzo et al. 2005; Kotzerke et al. 2008; Liu et al. 2009), alter microbial/metabolic activity and community composition (Underwood et al. 2011), and lead to the formation of antibiotic resistance genes (ARGs) and antibiotic resistance bacterias (ARBs) (Kumar et al. 2019a, b; Gogoi et al. 2018; Tao et al. 2014). Even though they are found in very low concentrations, they become a real environmental problem because of high persistence and ecotoxicity that can affect algae/bacteria (Chen et al. 2017). The effects of antibiotic pollution include the development of direct toxicity to micro-flora and micro-fauna and possible risks to human health by the consumption of contaminated non-target fauna (Rigos et al. 2004). Antibiotic contaminants present in the environmental matrices have a severe effect on aquaculture, the ecology, food chain, flora and fauna, and soil sediments. Hence, the removal of antibiotics contaminant is most important. The description of various removal techniques is given in the following section.

13.4 Removal Techniques

The techniques used to eliminate unwanted constituents (antibiotics) from water are known as removal techniques. There are two types of removal techniques; Ex situ (away from the contaminated site) and in situ (at the contaminated site). Detailed explanation is given in the following subsections. Table 13.1 shows the different removal techniques for different antibiotics contamination and corresponding removal efficiency.

13.4.1 Ex Situ Removal Techniques

A process in which contaminants are transported to the treatment plant to treat is known as Ex situ treatment processes. The overview of Ex situ treatment processes is as follows.

13.4.1.1 Conventional Treatment Processes

The application of filtration, coagulation, flocculation, sedimentation, and biological (activated sludge process, trickling filters) are often found in conventional treatment plants (Dong et al. 2016; Mutiyar and Mittal 2013). Filtration is the process in which sediments and suspended particles are removed by allowing the effluent passes through a granular bed layer which is made of non-cohesive earth material (fine/coarse sand), charcoal, and granular AC (activated carbon). Some of the particles can be retained in the granular bed due to the interstitial strain, but finer molecules must be brought to the surface where mechanism like electrostatic attraction, adsorption/absorption, ion exchange, etc., so that they retained on the surface of media.

In clariflocculator (coagulation/flocculation/sedimentation) treatment unit, coagulation is employed to increase the rate of settlement, precipitation, and agglomeration of colloids using chemicals reagents and subsequent settle down into the sedimentation tank. The commonly used coagulants are aluminum sulfate (alum), copper sulfate, ferric chloride, and sometimes polymers. The disadvantage of this technique is it requires subsequent treatment to remove the product of coagulation from the effluents. Biotic treatment like ASP is extensively used especially in factory liquid waste treatments. The biotic/biological process includes the degradation of the organic compound in the ASP tank, by using aerobic or anaerobic microorganism and by monitoring temperature and oxygen demand (COD) regularly. The immense initial concentration or high toxic compounds affect the efficiency biological treatment (ASP) because they are recalcitrant and toxic to the microorganism which is available in the tank (Britto et al. 2008). However, ASP can handle high hydraulic loading rates efficiently (Eckenfelder 2000), but not capable to handle a high concentration of antibiotics (Leung et al. 2012).

All over the world in the last couple of decades, various traditional wastewater treatment processes are tested for antibiotics removal from aqueous matrices. Wastewater/effluent having low initial concentration, as well as low toxic substances than these methods, work efficiently and effectively, because they are less harmful to the microorganism in the biological system. The WWTPs are located in Delhi

Table 13.1 Different removal techniques for antibiotics contaminants and corresponding removal efficiency

Removal techniques	Types of antibiotic	Removal (concentration) (%)	Remarks	References
Membrane techniques	Tetracycline	98.9	Hybrid carbon membrane (graphene oxide and activated carbon) 15 μm thickness is used This hybrid membrane is more effective than AC, GO, and carbon nanotube. Adsorption capacity is 449 mg/g because of the high surface area 414 m^2/g. Require lesser time and provide better efficiency	Liu et al. (2017)
	Sulfamethoxazole Trimethoprim Norfloxacin Roxithromycin	>99	Forward osmosis with the function of electrochemical oxidation (FOwEO) is established and used for the removal of antibiotics contaminants. The efficiency of FOwEO is far greater than forwarding reverse osmosis. No significant effect of mass flux rate on efficiency. The orientation of the membrane affects the removal. Rejection is decreased with an increasing concentration of draw solution	Liu et al. (2015)
	Sulfamethoxazole Flumequine	>70	Nanofiltration membrane (NFM) is better then ultrafiltration membrane (UFM). Adsorption is the main mechanism in UF. Increase in operating pressure rate of permeation is increased but the fouling increases. UF is more sensitive to fouling rather than NF. External fouling is predominat in NFM. pH effect negatively on UFM and slightly positive on NFM.	Acero et al. (2010)
Ozonation	Spectinomycin	100	Second-order reaction rates increased with increasing pH. Fast degradation around neutral pH. In 10 s, total degradation was achieved	Qiang et al. (2004)
	Amoxicillin	90	90% removal after 4 min and 18% mineralization after 20 min. Low degree of mineralization, even for long treatment times	Andreozzi et al. (2005)
	Ceftriaxone	95	COD removal was increased with increasing pH from 3 to 7. The addition of H_2O_2 had no advantage for COD removal kinetics over the direct ozonation Biodegradability represented in terms of BOD_5/COD was increased. After 60 min, 95% of degradation was achieved (45% TOC removal)	Balcıoğlu and Ötker (2003)
	Ampicillin Azithromycin Erythromycin Clarithromycin Ofloxacin Sulfamethoxazole Trimethoprim Tetracycline	>99	The efficiency of this process is highly dependent on ozone dose and hydraulic retention time. Inactivation of *E-coli* takes place at HRT = 40 min and dose = $0.25 gDOC^{-1}$. Maximum efficiency was achieved at HRT = 40 and 60 min. HRT of 40 min is optimum. Increase in oxidants concentration improves the efficiency of the treatment process	Iakovides et al. (2019)

(continued)

Table 13.1 (continued)

Removal techniques	Types of antibiotic	Removal (concentration) (%)	Remarks	References
	Sulfonamides Tetracyclines Microlide	85–100	Antibiotics are efficiently eliminated by ozone in the effluent of SBR. Dissolved organic matters also influence on the efficiency of treatment. HRT and sludge retention time is 10 and 45 days resp. The dose of ozone required high to treat the SBR effluents. At ozone dose, 13.3 mg/L/min with COD concentration of 190 mg/L, 96% removal takes place in 5 min	Ben et al. (2012)
	Amoxicillin Doxycycline Ciprofloxacin Sulfadiazine	95	Achieve the highest removal at 75 mg/L ozone dose. Degradation products found more water soluble and have acidic nature. With the increase in ozone dose removal is increasing up to a certain dose, after that saturation is achieved. Antibiotics removal from milk is efficient with the faster application of ozone	Alsager et al. (2018)
	Sulfonamides	17–92	Integration of ozonation and biological activated carbon (BAC) filtration. Ozonation efficiently removed the sulfonamides but BAC increasing the sulfonamides resistance bacteria. BAC alone achieve removal efficiency was 83–98% with the initial concentration of 50 ng/L. Optimum contact time is 20 min and pH range was 7.1–7.9	Li et al. (2018)
	Trimethoprim Norfloxacin Erythromycin Ofloxacin Ciprofloxacin Sulfamethoxazole Tetracycline	95–99 88–96 89–91 84–92 76–90 65–67 100	Combined the sponge membrane bioreactor and ozonation for the removal of hospital effluent. The main mechanism of removal is direct ozonation and reaction with hydroxyl radicals. Sponge MBR removes the total nitrogen as nitrification and denitrification take place simultaneously	Tim Kim et al. (2019)
Photo-Fenton	Amoxicillin	–	Amoxicillin degradation was not influenced by the type of irradiation or by the matrix. Its degradation was enhanced in the presence of ferrioxalate. The increase of the H_2O_2 concentration improved the efficiency of oxidation. After 10 min of irradiation, total degradation was achieved	Trovó et al. (2008)
	Tetracycline	−100	Under solar irradiation, it is a very efficient treatment for degradation of tetracycline within a 1 min of exposer using ferrioxalate. Photo-fenton treatment required lesser time to degrade tetracycline as compared to heterogeneous photocatalysis. Degradation of organic compound is directly related to the presence of iron concentration. Total degradation using $Fe(NO_3)$ in 1–1.5 min and using ferrioxalate it is in 8 min. Under black-light irradiation, tetracycline degradation favors in the presence of $Fe(NO_3)_3$, achieved total degradation in 1 min	Bautitz et al. (2006)

(continued)

Table 13.1 (continued)

Removal techniques	Types of antibiotic	Removal (concentration) (%)	Remarks	References
Photocatalysis	Tetracycline	41.9–90.6	70% TiO_2 and 30% calcite catalyst is the optimal combination for maximum removal. More than 90% removal takes place in the presence of UV irradiation and 82% in solar irradiation. Surface adsorption and formation of hydroxyl radical are the two factors that influence the degradation efficiency. Tetracycline species dominate in the 6–7.5 pH range. Efficiency decreases as initial concentration increases. 1.5 g/L of catalyst, 50 mg/L of tetracycline, and pH of 7 is the best combination for maximum removal	Belhouchet et al. (2019)
	Tetracycline	82.92	Magnetic graphene oxide cerium-doped TiO2 hybrid catalyst is used to enhance the degradation of tetracycline under visible light irradiation. It has a good adsorption capacity, high visible light photoactive, and magnetic separability as novel photocatalyst. The adsorption capacity of graphene oxide is more than bare Ce–TiO_2. Magnetic graphene oxide (MGO) enhances adsorption tetracycline antibiotics. MGO-Ce–TiO_2 works efficiently than Ce-doped TiO_2 under the same condition. For maximum removal, the optimum mass ratio of Ce-doped TiO_2/MGO is 10%	Cao et al. (2016)
	Amoxicillin	100	TiO_2 (Degussa P25) is the most efficient catalyst among all catalyst. Degradation amoxicillin increases with the increase in doses of catalyst up to 100–250 mg/L. The optimum dose of catalyst (Degussa P25) found to be 250 mg/L. This photocatalyst reaction is well described by first-order Langmuir Hinshelwood (L-H) kinetic model. Transformation of amoxicillin to by-product does accelerate in acidic condition. Catalyst Degussa P25 TiO_2 and UV-A irradiation is an efficient technique for the degradation of amoxicillin in water. Rate of degradation depends upon the ratio of substrate to oxidizing species	Dimitrakopoulou et al. (2012)
	Amoxicillin Ampicillin Cloxacillin	100 100 100	ZnO is a very efficient catalyst for the degradation of antibiotics. The optimal condition for complete degradation of antibiotics is a dose of ZnO is 0.5 g/L, irradiation time is 180 min, and pH is 11. A photocatalytic reaction followed pseudo-first-order kinetics. Low biodegradability is due to antibiotics by-products and dissolved zinc. Degradation is increasing with pH and ZnO dose	Elmolla et al. (2010a, b)

(continued)

Table 13.1 (continued)

Removal techniques	Types of antibiotic	Removal (concentration) (%)	Remarks	References
	Tetracycline	94.91	Visible-light-driven catalyst mostly used in the treatment of wastewater. Catalyst AgI (20% by wt.)/BiVO4 is a promising catalyst for the degradation of antibiotics. Heterostructure photocatalyst was synthesized by in situ precipitation method. AgI loading remarkably promoted the photocatalytic activity of BiVO4 during the photo-oxidation reaction. This photocatalysis reaction followed pseudo-first-order kinetics model. Increase in the initial concentration of tetracyclin leads to a decrease in efficiency and vice versa	Chen et al. (2016a, b, c)
	Oxolinic acid	76	The photocatalytic process is able to transform the target antibiotics into more oxidized by-products without antimicrobial activity and with low toxicity. The catalyst used is TiO2 (Degussa P-25). Increase in catalyst load improved the removal efficiency. Maximum removal takes place at pH (7.5) and 1 g/L of TiO2 dose and follows Langmuir isotherm model	Giraldo et al. (2010)
	Tetracycline	93	Magnetic activated carbon with TiO_2 showed good performance when coupling with ultraviolet light and ultrasonic light. Used catalyst has better performance due to the high reusability, recovery, good catalytic property, and high adsorption capacity. The optimal condition for maximum removal is pH (6), catalyst dose (0.4 g/L), and reaction time (180 min). Antibiotic concentration up to 10–20 mg/L degraded completely in 180 min. coupling of TiO_2 and magnetically activated carbon increases their photocatalytic ability over visible light	Kakavandi et al. (2019)
	Sulfachlorpyridazine	100	Nitrogen-doped reduces graphene oxide (N-rGO) metal-free as a catalyst is a use. Peroxymonosulfate (PMS) had excellent oxidation efficiency toward sulfonamide antibiotics through direct reaction. The results show that the PMS and (N-rGO +PMS) systems are applicable to remediate aquatic environment efficiently. Fresh catalyst takes 10 min for 100% removal of antibiotics	Kang et al. (2018)
	Erythromycin Doxycycline Clindamycin Penicillin G Ciprofloxacin Trimethoprim	100 80–85 90–95 65–70 30–35 100	At 254 nm UV, Clindamycin is not susceptible to direct photolysis and in pure water up to 2000 mJ/sqcm is not showing measurable degradation. At low- or medium-pressure UV lamp with or without hydrogen peroxide, degradation of antibiotics is expected to be better. Degradation under polychromatic UV irradiation in the absence of H_2O_2 is likely due to hydroxyl radical formation via nitrate photolysis. Doxycycline, penicillin-G, and ciprofloxacin are degraded directly by photolysis at 254 nm low-pressure UV lamp. Active transformation of the product was observed with irradiation from the low-pressure lamp, in the presence of H_2O_2 and not observed in pure water	(Keen and Linden 2013)

(continued)

Table 13.1 (continued)

Removal techniques	Types of antibiotic	Removal (concentration) (%)	Remarks	References
	Ampicillin	87	The test confirms that AMP is more stable in river water rather than Milli-Q water. Prescription of antibiotic is directly related to the occurrence of antibiotic in wastewater influent The concentration of antibiotic increases in monsoon season as compared to another season. Temperature does play a significant role in sorption and usually is inversely proportional to removal rates. A decrease in PCs was observed in the treated wastewater which may be attributed to the treatment process. Removal efficiency depends on detention time, temperature, inflow, quality of influent, and quantity of influent	Prabhasankar et al. (2016)
	Trimethoprim	44		
	Sulfamethoxazole	−99.41		
	Chloramphenicol	0		
	Erythromycin	−23.07		
	Naproxen	87		
	Ampicillin	87.83	The total production of antibiotics in India was more than 2332 Mt in 2006–2007, with a growth rate of 10%. Yamuna river water quality is so bad that photosynthesis is absent in a certain stretch. Removal efficiencies for antibiotics are varying with plants, their operations, geographic locations, and environmental factors. Conventional treatment does not remove all of the influent concentration with activated sludge process as the treatment process. Contaminated river water could possibly have harmful ecotoxicological effects on aquatic organisms. A significant gap is existing in understanding the effect of antibiotic interaction with the aquatic environment	Mutiyar and Mittal (2013)
	Ciprofloxacin	60.11		
	Gatifloxacin	55.47		
	Sparfloxacin	99.37		
	Cefuroxime	93.56		
	Chlortetracycline	70–95	ASP is not capable to remove all targeted antibiotics. The dominant mechanism in ASP which is responsible for the removal of antibiotics is adsorption and biodegradation. It is an efficient process than stabilizing pond and micropower biofilm method. Due to desorption, there may be chance to increase some antibiotics concentration in ASP treatment. ASP performed well in summer as well as in winter	Dong et al. (2016)
	Sulfamethoxazole	40–80		
	Roxithromycin	98–100		
	Ofloxacin	95–100		
	Ofloxacin	3–5	Convention treatment like ASP is not capable to handle higher concentration of antibiotic. Primary sedimentation tank efficiency is limited to 0–29%. Risk assessment indicated that antibiotic concentration found in the environment is susceptible to algae	Leung et al. (2012)
	Erythromycin	5–20		
	Cephalexin	70–80		

(continued)

Table 13.1 (continued)

Removal techniques	Types of antibiotic	Removal (concentration) (%)	Remarks	References
In situ removal techniques	Azithromycin Ciprofloxacin Clarithromycin Clindamycin Doxycycline Erythromycin Norfloxacin Oxytetracycline Sulfamethoxazole Tetracycline Trimethoprim Vancomycin	100 100 59 74 100 96 100 97 77 99 61	Constructed wetland serves an efficient and economical option for the removal of antibiotic as compared to the conventional wastewater treatment plant. Quinolones and tetracycline are not found at low concentration, and it may be possible due to adsorption to sediments. Antibiotics treatment using constructed wetland had no significant effect on bacterial diversity and evenness. The average removal efficiency does not fall below 59%. Antibiotic resistance genes found frequently in wastewater at varying concentration. Consequently, there is a need to explore alternative efficient and low-cost technologies that complement conventional methods of treatment	Berglund et al. (2014)
	Fluoroquinolones Lincosamides Sulfacetamide Sulfadiazine Sulfamethazine Trimethoprim Sulfamonomethoxine	100 78 23.8 10.3 95.1 100 100	Integrated constructed wetlands (ICWs) are efficient treatment technology for antibiotics contamination in rural areas. Removal efficiency is varied from 10 to 100%. The influent antibiotics loading rate is found to be 3479 and 199 μg/day for effluent, resp. Anaerobic degradation is a predominant mechanism for biodegradation of antibiotics. ICWs consist of floating microphytes, emerging microphytes, and stabilization pond	Chen et al. (2014)
	Erythromycin-H_2O Lincomycin Monensin Ofloxacin Sulfamerazine Sulfamethazine Novobiocin	17.9–98.5	Three hydraulic loading rates (HLRs) and four substrates (Oyster shell, zeolite, medical stone, and ceramic) are used to optimize the operation of wetlands. 20 cm/day HLR and zeolite are best for the removal of antibiotics. Biodegradation and adsorption are the dominant mechanisms in the removal process. Daily removal of COD, TN, and ammonia nitrogen is increased with an increase in HLR in zeolite CWLs	Chen et al. (2016a, b, c)
	Chlortetracycline Sulfamethoxazole Roxithromycin Ofloxacin	55–85 40–80 80–90 60–100	Constructed wetland work is efficient in summer as compared to winter. Due to desorption, there may be a chance to increase the concentration of antibiotics. Degradation and plant uptakes might be a removal pathway. Hydraulic retention time and temperature are the key factors which affect the removal process	Dong et al. (2016)

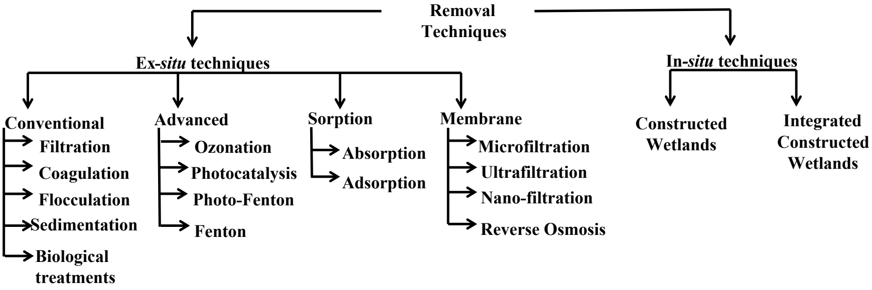

Fig. 13.2 Different antibiotics contaminants removal techniques

(India), in which treatment technique employed is ASP to remove contaminants from wastewater, and they have found that antibiotics removal efficiency is varied from 99.37% (Sparfloxacin) to 55.47% (Gatifloxacin), and it is not obvious in all the cases (Mutiyar and Mittal 2013). Similarly, the WWTPs are located in China which also employed ASP for removal and they have reported that the removal efficiency varies from 70 to 80% (Cephalexin) to 3–5% (Ofloxacin) (Leung et al. 2012). Sometimes there is a possibility to increase in the concentration of antibiotics, for example, WWTP's removal efficiency varies from −23.07% (erythromycin, influent concentration (CI) = 26 ng/L and effluent concentration (CF) = 32 ng/L) to 87% (ampicillin) (Prabhasankar et al. 2016). Complete removal does not occur always from conventional treatment plants.

Several researchers studied the performance of some physicochemical methods and found that their maximum efficiency is 30% in case of antibiotics contaminated wastewater. Physicochemical methods: In which physical as well as chemical processes are used to remove the pollutants, e.g., clarification. The removal efficiency of these treatments depends on many factors; 1) effluent: pH, temperature; 2) antibiotics: physicochemical properties, initial concentration, types; 3) Plant factors: SRT, HRT, this dependency makes the removal efficiency is a variable. Hence, this is the main disadvantage of the conventional techniques (Cizmas et al. 2015; Gao et al. 2012). Due to low efficiencies and disadvantages (as mention above) of these methodologies, these techniques are not used for antibiotic-contaminated water.

13.4.1.2 Advanced Treatment Processes

The advanced treatment to treat the antibiotics contaminated water is based on the oxidation process. Addition of oxygen or removal of hydrogen is known as oxidation. The wastewater influent brought to the WWTPs contains different contamination, and hence, it has heterogeneous nature, means influent carrying more than one pollutant, i.e., antibiotics, biological pathogens, chemical constitutes, etc. It is very difficult to treat such WW using conventional treatment processes, so the alternative for this is the advanced oxidation treatment processes (AOTPs). These AOTPs are based upon the producing of free hydroxyl radicals (OH^-), these radicals are highly reactive and having the potential of oxidants is 2.8 V, which is greater than ordinary or classical oxidants, made them highly effective and efficient to carry out the treatment of highly contaminated WW through an oxidation process (Hernandez et al. 2002). There are some oxidizing agents often used to produce hydroxyl radicals like ozone (O_3), hydrogen peroxide (H_2O_2) combined with semiconductor catalysts or UV radiation or metal catalysts. In this process, it is expected that pollutants get oxidized and reduced into less harmful products or converted into carbon dioxide (CO_2) and water (H_2O). It is also possible that sometimes, by-products produced after the oxidation is harmful than the parental compounds. Different AOTPs are as follows.

Ozonation

Ozone is known as effective or efficient oxidant because it has high oxidant potential ($E^0 = 2.07$ V) (Iakovides et al. 2019). Ozone has high redox potential than classical oxidants like hydrogen peroxides (H_2O_2), chlorine dioxides (ClO_2), Cl_2 gas, and hypochlorites. It has the ability to react directly or indirectly with contaminants. The degradation mechanism primarily has direct oxidation rather than indirect oxidation via OH (Ben et al. 2011, 2012). To carry out the direct oxidation using O_3, it is necessary to have a $C = C$ (carbon–carbon) or aromatic bonds with the N (nitrogen), O (oxygen), or S (molecules of sulfurs) because it reacts only and only with the nucleophilic molecules. If this condition is not fulfilled then the degradation of O_3 in WW to generate an OH^- (Hydroxyl radicals) takes place through the bellow mechanism (Alsager et al. 2018).

The reaction is as follows:

$$O_3 + OH^- \rightarrow O_2 + HO_2^- \tag{13.1}$$

$$O_3 + HO_2^- \rightarrow HO_2 + O_3^- \tag{13.2}$$

$$HO_2 \rightarrow H^+ + O_2 \tag{13.3}$$

$$O_2^- + O_3 \rightarrow O_2 + O_3^- \tag{13.4}$$

$$O_3^- + H^+ \rightarrow HO_3 \tag{13.5}$$

$$HO_3 \rightarrow OH + O_2 \tag{13.6}$$

As per reaction 13.1 and 13.2, these degradation reactions are pH sensitive, and hence, we can accelerate the initiation of degradation by improving the pH value.

$$OH + O_3 \rightarrow HO_2 + O_2 \tag{13.7}$$

Rate of above reaction (13.7) is fast and it helps to minimize the oxidation capacity of the matrix, as it required low DOC and alkalinity, and improves the efficiency of the treatment process.

AOTPs are very effective and efficient when the variability in inflow and composition of WW is high. In normal circumstances, these processes may be uneconomical because the cost of treatment units, maintenance, and energy requirement is high. There is limitation related to the mass transformation in the oxidation process with O_3, and hence, it is also one of the major disadvantages. This process works on the principle of phase transformation and requires to transform ozone molecules from the gaseous phase to the liquid phase so that it will attack on unwanted constituents in the WW. In most of the studies, it is reported that consumption of ozone is very high but the transformation of mass is limiting and reduces the efficiency of the process and increases the cost. Performance of this process is very sensitive toward some factors like the concentration of solids, the presence of microorganism/pathogens, CO_3 (Carbonate), HCO_3 (bicarbonate), HRT, ozone dose (Iakovides et al. 2019), pH, and temperature (Von Gunten 2003a, b).

Iakovides et al. 2019 work on the removal of mixtures of antibiotics (Ampicillin, azithromycin, clarithromycin, erythromycin, ofloxacin, sulfamethoxazole, tetracycline, and trimethoprim) using ozonation and suggested that the optimization in the treatment is necessary because excess ozone creates problems for the living organism in treated effluents. The ozonation is highly dependent on the ozone dose and HRT. They have used qualitative parameter like COD, BOD, TSS and considering the initial concentration of antibiotics is 100 μg per liters and pH range of 7.2 and 7.8, HRT varies from 10 to 60 min, and ozone dose varies from 0.125 to 0.75 gO_3 $gDOC^{-1}$, respectively. Increase with ozone dose and HRT in between 10 and 20 minute leads to the increase in rate of removal of all the parental antibiotics. The optimum HRT is 40 min, where the maximum removal at a minimum dose of ozone could be possible at microgram per liters concentration level. Increase in oxidant level leads to an increase in the rate of degradation of contamination. Sometimes it is also possible that using a sequencing batch reactor (SBR) with ozone for the decontamination of WW from the veterinary antibiotics has good removal efficiency (tetracyclines, macrolide, and sulfonamides) (Ben et al. 2012).

Ozone with H_2O_2 has better efficiency of antibiotics removal rather than ozone alone (Balcıoğlu and Ötker 2003). Antibiotics removal efficiency is about 98–100% at an ozone dose of 1.38 mg/L in pure water but at a dose of 37.3 mg/L, efficiency is dropped at 85–100% in the SBR treated effluents. The concentration of COD, DOM, and SS has a strong influence on the removal efficiency of antibiotics. To detect the concentration of the antibiotic in the milk, an instrument called high-performance liquid chromatography (HPLC) is used. Ozonation with properly optimized parameter is a promising technology for the removal of antibiotics contamination (Iakovides et al. 2019). Nowadays, the ozonation couple with some classical or advanced treatment processes is attracting researcher. The integration of ozonation with biological activated carbon filtration (Li et al. 2018) and combined sponge membrane bioreactor with ozonation to remove the different antibiotics contamination from water have better efficiency than conventional processes (Tim Kim et al. 2019).

Photocatalysis

Recently, photocatalysis techniques attracted researchers and scientific community more because of their advantages over different techniques available, and the advantages like economical and eco-friendly are known to be sustainable technology having negligible waste (Das 2014). Photocatalysis includes the elimination of contaminants from WW which have resistance to degradation and chemically stable. In SP, to carry out the degradation (Chen et al. 2016a) using oxidative mechanism requires three components, catalyst with photo-sensitive (e.g., TiO_2 or inorganic semiconductors), source of photon energy, and an efficient oxidizing agent (Ben et al. 2009; Belhouchet et al. 2019). The fundamental principle of this process includes the stimulating of semiconductor (generally used TiO_2 because of its immense stability, efficient performance, and cost-effectiveness easily available) by artificially means. Characterization of semiconductor is done by their valence and bandgap, and conduction bands, etc. The mechanism involves in this process are as follows; either TiO_2 (semiconductor oxide) get a chance to adsorbed contaminants causing quick oxidation or firstly change to adsorbed H_2O molecules producing OH. (Hydroxyl radicals).

$$\text{Photocatalyst (e.g. TiO}_2) \rightarrow \text{TiO}_2\left(\text{e}^- + \text{h}^+\right) \tag{13.8}$$

$$\text{h}^+ + \text{contaminaents} \rightarrow \text{contaminaents} \tag{13.9}$$

$$\text{h}^+ + \text{OH} \rightarrow \text{OH} \tag{13.10}$$

Reaction (13.8) shows the loss of electron and it means it is direct oxidation or photocatalysis. Reaction (13.9) shows indirect oxidation. The mechanism is shown in reaction (13.9) and is as fast as reaction (13.8). All the reported studies show that for the photo-mineralization, the presence of H_2O and molecular oxygen is necessary. The holes shown in Eq. (13.8) have huge oxidant potential to produce OH (hydroxyl radicals) from the H_2O molecules/OH^- adsorbed over the surface of semiconductors.

$$\text{TiO}_2\left(\text{h}^+\right) + \text{H}_2\text{O} \rightarrow \text{TiO}_2 + \text{OH} + \text{H}^+ \tag{13.11}$$

$$\text{TiO}_2\left(\text{h}^+\right) + \text{HO}^- \rightarrow \text{TiO}_2 + \text{OH} \tag{13.12}$$

The generated e^- are able to decrease the dissolved oxygen and producing the O_2^{-} (superoxide radical ion), which afterword converted into H_2O_2 (refer reaction 13.13–13.15).

$$\text{TiO}_2\left(\text{e}^-\right) + \text{O}_2 \rightarrow \text{TiO}_2 + \text{O}_2^- \tag{13.13}$$

$$\text{O}_2^- + \text{H}_2\text{O} \rightarrow \text{HO}_2 + \text{HO}^- \tag{13.14}$$

$$2HO_2 \rightarrow H_2O_2 + O_2 \tag{13.15}$$

H_2O_2 also acts like (e^-) receptor producing additional OH radicals as follows;

$$TiO_2\left(e^-\right) + H_2O_2 \rightarrow TiO_2 + HO^- + HO \tag{13.16}$$

The overall process of photocatalysis is divided into few steps: (1) transfer of reactants; fluid to surface, (2) sorption of reactants, (3) reaction in between adsorbed phase, (4) desorption of final products, and (5) finally the elimination of products.

The reported studies show that the decomposition of contamination not only occurs due to hydroxyl radicals but also occurs via other species of radicals which derive from the oxygen itself. The efficiency of the entire removal mechanism is influenced by some parameters such as pH, temperature, types of catalyst and its dose, the intensity of radiation and composition of WW. The major advantage of this process is the sunlight also used as the irradiation source. The industries application of this technology has been extensively reviewing because it is hard to pass radiation through the liquid waste which carries fine colloidal particle in suspension and difficult to eliminate the used catalyst after treatment. The separation of catalyst at the end of treatment is time-consuming and very costly. For resolving this limitation, researcher is performing the studies on catalyst immobilization. Variety of material is used to support the TiO_2 and the ideal supportive material has properties like strong adhesion toward the catalyst, sufficiently high surface area, and has good sorption leaning toward the pollutants and bonding process does not affect the performance of catalyst (Shan et al. 2010).

Most of the studies reported that this technique was the promising technology for the treatment of antibiotics contaminated WW. The application of this technique is to remove the residue of tetracycline antibiotics and found that the removal efficiency at 50 mg/L of initial concentration was 41.9–90.6% (Belhouchet et al. 2019). Removal of tetracycline is by employing SP techniques and they have used the hybrid catalyst which made up of magnetic graphene oxide cerium-doped TiO_2 so that the decomposition of contamination is accelerated (Cao et al. 2016). Performance of SP techniques is for the removal of amoxicillin antibiotics and they have used different dosed of TiO_2 catalyst and reported that 250 mg/L dose is the optimum dose for maximum removal (Dimitrakopoulou et al. 2012). The tetracycline elimination was also trying to understand several researchers (Chen et al. 2016a, b, c; Kakavandi et al. 2019). This is the promising technology for the removal of antibiotics contamination on the laboratory-scale laboratory model from several decades, but this technique is not used in the field for the WW treatment (Homem and Santos 2011) because of its certain limitations.

13.4.1.3 Sorption Techniques

Sorption (adsorption/absorption) processes are widely used to remove the unwanted constitute from liquid waste generated from community/industries. Basically, sorption means attraction of one molecule in the liquid phase on another solid molecule in the same phase by the chemical or physical forces. The adsorption process is the surface phenomenon, whereas absorption is an internal phenomenon. The term adsorption is generally used to describe the liability of the molecules in the liquid phase have to adhere to a solid surface. The force field creates a region near the solid surface either by a physical or chemical process, whose potential energy is low, resulting in the molecular density increase near the solid surface.

In adsorption phenomenon solute is transported in the bulk and adsorbate movement by the stagnant liquid film surrounding the adsorbent then film diffusion takes place and adsorbate transport along with the film then pores diffusion take place and then adsorbate diffusion through the porous structure to the active sites on the surface (molecular diffusion in the pore and/or in the adsorbent surface). Finally, adsorption takes place when there is an interaction between adsorbate and porous structure depending on the nature of the forces involved in the process; it can be divided into chemical adsorption or physical adsorption (Alsager et al. 2018; Homem and Santos 2011). The forces involved in this phenomenon is relatively week, involving week Van der Waals interactions forces or loose chemical forces. In chemical adsorption, the electron transfer and chemical bonds formation between adsorbate and absorbent occur; these interactions are strong and more specific rather than those existing in physical adsorption (Ingerslev and Halling-Sørensen 2000).

There are several mechanisms that are involved in the removal of the antibiotic from the wastewater using adsorbents, including ion exchange, pore filling and π–π electron interaction (Hu et al. 2019), the electrostatic mechanism (de Oliveira Carvalho et al. 2019), surface complexation and hydrogen bonding, etc., and they may occur individually or simultaneously. The removal by ion exchange mechanism depends upon the size of pollutants and SFG on the biochar used (Zhang et al. 2011; Premarathna et al. 2019). The pore structure of biochar facilitates the sorption of contaminants through the pore-filling mechanism (Ahmad et al. 2013).

The adsorption efficiency is dependent not only on adsorbent properties but also on phase or medium characteristics in which the process is happening. Adsorbent properties are namely surface area, porosity and pore diameter (Estevinho et al. 2007) and phase (liquid phase) characteristics such as pH, temperature, type of contamination and their concentration, and also the presence of different organic matters. pH has a major influence on the removal process because it directly affects the chemical properties of adsorbent and the surface activity of biochar or adsorbent. Sorption reaction is an exothermic reaction and hence it is dependent on temperature, with an increase in temperature adsorption rate is increases. It is important to notice that the process efficiency is dependent not only on the trace compounds of concern but also on dissolved naturally occurring organic matter present in any liquid. A major effect of the organic matter on the removal efficiency is its direct competition to the targeted molecules for the available adsorption surface/sites. Nature of the adsorbent, i.e., physicochemical, is a major influence on the rate of adsorption rate and its capacity.

Some of these adsorbents require a pre-activation treatment and it may be chemical or thermal activation in order to increase their surface areas and consequently, the adsorption efficiency, and to improve the presence SFG. The absence of SFG leads to a decrease in the adsorption process because the rate of chemical interaction is dependent on the presence of SFG. Chemical interaction between adsorbent and adsorbent is the main mechanism in adsorption processes. Hence, pre-activation treatment is required to enhance the availability of SFG so that it help to increase the chemical interactions, and thus the capacity of adsorption increases by increasing the specific SFG, and sometimes it may lead to the negative influence on the process depending on the SFG composition. The existence of anions/cations on the adsorbent can enhance the capacity of ion exchange, as this is the most influencing mechanism in the process of heavy metal contaminants removal.

The widely used adsorbents are granular ACs, but their high cost and difficult to synthesize are the major disadvantages. Therefore, the interest in finding alternative adsorbents which can replace the AC is grown up, with the purpose of finding new low-cost adsorbents, easy to generate or as by-products or waste materials from industrial or agricultural productions. The low-cost adsorbent produced from agricultural waste and industrial waste, till now used in the decontamination of antibiotic-contaminated water, is activated carbon produced from agricultural waste. Different adsorbent materials and corresponding removal efficiencies are shown in Table 13.2. The literature proves that the sorption techniques for the removal of antibiotics are promising and economical technology, as they used various waste materials to produce low-cost adsorbent. This process is able to treat low as well as high concentration contaminated liquid waste. However, this process is transferring the contaminants from the liquid phase to the solid phase. The solid/sludge that is produced from this process is easily treated by incineration. It is found from the previously published research that there is a need to check the feasibility of the developed biochar/treatment process and to have an emphasis on the pilot-scale model rather than the laboratory experiment studies.

13.4.1.4 Membrane Techniques

These techniques come under the physical treatment process. Membrane techniques are extensively used to treat contaminated wastewater. These techniques are a diffusion process applied where unwanted molecules and ions are removed from liquid waste generated from different components. In these processes, water is passed through the semi-permeable membrane with the help of mechanical forces (pressure is applied) so that unwanted substances retain over the surface and effluent must be contamination free. This technique does not degrade the contaminant just retained over the surface or just transference of new phase where the concentration of this contaminant is more than the initial concentration. Size of the membrane varies from

Table 13.2 Different adsorbent used to removed different antibiotics and corresponding removal efficiency

Antibiotic	Adsorbent	Efficiency (%)	References
Ciprofloxacin	Polysaccharide-based sodium alginate/κ-carrageenan double-network gel beads	55–60	Li et al. (2019)
	Activated carbon produced from Jerivá	93.43	de Oliveira Carvalho et al. (2019)
	ACs from *Albizia lebbeck* seed pods by KOH chemical activation	96.12	Ahmed and Theydan (2014)
	montmorillonite, rectorite, and illite	95	Wang et al. (2011)
	Nano-hydroxyapatite	47.3	Chen et al. (2015)
	Modified coal fly ash		Zhang et al. (2011)
	Nano-hydroxyapatite $[Ca_{10}(PO_4)_6(OH)_2]$	47.3	Chen et al. (2015)
	Hazelnut shell activated carbon	92.67	Balarak et al. (2016)
Norfloxacin	ACs from *Albizia lebbeck* seed pods by KOH chemical activation	98.13	Ahmed and Theydan (2014)
	Trapa natans husk-activated carbon	90.7	Xie et al. (2011)
	Nano-hydroxyapatite	51.6	Chen et al. (2015)
	Aquatic plant residue Trapa natans husk Used H3PO4 activation method.	90.7	Xie et al. (2011)
	Nano-hydroxyapatite [Ca10(PO4)6(OH)2]	51.6	Chen et al. (2015)
Penicillin G	Dried Rhizopus arrhizus	78.3	Aksu and Tunç (2005)
	Dried activated sludge	61.1	
	Activated carbon	64.4	
	Dried duckweed (*Lemna minor*)	94.6	Balarak et al. (2015)
	Decaffeinated tea waste	39.3	Gharbani et al. (2015)
	Activated carbon nanoparticle from vine wood	38.98–81.26	Pouretedal and Sadegh (2014)
Tetracycline	Graphene oxide	71.4	Gao et al. (2012)

(continued)

Table 13.2 (continued)

Antibiotic	Adsorbent	Efficiency (%)	References
	NaOH-activated carbon prepared from macadamia nut shells 3 NaOH: 1 CHAR	100 pH = 3 80 pH = 4 70 pH > 5	Martins et al. (2015)
	Ferric-activated sludge-based adsorbent from biological sludge	– NA–	Yang et al. (2016)
	Multi-walled carbon nanotube modified MIL-53(Fe)	– NA–	Xiong et al. (2018)
	Biochar derived from Alfalfa hays and activated by NaOH	– NA–	Jang et al. (2018a, b)
	Iron and zinc-doped sawdust biochar	– NA–	Zhou et al. (2017)
	H_3PO_4 modified biochar derived from rice straw and swine manure	91.7	Chen et al. (2018)
	Ferric-activated sludge-based adsorbent	– NA–	Yang et al. (2016)
	Pinus taeda-derived activated biochar	– NA–	Jang et al. (2018a, b)
	Waste expanded polystyrene	– NA–	Hu et al. (2019)
	Magnetic nanocomposite (chitosan, diphenylurea, formaldehyde, and magnetic nanoparticle $MnFe_2O_4$)	– NA–	Ahamad et al. (2019)
	Activated carbon nanoparticle from vine wood	57.69–88.17	Pouretedal and Sadegh (2014)
Sulfadiazine	Expanded graphit	80	Zhang et al. (2017)
Enrofloxacin	Natural zeolite	– NA–	Ötker and Akmehmet-Balcioglu (2005)
	Clinoptilolite Natural zeolite	– NA–	Ćurković et al. (2018)
Amoxicillin	Activated carbon	94.67	Putra et al. (2009)
	Bentonite	88.01	

(continued)

Table 13.2 (continued)

Antibiotic	Adsorbent	Efficiency (%)	References
	Activated carbon nanoparticle from vine wood	26.31–60.23	Pouretedal and Sadegh (2014)
Oxytetracycline	Graphene oxide	71.4	Gao et al. (2012)
	Multi-walled carbon nanotube modified MIL-53(Fe)	– NA–	Xiong et al. (2018)
Doxycycline	Graphene oxide	71.4	Gao et al. (2012)
Chlortetracycline	Multi-walled carbon nanotube modified MIL-53(Fe)	–	Xiong et al. (2018)
Chloramphenicol	Typha orientalis via phosphoric acid activation	65.6	Li et al. (2018)
Sulfamethoxazole	Biochar from pine wood	–	Jang et al. (2018a, b)
Cephalexin	Activated carbon nanoparticle from vine wood	43.52–76.02	Pouretedal and Sadegh (2014)

0.001 to 0.02 μm. There are several membrane techniques that are used to treat the wastewater such as reverse osmosis (forward, reverse, and backward), ultrafiltration, nanofiltration, microfiltration, etc. These membrane techniques are classified based on the opening of the membrane. Membrane processes used to treat the liquidwaste generated from domestic, industrial-like food, pharmaceutical, chemical, etc. It appears to be a rational option to treat contaminated water. Membrane techniques such as reverse osmosis and nanofiltration techniques are very effective to treat the antibiotics contaminated water after wastewater treatment processes (Acero et al. 2010) but energy requirement of this technology is high and hence they are not economical.

Microfiltration is the membrane which has a pore size/diameter in 0.1 to 10 μm. It is used for the wastewater which carries large suspended particle, pathogens, large microbes, etc. MF is used before nanofiltration and reverse osmosis so that large suspended molecules removed before the effluent is reached to these processes. It has high yield but has lesser efficiency of removal. The sieving due to physical forces is the major mechanism in MF. Backwashing by air/water is used for cleaning the membrane, as pore size is more. Clogging due to mud is advantageous in the MF because it is used to retain non-targeted fine molecules. Membrane bioreactor is a very useful and promising technology in the traditional wastewater treatment plant, as MF is a principal component of this technology. The major limitations of this technique are fouling of the membrane, operating on low mass flux, energy requirement is high and the high initial cost.

Ultrafiltration is the membrane which has pore size/diameter in 0.001 to 0.2 μm. It is used for the effluent which carries the suspension of colloids having size ranges from 0.001 to 1 μm. UF is primarily used to treat wastewater (WW) generated from the paints industries, dye industries, leather industries, etc. and where the recycling of WW is prior concerned. Also used as pretreatment where NF or RO is used. Better efficiency then MF but having the same disadvantages as MF.

Nanofiltration (NF) is the membrane which has pore size/diameter in between UF and RO. It has better efficiency than UF and requires low pressure to operate as compared to RO. Mechanical sieving is the dominant mechanism in the removal of colloidal molecules, and however, chemical interaction is the dominant mechanism in the removal of metals ions. Nanofiltration membrane technique is efficient then ultrafiltration membrane in the removal of antibiotics contaminant. In UFM, adsorption is the predominant mechanism, whereas in NFM, the size of exclusion and electrostatic repulsion is dominant retention mechanism (Acero et al. 2010). pH has a negative effect on the NFM process and slightly positive on UFM. Membrane fouling, cake formation, and blocking of pores are the main problems in the UFM as well as in NFM.

Reverse osmosis is the first membrane process which extensively used to treat the contaminated water. In RO process, flow takes place against the osmotic pressure gradient and size pores in the membrane are very small due to these factors as the energy requirement of this technique is high. RO techniques are very efficient to reduce the high concentration dissolved salts but it has certain drawbacks in the removal of an organic contaminant. Effectiveness of these membrane processes depends upon the mechanical and chemical properties of membrane material like porosity, mechanical resistance, etc. In RO, mostly polymeric material for the membrane is used. This treatment does not require thermal energy but requires electrical energy for the pump so that, pump feeds inffluent. Membrane fouling or damaging is the frequent problem rising in the RO process. Sometimes RO techniques not able to retain fine chemical molecules due to this RO with carbon filters are provided. The yield of this process is very low, whereas the efficiency of removal is very high as compared to other membrane techniques. The research have been done to modify the conventional osmosis process like forward osmosis (Zheng et al. 2015), forward osmosis combined with electrochemical oxidation (Liu et al. 2015) (Table 13.3).

13.4.2 In Situ Treatment Processes

A process is used to treat contaminants at the field itself is known as in situ treatment processes. There are two types of in situ treatments that are constructed: wetlands and integrated constructed wetlands.

13.4.2.1 Constructed Wetlands

A constructed wetland (CW) is a man-made wetland constructed to treat municipal or industrial effluent (Chen et al. 2016b, c), greywater or stormwater runoff, etc. It

Table 13.3 Different types of membrane techniques

Types of filtration Different characteristics	Microfiltration	Ultrafiltration	Nanofiltration	Reverse osmosis
Membrane	Porous isotropic	Porous unisotropic	Finely porous unisotropic	Semi-permeable
Mechanism	Sorption and sieving	Dominant sorption and sieving	Electrostatic and diffusive, sorption	Diffusive
Governing equation	Darcy's	Darcy's	Fick's	Fick's
Able to remove	solid suspension	colloidal and macromolecules	Nanoparticles and ions	Nanoparticles and ions, very fine molecules
Mass flux ($L/m^2/h$)	500–100,000	100–2000	20–200	10–100
Pressure required in atm	0.5–5	1–10	7–30	20–300

may also be useful for land reclamation in the mining area or as a remediation step for naturally lost areas to develop the land and to enhance the aesthetic appearance and landscape enhancement (Knight et al. 2000; Handbook on CW by EPA 2015).

CW is the transitional areas between land and water. The boundaries between wetlands and high-grade lands or deep water are sometimes distinct sometimes not. The term "wetlands" encompasses a wide range of wet environments matrices, including bogs, swamps, wet meadows, tidal wetlands, floodplains, marshes and ribbon (riparian) wetlands along natural stream channels. Vegetation in these wetlands was dominated by Phragmites australis and Typha latifolia (Berglund et al. 2014). The hydrology of wetlands is generally provided as slow flows and shallow waters or saturated substrates so that the hydraulic retention time should be sufficient to interact with the contaminant and surface of wetlands. Most of the wetlands support dense vascular plants adjusted to saturated conditions. This dense vegetation slows down the water flow so that it will create microenvironments within the water column itself and provides suitable and sufficient attachment sites for the microbial community (Handbook on CW by EPA 2015). It can be classified into a surface flow and subsurface flow wetlands (vertical or horizontal) according to their hydrology and flow path (Chen et al. 2016b, c).

The wetlands are used traditionally for improvement of water quality, cycling of nutrients, habitat for fish- and wildlife and to treat wastewater also, in the last couple of year researcher trying to find out the wetlands efficiency to treat the antibiotics contaminated water (Dong et al. 2016; Chen et al. 2014, 2016a, b, c; Berglund et al. 2014). Recently, it has been reported that treating effluent using CWs can serve as a cost-effective and promising alternative to conventional WWTPs for removing or reducing the levels of nitrogen, phosphorous, pharmaceuticals (Antibiotics), and the biological oxygen demand (BOD) in treated water (Berglund et al. 2014). The ecological wastewater treatment (i.e., constructed wetlands) processes usually have a high surface to equivalent-inhabitant ratio, relatively low cost, simple operation, and maintenance. Sometimes they are planned and constructed to use as the secondary or tertiary treatment processes for wastewater are in rural areas of China (Dong et al. 2016). In several studies, researches reported that CWs are very effective in the reduction of antibiotics and ARGs by the optimized CWs could be achieved at relatively similar or higher rates than conventional WWTPs (Chen et al. 2016a, b, c). The finding has demonstrated that the concentration levels of most detected antibiotics in the rural domestic sewage could be efficiently reduced up to 78–100% through the wetland treatment systems (Chen et al. 2014). In CW, removal of target contaminants in treatment processes of horizontal subsurface flow can be possible by both mechanisms, i.e., sorption and biodegradation could contribute to the elimination (Chen et al. 2014) and finding the percentage contribution of both the mechanism is an open question for the researcher.

13.4.2.2 Integrated Constructed Wetlands

Integrated constructed wetlands (Conventional WWTPs with CW) have been scientifically tested and constructed for onsite treatment in a rural area for small towns and villages due to their low investment and operation costs (Shao et al. 2013). Integrated CWs consist of floating macrophytes, emerging microphytes, and stabilization pond (Chen et al. 2014). The antibiotics removal efficiency of CW is varied from 10.3% (Sulfadiazine, Chen et al. 2014) to 100% (Ciprofloxacin, Berglund et al. 2014). CWs could be a promising technology for rural wastewater in case of antibiotics contaminants (Chen et al. 2014). CWs treatment techniques for antibiotics contaminants are the complement to conventional methods of treatment but it is useful for the small locality or town (Shao et al. 2013).

13.5 Challenges

The challenges facing while monitoring the antibiotics contaminants are as follows:

- There is no standard regarding permissible limits of antibiotics concentration in the various compartment of the environment.
- There is a lack of understanding about the effects of antibiotics contaminants on the natural habitat.
- Antibiotics contaminants are not commonly monitored in the environments.
- Common peoples are not aware of the effects of antibiotics contaminant.
- Antibiotics present in very small quantity (ppt) in various aqueous matrices, hence it is very difficult to detect.

- It is very difficult to remove antibiotics from water because it is a highly polar substance.
- Conventional treatment is not able to degrade the pollutants and hence generating the new solid waste after treatment (Homem and Santos 2011).
- Activated sludge processes in conventional treatment are not capable to handle a high concentration of antibiotics (Leung et al. 2012).
- Advanced removal treatment processes like ozonation and photocatalysis are not feasible for large scale treatment because of economic constraints.
- The membrane processes are efficient but they have not degraded the residues of the antibiotics, and hence they form high concentrated retentate, very difficult to decompose.
- Sorption processes are most efficient techniques for removal of the antibiotic contaminants but the formation of sludge after treatment create disposal problems.
- Constructed wetlands cannot handle the high hydraulic loading rate and hence not used for a populated area.

13.6 Summery

Day by day, the frequency of detection of antibiotics traces in the water system is increasing as the use of antibiotics is extensive in all sectors. These antibiotics residue are enduring and having high resistance to decomposition, hence deposition is increasing in the different environmental matrices. These residues are harmful to the human as well as an ecosystem or aquatic life at its detectable limit (i.e., at very low concentration). Due to this, the several removal techniques come into the picture to resolve antibiotics contamination problems efficiently and effectively. Treatment units used in conventional WWTPs and DWTPs are coagulation, flocculation, sedimentation, filtration, and biological process (ASP or trickling filter or biological reactor barrier), and they have partially removed these contaminants (Mutiyar and Mittal 2013; Dong et al. 2016; Leung et al. 2012) and need to develop new efficient and effective techniques.

Because of the fractious nature of effluent which contains antibiotics contamination, the used AOTPs come out as a substitute. In the last decades, photocatalysis and ozonation are frequently tested techniques. Ozonation technique has an advantage that it can effectively work even though there is fluctuation in flow rate and composition of WW, but the demerits are the high cost and energy requirement. Sometimes there may be a low rate of mineralization for longer times that leads to the generation of new by-products which is more dangerous than the parental compounds (Balcıoğlu and Ötker 2003; Li et al. 2008). Photocatalysis is also most employed removal techniques for antibiotics contamination (Cao et al. 2016). This technique generally used semiconductor like zinc oxide (ZnO) and titanium dioxide (TiO_2). ZnO is a better option for TiO_2 because the photodegradation mechanism is similar. When the energy source is sunlight, then mostly prefer the ZnO catalyst as its performance is better in the presence of sunlight.

Sorption techniques are widely used remediation techniques for antibiotics contamination. Many studies reported that adsorption techniques are an alternative to oxidation techniques. In all the reported studies, this technique was efficient for the removal of antibiotics (i.e., efficiency is almost greater than 50%), in spite of that, it has disadvantages as it produces new waste material. Classically, activated carbon is used as adsorbent, but it is very costly. In recent decades, there have been studies in which the researcher used agricultural waste as biochar (Balarak et al. 2016; Huijun et al. 2010) and finds that the biochar produced from agricultural waste has the potential to replace the activated carbon.

Practically, ecological treatment processes, i.e., constructed wetlands are economical and sustainable and also effective for the low antibiotics hydraulic loading rate, but they are applicable for low populated areas. Also, the combination of two removal techniques is a better option for practical purposes, for example, a combination of Fenton's oxidation with two-stage reverse osmosis.

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Chapter 14
Antibiotic Resistance, Its Health Impacts and Advancements in Their Removal Techniques with a Focus on Biological Treatment

Rajneesh Kumar, Payal Mazumder, and Mohammad Jawed

14.1 Introduction

Lately, antibiotics have become an essential part and parcel of human health as it provides an indispensable role in the cure of various microbial infections. About 90,71,847 kg of antibiotics are manufactured yearly for utilization in human and animal health, aquaculture and agriculture activities, as a consequence of which they are emancipated into the water environment in many ways. Some of these compounds are crucial in our present society. The unregulated organic pollutants, called emerging pollutants, have been lately instigated or found with the help of facilitated analytical tools (Richardson 2011). Effluents from pharmaceutical industries and hospitals hold very high amount of these antibiotics, while the concentration detected in ground and surface waters varies from a few parts per billion (ppb) to many parts per million(ppm) (Hernando et al. 2006; Watkinson et al. 2009).

Antibiotics are extensively utilized in medicine and animal farms. However, a very small tranche (10%) can be metabolized by animals and humans, and about 90% is liberated into the environment (Nguyen et al. 2017). Another major source of antibiotics in water is sewage due to unsafe disposal by consumers. The expiry date on the medicines does not indicate that the medicine has completely lost its potency and is no longer effective or harmless after it is discarded in water bodies. Common practices all around the world for unused medicines to flush in the sink

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or disposed of in garbage has been reported by Tong et al. (2011a, b). For instance, ciprofloxacin (CIP) is generally employed to cure bacterial infection and is often found at high concentrations in secondary effluent, pharmaceutical industry wastewater (6.5–31 mg L^{-1}) and hospital wastewater (10–200 $\mu g\ L^{-1}$) (Larsson et al. 2007; Tran et al. 2018). It has been reported that CIP causes the occurrence and transfer of antibiotic resistance genes (ARGs) in microbes in the environment (Martínez 2008; Zhang et al. 2013; Turolla et al. 2018). However, ARGs are a part of pristine environment as well as human influenced systems, and therefore, background and baseline concentrations need to be well studied before concluding impact due to anthropogenic use (Durso et al. 2012; Rothrock et al. 2016). From past few decades, reports on wastewater traits have attracted attentiveness toward the appearance of a number of newly discovered substances of anthropogenic origin. They are also newly found in waste water treatment plant (WWTP) effluents, natural surface waters, sediments, sludge, water used for drinking and even in groundwater. Moreover, they are thought to invoke the evolution of ARGs in soil microbiota (Gogoi et al. 2018). Different techniques, viz., chlorination, biodegradation, photolysis, ozonation and adsorption processes, are applied for the elimination of antibiotics from wastewater (Ikehata et al. 2006; Navalon et al. 2008; Jiao et al. 2008; Yang et al. 2012a, b; Álvarez-Torrellas et al. 2016). While, the motive of typical drinking water treatment is assuring safety of water for human use and is free from physical, chemical and microbial contaminations, viz., suspended particles, heavy metals and pathogenic microbes, respectively. These treatment plants are mostly not planned to remove ARGs and can even stimulate the occurrence, dispersal and transfer of antibiotic resistance bacteria (ARBs) via horizontal gene transfer, thereby, elevating health risk in human (Sanganyado and Gwenzi 2019). Although these antibiotics, ARBs and ARGs, have entered the environment for several decades now, but inquisition on their harmful effects on aquatic organisms have begun only recently. A huge number of (>160) variety of pharmaceuticals have been investigated in aquatic systems at minute quantities, generally in the range of ng L^{-1} to $\mu g\ L^{-1}$ (Kummerer 2010).

The antibiotics possess antibacterial property which imparts harmful impact not only on aquatic but terrestrial organisms too and also on human health. The occurrence of antibiotics in open environment is now a serious matter of concern among the global scientist's community, engineers, as well as the civilians. The presence of trace organic contaminants (TrOCs) with certain biologically active compounds can largely affect the aquatic ecology and hence should be addressed (Clara et al. 2012; Luo et al. 2014; Dong et al. 2015; Tran et al. 2018). Other noteworthy impact is the development and multiplication of antibiotics resistance microorganisms in the environment (Halling-Sørensen et al. 2000; Martínez 2008). ARBs are reported to alter the normal functioning of natural aquatic ecosystems and affect processes such as nitrification (Costanzo et al. 2005). The toxic effect of such antibiotics were studied by Gonzalez-Pleiter et al. (2016), and the adverse effects of various such compounds were observed on lower organisms further, emphasizing that proper monitoring and regulation standards needs to be employed for effluent discharge.

There is very little information about the eco-toxicological effects of antibiotics on aquatic and terrestrial organisms. Therefore, this chapter mainly deals with the health impact of antibiotics and antibiotic resistance (AR) and their removal techniques (Fig. 14.1; Tables 14.1).

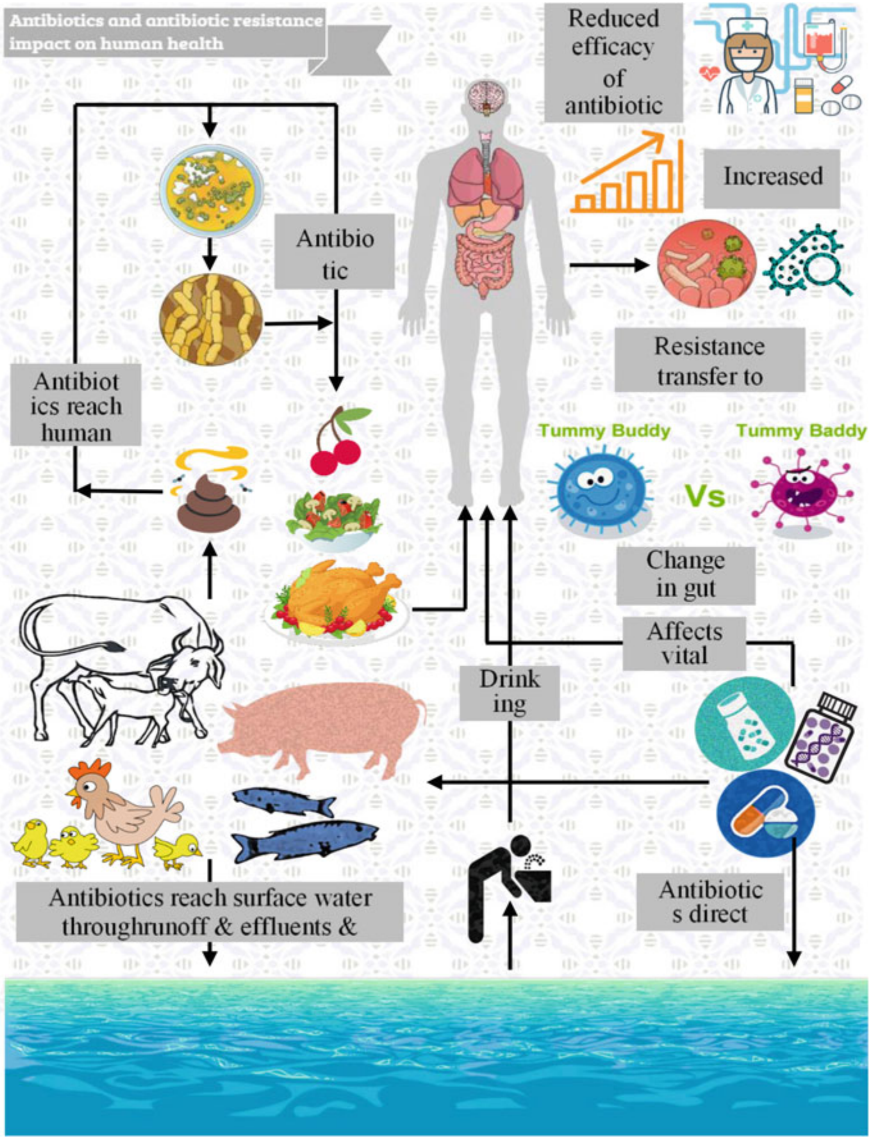

Fig. 14.1 Antibiotics and antibiotic resistance spread in the environment and its adverse impact on human health

Table 14.1 Various treatment methods for antibiotics, ARBs and ARGs

Treatment type	Antibiotic/ARB/ARG	Class	Removal efficiency	References
Physical treatment				
Sedimentation	sul1, sul2, tetO, tetM, tetQ, tetW, tetT, tet, OXA-1, OXA-10, ermB	–	96.8–99.9%	Zhai et al. (2016)
Adsorption (GAC-based)	Tetracycline and doxycycline-hyclate	Tetracyclines	>68%	Choi et al. (2008)
Adsorption biochar/H_2O_2	Sulfamethoxazole, sulfadiazine, sulfamethazine, sulfadimethoxine	Sulfonamides	~60%	Sun et al. (2018)
Lateral flow sand filters	sul1, sul2, qnrS, tetO, ermB, bla_{TEM}, 26 $bla_{CTX\text{-}M}$, mecA, vanA, int1, HF183, 16S rRNA	–	2.9–5.4 log	Heyward et al. (2019)
Constructed Wetland (Zeolite-based)	sul1, sul2 and sul3, tetG, tetM, tetO, text, ermB and ermC, qnrB, qnrD, qnrS, cmlA, fexA, fexB, floR, int1 and int2	–	50.0–85.8%	Chen et al. (2016)
	Erythromycin-H_2O, lincomycin, monensin, ofloxacin, sulfamerazine, sulfamethazine and novobiocin	Macrolides, sulfonamides, flouroquinolones, lincosamides	17.9–98.5%	
Chemical treatment				
Coagulation	tetQ, tetO, tetW and IntI1, sul1 and sul2	–	0.5–3.1 log	Li et al. (2019)
Chemical oxidation	sul1, sul2, tetO, tetM, tetQ, tetW, tetT, tet, OXA-1, OXA-10, ermB	–	78.7–85.7%	Zhai et al. (2016)
Thin TiO_2 Film +UV	Methicillin-resistant *Staphylococcus aureus* and *Pseudomonas aeruginosa*	Gram +ve and Gram −ve	4.5−5.8 log	Guo et al. (2017)
Cu@TiO_2photocatalysis	Ciprofloxacin	Fluoroquinolones	97.64%	Gan and Tan (2019)

(continued)

Table 14.1 (continued)

Treatment type	Antibiotic/ARB/ARG	Class	Removal efficiency	References
Biological treatment				
Bioelectrochemical systems	Oxytetracycline	Tetracyclines	99%	Yan et al. (2018)
	Sulfamethoxazole	Sulfonamides	83.3%	Miran et al. (2018)
	Choramphenicol	Choramphenicols	92.50%	Guo et al. (2018)
	Cefazolin sodium	Cephalosporins	>70%	Zhang et al. (2013)
Constructed wetland (*Plant* spp.-based)	sul1, sul2, sul3, tetG, tetM, tetO, tetX, ermB, ermC, cmlA and floR	–	63.9–84.0%	Chen et al. (2017)
Vertical up-flow constructed wetland	Sulfamethoxazole, tetracycline and sul, tet	Sulfonamides and tetracyclines	>98%	Song et al. (2018)
Constructed wetland [*Phragmitesaustralis* (Cav.) Trin. ex Steud]	Enrofloxacin, ceftiofur and *Enterobacteria*, *Enterococci*	Flouroquinolones, cephalosporin and Gram +ve and Gram −ve	>90%	Mohammed et al. (2019)
Fungal bioreactor	b-lactams, fluoroquinolones, macrolides, metronidazoles, sulfonamides, tetracyclines, trimethoprim and ermB, tetW, bla$_{TEM}$, sulI, qnrS	Macrolides, sulfonamides, flouroquinolones, tetracyclines	77%	Lucas et al. (2016)
Microbial fuel cell	Aureomycin, roxithromycin, norfloxacin, sulfadimidine	Sulfonamides,	99.9–100%	Mao et al. (2018)
Membrane biological reactor	tetW, tetO	–	2.57–7.06 log	Munir et al. (2011)
	aac(6’)-Ib, bla$_{CTX-M}$, bla$_{SHV}$, ermB, sul1, sul2, tetM, tetO, and intI1	–	Up to 4.8 log	Le et al. (2018)
	bla$_{NDM-1}$, bla$_{CTX-M-15}$ and bla$_{OXA-48}$	–	2.76–3.84 log	Waseem et al. (2018)

(continued)

Table 14.1 (continued)

Treatment type	Antibiotic/ARB/ARG	Class	Removal efficiency	References
	Aeromonas Spp.	Gram −ve	Significant reduction	Le et al. (2018)
	Escherichia coli, Klebsiellapneumoniae		Significant reduction	Shields et al. (2017)
Sequencing-batch membrane bioreactor	Sulfadiazine, sulfamethazine, sulfamethoxazole, tetracycline, oxytetracycline, chlortetracycline, norfloxacin, ciprofloxacin and ofloxacin	Sulfonamides, tetracyclines and fluoroquinolones	70–90%	Xu et al. (2019)
Membrane bioreactor	bla_{TEM}, ermB, tetW, tetO, sul1, sul2, addD, qnrS and int1	–	1.5–7.3 log	Li et al. (2019)

14.2 Human Health Impacts of Antibiotics and Antibiotic Resistance

The prevalence of emerging contaminants (ECs) including pharmaceuticals such as steroid hormones, antibiotics, industrial sewage, municipal sewage and water bodies receiving sewage effluents (both surface and groundwater) is of substantial concern to human and ecological health. It is conjectured that by the year 2050, AR will be elucidated for 1000,000 deaths and an economic strain of around US$100 trillion (O’Neill 2016). Due to the absence of sufficient reports on the harmful effects, fate, background and anthropogenous concentrations of antibiotics in the environment make it difficult for government and policy makers to implement jurisdiction on their utilization and also managing the levels that are already prevalent. According to the best knowledge of the authors, no record/data of codes or commissions emphasizing the permissible/allowable limits of antibiotics concentration in wastewater effluent discharge, drinking water and/or in the water environment was available. In a review by Kummerer (2009) it was reported that 20–90% of fluoroquinolones in aquatic environment persisted in both metabolized and its unmetabolized derivatives, leading to adverse effects on phytoplankton, zooplankton and other such lower forms of life. AR can be transported from the water bodies to drinking water and can be a major risk to human health such as protracted rate of illness and escalate rate of deaths (Ashbolt et al. 2013; Chamosa et al. 2017). However, thorough study and detailed research are required to conclude the impact of human exposure to such ARBs and ARGs from food, water, air, etc., in the environment. ARGs in general can transfer AR in microbial communities (e.g., biofilms, soil microbes, etc.) via horizontal gene transfer (HGT) (Wang et al. 2019). HGT betides when AR encoding mobile genetic material (plasmids, transposons and/or integrons) is transferred from resistant strains to non-resistant microorganism (Berendonk et al. 2015; Bengtsson-Palme et al. 2018). Another study by Qamar et al. (2018) report traced the cause of typhoid fever as result of *E. coli* and *Salmonella enterica* ser. Typhi (ceftriaxone-resistant) due to contaminated drinking water. Prior to that in the year 2015, an azithromycin and nalidixic acid resistance *Shigella* outbreak in a lower primary school in China was reported due to poor quality of drinking water and food (Ma et al. 2017). Yet in another report by Finley et al. (2013), intake of multi-drug-resistant (MDR) *Salmonella typhi* contamination present in the treated water caused ~100 deaths. A Cholera outbreak case was investigated, and it was found that the stool samples of the patients contained cotrimoxazole and ampicillin resistance in *Cholera vibrio* (Gupta et al. 2016). ARB such as carbapenem resistance *Klebsiella pneumoniae* are the supreme reasons for worldwide reason for urinary tract infections (UTIs), lower respiratory tract infections and infections of blood.

Once bacteria evolve resistance to customary primary antibiotics (first line drugs), treatment of human bacterial invasions and diseases becomes intricate and expensive, as it will demand doses of last antibiotics available or even require the discovery of new drugs (World Health Organization (WHO) 2017). Although, AR is a worldwide issue, risks on human health remain more conspicuous in developing countries and seem higher than that in developed ones. The reason behind this may be that developing countries lack better healthcare facilities and are deprived of basic technology, medications and equipment. Also, tropical environments aid more diseases, which in turn demand incessant use of antibiotics. In Asian and African countries with underdeveloped conditions, impoverished sanitization and unreliable drinking water quality, *Shigella* spp. with ciprofloxacin resistance may persists, causing conditions like dysentery and diarrhea, which is oftentimes malignant in children. In 2017, WHO listed couple of medium that serves list of critical priority pathogenic ARBs possessing serious threat to human health and endorsed worldwide scrutiny of these pathogenic ARBs (Barancheshme and Munir 2018).

14.3 Trending Treatment Techniques for ARB/G Removal

14.3.1 Efficient Physical Treatment

From last few decades, a large variety of technologies such as, filtration, oxidation (both simple and advanced oxidation techniques), adsorption and improved membrane technologies are employed in the treatment of wastewater in WWTPs for the removal of antibiotics. Adsorption process uses permeable solid adsorbent such as silica gels, activated carbon, artificial pumice to adsorb pollutants and nutrients from waste to eliminate contaminants or regain nutrients, thereby edulcorating the media. Various studies have analyzed many substances, viz., activated carbon, carbon nanotubes, iron, permeable resins, etc., immobilized on alumina for the removal of norfloxacin (NOR) (Liu et al. 2011; Yang et al. 2012a, b). Similarly, adsorption studies with silica, mesoporous alumina, biomass obtained from cork, etc., have been done for the removal of ofloxacin (OFL) (Goyne et al. 2005; Crespo-Alonso et al. 2013).

Yet another technique is the photolysis, in which chemical contaminants are lysed or decomposed with the help of light. When applied in water treatment, indirect photolysis is enhanced by H_2O_2, O_3 or persulfates. Another method, electrochemical oxidation, generates hydroxyl ions in situ at ambient temperature and pressure, without any addition of chemicals. Moreover, electrochemical oxidation is the most promising process to eliminate the toxicity. Antibiotics mineralization is poor when an electrochemical process is employed alone (Guo et al. 2016). Furthermore, ozone splits into hydroxyl radicals in water, which by their very nature are even more strong oxidizing agents. Specific pollutants are targeted to be oxidized directly in the presence of ozone or indirectly by hydroxyl radicals. However, there is difference in their oxidizing mechanism. Ozone oxidation is more specific and at a higher rate, while hydroxyl radicals oxidize indiscriminately. Henry John Horstman Fenton in 1894 discovered the Fenton's reaction, a special type of oxidation process which involved the exploitation of properties of certain metals that can transfer oxygen thereby creating hydroxyl radicals with strong reactivity. These entities were generated via free radical chain reaction and had immense catalytic power. The breakdown of hydrogen peroxide into $^{\bullet}OH$ radicals via an Fe-salt-based decomposition process can be utilized for degradation of antibiotic compounds. Implementation of ultrasonic technique to treat wastewater is also in trend, and a couple of recent publications have reported antibiotic treatment via ultrasonication.

To address the issue of carbon sequestration, energy and economic factor, as well as waste material recycle, biochar is considered as a propitious substitute for the treatment of wastewater. Biochar is reported to be efficacious for alleviating diverse number of antibiotics (Yao et al. 2012; Wu et al. 2013a, b). Adsorption of sulfapyridine (Xie et al. 2014; Inyang et al. 2015), sulfamethazine (SMT) (Vithanage et al. 2014; Peng et al. 2016), sulfamethoxazole (SMX) (Jung et al. 2013; Zheng et al. 2013; Calisto et al. 2015) and sulfadiazine (SDZ) (Peng et al. 2016) with the help of biochar and/or activated/functionalized biochar have been studied. Additionally, biochar was investigated to decompose H_2O_2 or $SO_4^{\bullet-}$ to form highly reactive species that were capable of removing the organic pollutants (Fang et al. 2015). Lately, metal-organic frameworks (MOFs), e.g., zirconium-based MOF(PCN-128Y), MIL-101(Cr)–SO_3H, etc., consisting of an inorganic part developed from metal subunits and the other part organic ligands, gained extensive research focus through modifying the functional groups and also the structure of MOFs their utility capacity in many areas, viz., separation techniques, catalysis of reactions and adsorption (Lee et al. 2009; Sumida et al. 2012; Huang et al. 2015a, b). In contrast, graphene derived and carbon nanotubes are largely restricted at the laboratory scale and are seldom applied to treat antibiotic containing wastewater. Biochar was promulgated to be meagerly efficacious in terms of adsorptive removal capacity than activated carbon from aqueous media due to lesser surface area and various other abiotic and/or biotic phenomena influence on its properties (Anderson et al. 2013). Therefore, biochar conglomerations obtained by inculcating biochar with certain substances that further increase its surface area, e.g., clay, were analyzed for antibiotics adsorption (Chen et al. 2017). Besides these, the environmental factors such as pH, concentration of adsorbates, temperature, organic substances also play crucial role in the adsorption of antibiotics in water (Table 14.2).

Subsequent to adsorption, diverse techniques, viz., centrifugation followed by filtration, micro- and/or nanopore filters, are implemented to segregate the adsorbent-adsorbate complex from the media. Among these techniques, centrifugation followed by filtration is costly due to lofty energy demand. Also, other techniques like paper filtration separation process take a lot of time and care, while unification of membrane filtration technique with adsorption is advantageous in several ways. Membrane technique is sustainable as it provides many naturally occurring substances/wastes for membrane production, entails little space and less travail to operate. One of the voguish membranes nowadays is the ceramic membranes which are more resistant to harsh environment, in contrast to polymeric membranes. They are also relatively more immune to degeneration by microorganisms and can withstand extreme pressures. Integrating microfiltration (MF) with membrane technology is commendatory than that of nano-filtration (NF) and/or ultra-filtration (UF) for it obtains more intense flux and lesser membrane fouling. Consequently, for the removal of antibiotics from wastewater, employing membrane technology with sustainable membranes and cost effective adsorption processes seems propitious.

14.3.2 Cost-Effective Conventional Biological Treatment

In the past few decades, wastewater analysis has attracted the attention toward appearance of these newly detected compounds of anthropogenic origin in the environment. The main objective of wastewater treatment is normally to permit domestic and industrial wastewater to let through after attaining permissible limits to avoid any vandalization of the environment or cause negative impact on human health. The characteristic of wastewater is the main parameter for the selection, design, suitability and effectiveness of relevant wastewater treatment technologies. The biological treatment step is designed to remove the organic matter from wastewater, but the unknowingly addition of antibiotics impart negative impact on treatment plant. The biodegradation process of each antibiotics is dissimilar feasibly because of their distinct chemical compositions and structures (Li and Zhang 2010; Kumar et al. 2016; Das et al. 2015; Kumar et al. 2010; Singh et al. 2019, 2020). In biological process, adsorption and biodegradation both take place and mechanism is determined by the chemical structure of the antibiotics. The disintegration rate also differs on the basis of the class of antibiotics. The different cellular enzymes are involved in biodegradation of antibiotics.

Many reports on wastewater treatment plants (WWTPs) suggested that such plants are the ARGs (Neudorf et al. 2017; Guo et al. 2018). In the first place, WWTPs

Table 14.2 Major antibiotics and their concentrations detected in water/wastewater worldwide

S. No.	Country	Number of samples/sites	Antibiotics	Concentration range (μg/L)	Water type	References
1	China	152	Cefazolin, cefmetazole, cefotaxime, azithromycin, clarithromycin, roxithromycin, ofloxacin, norfloxacin, flumequine, sulfadiazine, sulfapyridine and sulfamethoxazole	ND-73100	Songhua river	Wang et al. (2017)
2	Portugal	–	Minocyclin, tetracycline, epimerepitetracycline and doxycycline	ND-350	Hospital effluent, wwtp influent and effluent	Pena et al. (2010)
3	Sri Lanka	50	Sulfadiazine, sulfamethoxazol, amoxicillin, ampicilline, oxytetracycline, tetracycline and erythromycin	ND-24	Hospital effluents water and sediment	Liyanage and Manage (2016)
4	South Africa	15	Acetaminophen, ibuprofen, erythromycin, sulfamethazine, sulfamethoxazole, trimethoprim, carbamazepine, clozapine, metronidazole, ibuprofen, trimethoprim and caffeine	ND-59.28	Umgeni river	Matongo et al. (2015)
5	China	63	Erythromycin, roxitromycin, azithromycin, clarithromycin, sulfadimidine, sulfamethoxazole, sulfadiazine and trimethoprim	0.002–0.145	Dongjiang river and sewage water	Zhang et al. (2012a)

(continued)

Table 14.2 (continued)

S. No.	Country	Number of samples/sites	Antibiotics	Concentration range (µg/L)	Water type	References
6	Tunisia	–	Chloramphenicol, thiamphenicol, florfenicol, paromycin, dihydrostreptomycin, kanamycin B, aparamycin, streptomycin, amikacin, sisomycin, neomycin and gentamycin	ND-0.016	Pharmaceutical industrial wastewater, wastewater treatment plant and sea waters	Tahrani et al. (2016)
7	China	–	Ofloxacin, norfloxacin, ciprofloxacin and enrofloxacin	0.078–2.029	Raw and treated sewage and in receiving waters	Tong et al. (2011a, b)
8	China	58	Enrofloxacin, ciprofloxacin and florfenicol	0.0–7.49	Animal wastewater, animal farm-effluent, river water, and pond water	Wei et al. (2012)
9	China	6	Trimethoprim, sulfadiazine, sulfamethoxazole, sulfachloropyridazine, ciprofloxacin, ofloxacin, tetracycline, oxytetracycline, erythromycin and roxithromycin	0.027–0.210	Haihe river	Luo et al. (2011)
10	South Africa	15	Ciprofloxacin, aspirin, ampicillin, nalidixic acid, ketoprofen, bezafibrate, diclofenac, ibuprofen, acetaminophen, sulfamethoxazole, atenolol, caffeine, streptomycin, tetracycline, erythromycin, chloramphenicol, andtylosin	0.46–2.75	Umgeni river	Agunbiade and Moodley (2014)
11	Pakistan	–	Ofloxacin, ciprofloxacin, sparfloxacin, moxifloxacin and gemifloxaci	0.2–224	Hospital waste	Ashfaq et al. (2016)

(continued)

Table 14.2 (continued)

S. No.	Country	Number of samples/sites	Antibiotics	Concentration range (µg/L)	Water type	References
12	China	50	Sulfonamides, trimethoprim, norfloxacin, ofloxacin, ciprofloxacin, enoxacin, enrofloxacin, erythromycin, azithromycin, clarithromycin, roxitromycin, sulfadiazine, sulfamethoxazole, sulfamethazine and trimethoprim	ND- 13.6	Sea and river water	(Zhang et al. 2012b)
13	China	–	Sulfadiazine, sulfathiazole, trimethoprim, sulfamethazine, sulfamethoxazole, sulfamerazin, ofloxacin, norfloxacin, ciprofloxacin,, lomefloxacin, tetracycline, oxytetracycline, chlorotetracycline, doxycycline, erythromycin dehydrate, clarithromycin, azithromycin and roxithromycin	ND-0.381	Surface and ground water	Tong et al. (2014)

(continued)

Table 14.2 (continued)

S. No.	Country	Number of samples/sites	Antibiotics	Concentration range (µg/L)	Water type	References
14	Mexico City	26	Clofibric acid, salicylic acid, ibuprofen, ketoprofen, gemfibrozil, naproxen and diclofenac	ND-0.464	Groundwater, surface water (dams), and mixed water (tanks)	Félix-Cañedo et al. (2013)
15	Korea	–	Tetracycline, sulfamethoxazole, sulfonamide, chlortetracycline, oxytetracycline, sulfamethazine, sulfathiazole and tylosin	ND-5.35	Water	Ok et al. (2011)
16	Hong Kong	25	Sulfadimidine, sulfamethoxazole, sulfadiazine, sulfapyridine, doxycycline and ofloxaci	ND-0.580	Sewage influent and effluent, river water	Deng et al. (2016)
17	Iraq	36	Ciprofloxacin, levofloxacin and amoxicillin	0.020–0.146	Drinking water treatment plants	Mahmood et al. (2019)

ND Not detected

acquire wastewater from hospitals and municipal sewages where antibiotics are predominantly utilized, which leads to the presence of considerably large amounts of ARGs (Rodriguez-Mozaz et al. 2015). Second, prolonged selective pressures from the antibiotic remnants at sub-inhibitory concentrations in these wastewater on the microbes in the activated sludge naturally favor the occurrence of ARGs (Kim et al. 2014). Another cost-effective design to treat wastewater is constructed wetlands (CWs) which include several steps of natural procedures employing live flora, soil/sludge/sediment and microbes that can reduce the pollutants (Vymazal 2011). In contrast to techniques like activated sludge, the benefits of CWs are many including cheaper construction, less energy intensive, low maintenance, minimal labor and high treatment efficiency. These benefits allow the CWs to be more sustainable and a better substitute in developing countries with majority of rural areas (Fernandes et al. 2015; Huang et al. 2015a, b). Guo et al. (2015) studied the efficiency of activated sludge, Fenton process activated sludge and individual Fenton process. When the concentration of amoxicillin was less than 350 mg/L, 69.04–88.79% of the antibiotic was removed. Meng et al. (2017) investigated the continual effect of cefalexin (CFX) on the microbial community and efficiency of an expanded granular sludge bed (EGSB) treatment system. The addition of CFX to the reactor had affected the COD removal efficiency and reactor tried to recover after 122 d of operation. Yu et al. (2019) studied the effect of ampicillin on the reactor efficiency, rate of nutrient removal, microbial community structure, evaluation of extracellular polymeric substances (EPS) and enhanced enzymatic activity in the activated sludge of a sequencing batch reactor (SBR) system. Ampicillin was found to inhibit the sludge activity and enzyme activity at a concentration of 20 and 30 mg/L. The mode of action of antibiotics is precise and basically inhibits the cellular machinery function which includes inhibition in cell wall synthesis, inhibitors of bacterial beta lactamases, inhibitor for protein synthesis, inhibits transcription and translation and inhibition of DNA replication (Gothwal and Shashidhar 2015).

Laboratory-based research indicated the possible risks of ARG distribution when vertical up-flow constructed wetlands (VUF-CWs) are operated for the removal of antibiotic containing wastewaters. The results showed high removal effectiveness of >98% for both tetracycline (TC) and sulfamethoxazole (SMX) (Song et al. 2018). Diverse mesocosm horizontal subsurface-flow CWs containing various design frameworks with *Cyperus alternifolius* L. plants were assessed by Chen et al. (2016). Many researchers also used zeolite, oyster shells, ceramic, medical stone, etc., in order and optimized the best combination for treating wastewater. In the attempt, ~ seven antibiotics, viz., lincomycin, erythromycin-H_2O, ofloxacin monensin, sulfamerazine, novobiocin and sulfamethazine, and 18 genes (fexA, floR, fexB, sul1, sul2 and sul3, ermC, ermB, tetG, tetO, tetM, tetX, qnrB, qnrS, qnrD, cmlA, int1 and int2) were found significant in the domestic wastewaters. In these CWs, the obliterations (%) of the antibiotics were found to be in between from 17.9 to 98.5%, whereas that for the ARGs ranged between 50.0 and 85.8%.

In WWTPs with submerged aerated filters and dribbling kind of filters, the overall plethora of bacteria resistant to tetracycline declined by N2 log units CFU/100 mL as reported by Fry and Day (1990) and Galvin et al. (2010) and b1 log units CFU/100 mL

(Novo and Manaia 2010), respectively. Tong et al. (2019) reported that horizontal gene transfer (HGT) occurs in observed ARGs in six municipal WWTPs in the aerated tanks, while anoxic tanks alleviated the ARGs. Mahfouz et al. (2018) studied the entire gene sets of *E. coli* strains in clinics and WWTPs which did not show any variance in the influent or the effluent. Therefore, it can be concluded that conventional WWTPs declines the concentration of microorganisms, while the resistivity of bacteria toward antibiotics cannot be diminished. Moreover, the municipal pan-genome is substantial than alike and same size of hospital pan-genome due to attainable HGT in wastewater.

14.3.3 Advanced Membrane Bioreactor Treatment

Employing alternative technologies like membrane bioreactors (MBRs) provides a feasible substitute to remove ARB and ARGs from wastewaters. For example, Du et al. (2015) found decline in tetracycline resistant genes (viz., tetG, tetW, tetX) and sul1 genes by N5 log unit gene copies/100 mL in a MBR (0.1–0.4 μm pore size). Munir et al. (2011) reported 1–3 log unit gene copies/100 mL more removal efficiency of ARGs in MBR than conventional wastewater treatments. Moreover, 3–5 log decline of tetracycline and sulfonamide resistant genes CFU/100 mL), respectively, was delineated. *E. coli* bacteria that are non-resistant or wild type, more elevated removal efficiencies, viz., N6 log units, were reported for MBR treatment (Luca et al. 2013; Marti et al. 2011). More research is suggested to corroborate the delineated MBR treatment process for antimicrobial resistance (AMR) removal efficiencies to interpret the basic principal. Membranes for MF are formulated to minimize inorganic particles and organic load/compounds and vary in size (viz., 0.1–1 μm). On the other hand, UF with pore size 0.01–0.1 μm, most microorganisms (bacteria and viruses), can also be retained. NF, with membrane pore size 0.3–2 kDa and reverse osmosis (RO) with size up to 100 Da, is frequently solicited for water treatment where the quality demand for water is high (e.g., drinking purpose) and are competent to remove impurities like bacteria, viruses and dissolved ions. Breazeal et al. (2013) revealed a hefty reliance of ARG removal on the membrane pore size of MF, UF and MF, for the gene bla_{TEM} with ~1 log unit gene copies/100 mL in the pore size of 0.45, 0.1 μm, 1.7 log units in 100 kDa, 4.7 log units for 10 kDa and N 5.7 log units for 1 kDa, respectively. The authors of these reports proposed the link of ARGs removal to DNA-colloid interactions.

Le et al. (2018) elaborated that the antibiotics such as ciprofloxacin, azithromycin, amoxicillin, chloramphenicol, minocycline, meropenem, vancomycin, oxytetracycline and sulfamethazine had greatest removal efficiencies by MBR or conventional activated sludge (CAS) treatments with median value >70%, while antibiotics like trimethoprim and lincomycin were unmanageable in CAS (~removal efficiency <50%). ARB in the secondary effluent of the CAS set-up abated as compared to the influent (i.e., lesser by 2–3 times), and ARB was absent in the secondary effluent of the MBR. Furthermore, ARGs in the same varied from less than method quantification limit (<MQL) and up to 10^4 gene copies/mL concentration. It is notable that many ARGs, viz., bla_{SHV}, sul1, bla_{KPC}, ermB, intI1, bla_{NDM} and tetO, were present in the secondary effluent at significant levels (average concentration ~103 copies/mL). Predominantly, MBRs mitigated the ARGs with better removal efficiencies than other processes. Xu et al. (2019) investigated the prevalence of nine compounds classified under three clusters of frequently applied veterinary antibiotics, viz., sulfonamides, tetracyclines and fluoroquinolones. The obliteration of these antibiotics by sequencing-batch membrane bioreactor (SMBR) was investigated and found that the tetracyclines, and the sulfonamides were effectively reduced by SMBR (>90%), while the removal efficiency of fluoroquinolones was <70%. Mass balance analysis was done to substantiate the underlying mechanism, i.e., biodegradation/biotransformation. Besides, membrane retention and sludge adsorption was also contributing factors for the antibiotic removal. It was adumbrated that out of these three domains of antibiotics, fluoroquinolones and tetracyclines were more susceptible to accrued in biosolids. Moreover, antibiotics were found to temporarily perturb SMBR efficiency by restricting sludge growth and activity. The amount of microbial by-products (soluble) and EPS in the slurry was also found to be elevated. Nonetheless, swine wastewater was remediated with >60% obliteration of nutrients and organic matter by SMBR systems. Noticeably, the most persistent ARGs in influents, like the macrolide resistance gene ermB, sul1 and int1 (concentrations 106.39–107.79 copies/mL), were profoundly depleted by MBR systems (1.5–7.3 log removal) than conventional techniques such as sequencing batch reactor or oxidation ditch (0.8–3.4 log removal) (Li et al. 2019). In conclusion, MBR eclipsed CAS in the abrogating antibiotics, ARBs and target ARGs.

14.4 Conclusions

Comprehensive study of the underlying principal of AR removal in WWTPs and their transport and persistence in drinking water and in the environment as such is of crucial importance for human health risk assessment. A number of latest techniques has been engineered and are presently employed for water treatment (e.g., advanced oxidation processes, adsorption, micro- and ultra-filtration, nano-filtration, membrane filtration, etc.), but their efficiency in AR removal and persistency is still poorly understood. Also, strict guidelines, standards and permissible limits of wastewater treatment plant effluents should be tabulated and followed to minimize the future uncertainty of hazards related to AR. Thorough monitoring should be performed on the excessive production and unethical disposal of surplus and expired antibiotics. In underdeveloped/developing countries, cost-effective cheap water treatment techniques) are applied rather than traditional and super advanced wastewater treatment methods. Although, the effectiveness of cost-effective water treatment systems on AR removal is scarcely perceived, may be due to lack of research, techniques and analysis equipment in the poor countries. International collaborations between researchers/institutes and companies from developing and developed countries will serve to address the purpose of detection, caution, prevention and advanced effective treatment of AR.

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Chapter 15
An Overview of Natural Water Contamination and Sustainable Attenuation Techniques: Challenges and Opportunities

Nivedita Pradhan, Santanu Mukherjee, and Manish Kumar

15.1 Introduction

India with a population of more than 1.30 billion shares nearly 17% of the world population and holds nearly about 4.2% of global freshwater supply. It is estimated that approx. 20 Indian cities will have scarcity of fresh/drinking water (40% of Indian population) by 2030. According to Composite Water Management Index' (CWMI) report (CWMI 2018), there is a dire necessity of Sustainable Water Management Practices (SWMP) to manage aquatic ecosystems both in terms of quality and quantity which on the other hand will impair the food security of the nation. The supply of fresh and quality water is utmost important to have better crop production, regulation of daily human activities, industrial operations, recreational operations, and some other major horticultural operations. The contamination of water resources exacerbates the ecological balance by causing problems to human health and restoration of surface water bodies. Therefore, the fate, occurrence, and sources of different contaminants and their regulations along with their different types are summarized in this section. This is explained in Fig. 15.1, where spreading of contaminants arising from land use management and anthropogenic activities has been depicted along with their natural attenuation strategies through rainfall and surface runoff activities to the nearby waterbodies.

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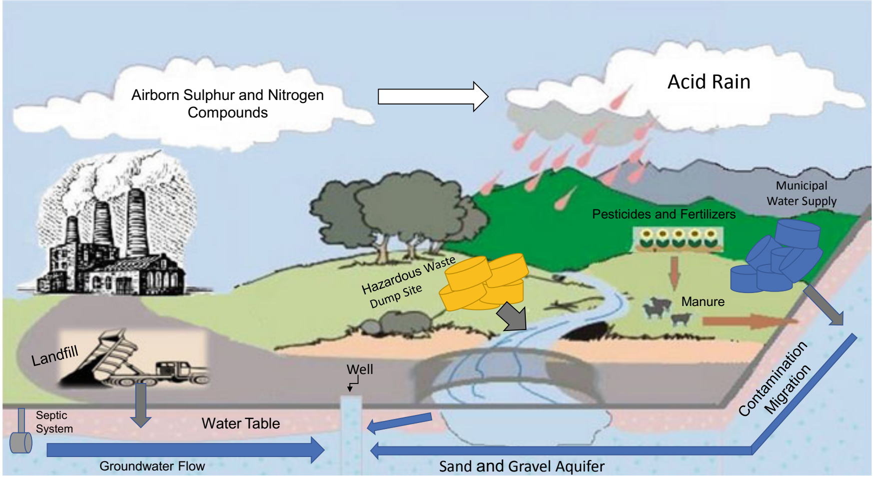

Fig. 15.1 Sources and migration pathways of contaminants through the environmental compartments

15.1.1 Background and Overview of Contaminants

The problem of water contamination is not only limited to India rather it is found all over the world. There can be different types of contamination based on geological or anthropogenic in origin. Therefore, it is utmost important to maintain and balance sustainable water ecosystems which otherwise will be a cause of damage of food-energy-water nexus in the context of freshwater resource management system. The problem is more serious for developing countries like India, China, Brazil, Russia, etc., than for developed nation, where industrial discharge to the nearby water bodies mostly pose a significant problem with due course of time and therefore maintaining water security along with food security is considered as one of the biggest challenges of the twenty-first century.

The types and nature of the contaminants depend on the geological formation of the area and lithological characteristics through which groundwater pass and carry over a suite of natural elements of environmental significance like As, Mg, Ca, F, NO_3^-, Cl^-. etc. (Kumar et al. 2016; Singh et al. 2019; Singh et al. 2020). The presence of such geogenic contaminants can be present in water to the extent of unacceptable level and can be mixed up with other industrial effluents which carry a suite of heavy metals and different organic/inorganic moieties (like Cd, Pb, Cu, Se, Hg, Cr, etc.) in their backbone (Grützmacher et al. 2013). Some types of contaminants (mostly metallic) can easily be identified by their physico-chemical appearances and can come in touch with the pathogenic and/or biological agents and develop resistance genes and traits as documented by Favas et al. (2019). The presence of unwanted materials like organic materials, clay/silt, leaf litters, plant debris, sand/algae, etc., can result into poor quality water with bad taste, though the immunity level varies greatly from infant to adult people to such noxious substances.

In general, it is well known that four different types of contaminants are primarily important for taking into account different environmental maladies, namely organic, inorganic, radiological, and biological contaminants. The major sources of organic contamination are stemming from different industrial, domestic, and agricultural activities which on the other hand can create dysfunction of human organ and cause different diseases at ultra-trace to trace level. Pesticides and chlorinated byproducts are considered as one of the most harmful products among these carcinogens. The use of pesticides and other chemicals can have adverse effect on the environment. Some of the chlorinated- and phosphorus-based pesticides are really harmful for disruption of metabolic activities of non-target pests. Though CIB and EPA have set down some maximum contamination level (MCL) for such toxicants, still it is usually found in the environmental compartment above their MCL.

In addition to the different volatile organic compounds, dyes and emerging contaminants consist of a series of pernicious chemicals which has acute and chronic effects on human health. Figure 15.1 shows the sources and migration pathways of contaminants through the environmental compartments and their dissipation routes by natural meteorological events. Additionally, dyes and other emerging contaminants like pharmaceuticals, antibiotics, and PCPs can be the significant carcinogenic chemicals which can be stemming from different industrial effluents and anthropogenic activities (Pagga and Brown 1986). Water treatment by-products, flame retardants, plasticizers, personal care products, petroleum hydrocarbons, cationic and anionic dyes, different surfactants, chemical solvents, analgesic products, fragrances, etc., through their physical, chemical, and biological degradation can create environmental benign/malign by-products that may induce non-esthetic pollution and non-point source of pollution of water bodies.

15.1.2 Link Among Fate, Sources, and Occurrence of Environmental Contaminants

There are a suite of other categories of contaminants prevailing in the water bodies which play important roles in spreading human diseases. Among them, algae, protozoa, fungi, bacteria, or viruses can play a vital role in deterioration of water quality in terms of its taste, appearances, and odor/color. The slime or molds produced by a group of entomopathogenic bacterial population can be quite harmful for the infants and adult people who have no options for fresh drinking water in rural areas and ultimately can damage the different essential metabolic activities. Some group of iron/sulfur bacteria, protozoans, and viruses (polio, Hepatitis, etc.), blue-green algae, and other microcystis population are responsible for various infectious diseases, and they can appear in different hospital and industrial wastewater streams. They are responsible for multiple diseases like diarrhea, chlorea, typhoid, nausea, gastroenteritis, dysentery, fatigue, etc., through their toxin liberation mechanism and unwanted slime growth that usually creates problems in the water of streams, rivers, and lakes, which are often found to be associated with fecal (*E. coli*) contamination along with such microscopic single-celled anthropogenic markers.

Some other types of contaminants along with inorganic contaminants are quite common in the mining areas or excavation sites or in the industrial legacy dumping sites, where the source of radioactivity can be from soils, or geogenic process (water passes through the rocks) or erosion activities of natural deposits. Usually, natural deposits of radiological elements ($Ra^{226/228}$, U^{226}, Rn^{228},etc.) are detrimental for human health considering their radioactive properties. These all may lead to the enhancement of carcinogenic activities if they are present in groundwater above their MCL (Binesh et al. 2010; Hakl et al. 1995). A large variety of inorganic contaminants such as Cd, Pb, Se, Cr, Hg, Cu, Ni can be present in groundwater in the vicinity of landfill/electroplating metal/leather industry sites, where surface runoff or leaching phenomena can induce wide ranges of neurological and developmental difficulties that might result into damage of spleen, liver, cardiovascular systems, dental/skeletal problems, etc (Shim et al. 2019a, b; Mukherjee et al. 2020). Therefore, it is utmost important to know the sources, pathways, and actual mode of action of such noxious metals. Usually, it is found that besides the presence of major cations and anions (rendering hardness problem in water bodies), co-occurrences of Sb, Be, cyanide, etc., lead to the deterioration of water quality. These results into subsequent health risks stemming from natural/industrial and plumbing sources, acting as a potential agent for endocrine disruptors and reproductive disorders.

In general, it is found that point source of pollution can be derived from spatial discrete spaces. Industrial outputs, buried septic tanks, municipal solid wastes, hospital effluents, and landfill sites can often contribute to aquatic ecosystems in a large diverse manner. On the other hand, diffuse sources of pollution can be derived from large geographical scales and therefore contribute to the lower amount of environmental burden compared to the point sources. These pollutants are difficult to quantify and monitor for long-term scale, thus they may pose real threat to the ground and fresh water resources as suggested by Sharma and Bhattacharya (2017). Most of the studies and researches so far have been focused on direct or point sources of pollution which can be taken into account for the contamination of different natural water resources, commonly used for artificial water recharge purposes. The acute or chronic effects of contaminants can be assessed based on the fate and transport phenomenon of such agents which is affected by different water treatment processes. The fate of such compounds largely depends on the physico-chemical properties, i.e., K_{ow}, $D_{\text{ow,}}$ and chemical features of intricate molecular bindings which on the other hand control the fundamental processes of contaminant transport, namely sorption, ion exchange, microbial degradation, etc. Ground water residence time, redox conditions, total chemical loading, hydraulic features, geological control, etc., determine the surface/subsurface processes of groundwater resources and depict the attenuation process of contaminants through natural processes in the saturated/unsaturated

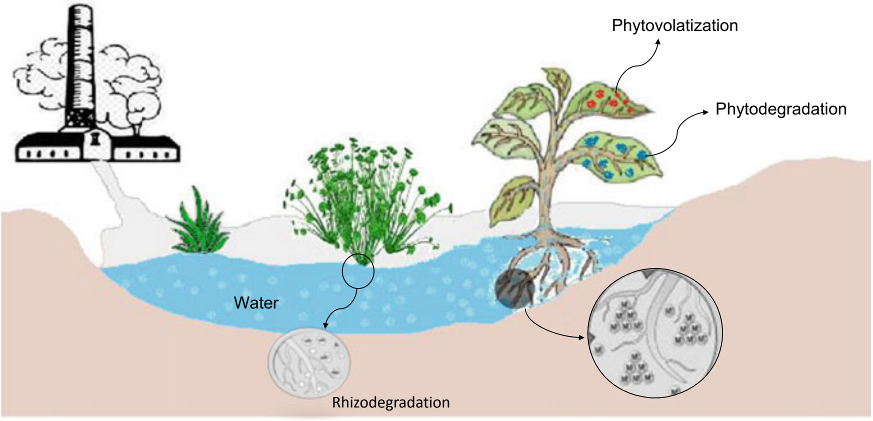

Fig. 15.2 Natural dissipation of contaminants removal by different removal mechanism

zone of recharge activation processes. Figure 15.2 depicts the way by which contaminants dissipates naturally by different removal mechanisms and showing the rate of biodegradation along with their redox control mechanisms.

In general, it is reported that contaminants with a high range of concentrations (mg L^{-1} to μg L^{-1}) undergo dilution and dispersion mechanism which often allow them to come in the flow of direct/indirect sources. Sometimes, the concentrations are in the range of >100 ppb in case of mixture of compounds which possess global impact on largescale due to their frequency of occurrence in the groundwater and combined toxicity effect on the groundwater quality (like Atrazine and other caboxamide group of fungicides along with some emerging contaminants such as bisphenol, diclofenac, ibuprofen, caffeine, etc.). Due to occurrences of such compounds in small numbers, their mean values are often taken as representatives of contaminants pool. Usually, anaerobic situations persist beneath the aquifer represent their calcitrant behavior of the EOCs considering their slow movement from the base of the lagoon. In general, it is found that alternate saturated/unsaturated conditions govern the natural attenuation and treatment processes mostly in case of phenolic, carboxylic, and amide/carboxyzole group compounds. Usually, neutral charge and hydrolysis resisting conditions that prevail in the groundwater and surface water situations prevent further interaction with minerals which helps in the further spreading of the contaminant plume under unsaturated conditions in the shallow alluvial aquifers.

15.1.3 Regulation of Contaminants in the Scenario of Environmental Quality Standards

Numerous reports have been published to validate the occurrences of contaminants in surface and ground water. Many researchers (Cooper and Harrison 2009; Fawell et al. 2006; Zhang and Li 1997) have published a wide range of contaminants fate in the literature which shows the contaminants concentration in the various ranges from μg to ng L^{-1}. Table 15.1 is showing different contaminants level at MCL level or lowest predicted no effect concentration (PNEC) as per the guidelines set by USEPA 2009a, b. Different steroids, tylosin, and carbazole/carboxamide, natural hormones, estrone, and oestradiol compounds are found in surface and subsurface

Table 15.1 Contaminants types, nature, and maximum contamination level (MCL)

	MCL, mg/L	Nature/Type
(1) Organic contaminants		
Ethylene dibromide	0.05	Insecticide
Toxaphene	3	Insecticide
Methoxychlor	40	Insecticide
Dioxin	0.0003	Herbicide
Simazine	4	Herbicide
Diquat	20	Herbicide
Dalapon	200	Herbicide
Endothall	100	Algicide
Carbofuran	40	Nematicide
Dibromochloropropane	0.2	Nematocide
Pentachlorophenol	1	Fungicide
(2) Inorganic contaminants		
Aresenic	0.01	
Barium	2	
Beryllium	0.004	
Chromium	0.1	
Cyanide	0.2	
Copper	1.3	
Mercury	0.002	
Selenium	0.05	
Lead	0.015	
Antimony	0.06	
(3) Radioactive contaminants		
Uranium	30 μg/L	Radioactive
Beta particles and photon emitters	4 merms/year	Radioactive

freshwater of different lakes in Europe with a frequency of detection of nearly 20%. Surface water is found to be less contaminated in comparison with ground water, though triclosan, sulfamethoxazole, and other regional and national level emerging contaminants are likely to have a comparable range of concentrations which can be fitted into reconnaissance surveys having different median values. A comparable value can be estimated from the log-normal distribution of qualitative tracers, where important numerical estimation of tracers can be evaluated for groundwater dating and characterization of emerging contaminants (EOC) ratios. Some univariate statistical calculations have been done by previous researchers to calculate the minimum detection level and intrinsic properties of the target compounds.

Long history of uses of chemicals in North America and Europe resulted into the appearance of legacy pollutants in the particular depth of water level (>1 m) which can be crucial for the formulation of pollutant transport dynamics under the regime of saturated/unsaturated zone. This is very much important to understand that the attenuation dynamics and cumulative distribution of number of EOC compounds are significantly different than other comparative studies, for which long-term investigations with more sample sizes and analytical parameters are required. Long-term migration of high conc. series of contaminants is usually arisen from the event of wastewater pollution and from the residuals after the treatment techniques of individual molecules. It is observed that with the advancement/evolution of state-of-the art treatment technology and many other attenuation techniques detection of contaminants in several river basins becomes easier and less time consuming. As a result of river bank, natural filtration and dilution effect ecological assessment of EOCs concentration in the range of 10^2–10^4 ppb-ppt are reported by some authors.

15.1.4 Purpose and Scope of the Present Chapter

There are numerous publications which deal with the environmental behavior of different pollutants in the soil and water/sediment distribution medium. It is a well-known fact that source partitioning of such pollutants, coming from different sources and emission sites has high K_d/K_{ow}values and exists in environment due to their incomplete removal and dissipation process in sewage treatment plants. Usually, different environmental processes such as conjugation, photo degradation, biodegradation, sorption/desorption, etc. are the common determining factors for the fractions of metabolized and unmetabolized residues that are percolating in the nearby water-bodies. Although nearly 30–50% of the bound residues are formed due to slow kinetic action of contaminant dissipation, it is very much important that complete removal of such noxious chemicals and metabolites lead to the less chances of remobilization and leaching effect (Das et al. 2015; Kumar et al. 2010).

Though many papers have described the traditional treatment technologies in the context of environmental cleanup, an iota of publications has discussed the advantages and disadvantages of the suitable technologies along with their societal challenges and process based environmental techniques. In this chapter, our focus is to represent an overview of the performance-based sustainable technologies and their suitability in the context of performance-based case studies. Different remedial/clean up procedures have been discussed in the light of state-of-the art separation and degradation technologies. Some new emerging technologies such as hybrid membrane based and electrocoagulation clean up procedures have also been discussed in the context of natural and synthetic wastewaters treatment. The most conventional and integrated system-based solutions based on electrochemical technologies and photo catalysis along with microbial eco technology have been highlighted to discuss the rapid removal of compounds mostly for emerging recalcitrant compounds such as carbamazepine, carboxamide, mono- and bromo halo derivatives, chlorinated solvents, dichloro acetic acids, atenolol, etc.

15.2 Process-Based Environmental Remediation Approaches

There are several science-based ecofriendly and cost-effective sustainable approaches which are categorized based on their source and performance toward several water treatment steps. Basically, the availability of raw water, cost-input, infrastructure, different purification methodologies, etc., are some of the governing factors that control the mitigation of contaminants through several problem solving approaches particularly in the mixture of components. Separation between water and other miscible/immiscible liquid usually occurs through different membrane separation/catalytic techniques which on the other hand use different physico-chemical driven forces to physically separate unwanted materials from the plume of wastewater. Some of the important methods are summarized below and Fig. 15.3 shows the detoxification mechanism of inorganic metals/substances from environmental compartments.

15.2.1 Physico-Chemical Approaches

There are many environmental compatible techniques which are often regarded as useful methods for the removal of major contaminants. These methods are often widely accepted because of their high energy efficiency and ease of post-operation, versatility and cleanenv. treatment technologies, easy handling, automation process, and best operative conditions. Some of the promising methods are mentioned as follows:

(a) Adsorption
(b) Ion exchange

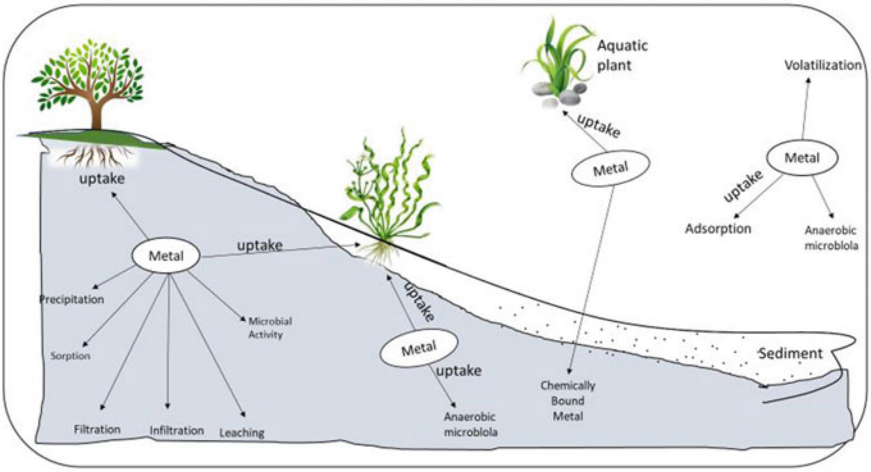

Fig. 15.3 Mechanism of metal removal in aquatic system (modified image, Favas et al. 2019)

(c) Distillation
(d) Catalytic and membrane based techniques
(e) Precipitation and coagulation.

15.2.2 Biological and Eco-friendly Techniques

Usually, the removal of contaminants happens with the help of biological substances like plant, microbes, and some other living/non-living substances (biomass/biosorption). The process involves different process-based mechanisms by which microbial actions are performed, i.e., phytostabilization, phytoremediation, phytoextraction, rhizofiltration, etc. In this whole process of removal techniques, the metal contaminants get detoxified by accumulation, precipitation, and absorption process with the use of plant roots and shoots (Thompson 1994; Bridges et al. 2000; Naidu 2013). Plant enzymes through metabolic transformation and degradation help in the concentration of toxicants into their harvested parts and plays a big role in accumulation/elimination of such toxicants through cellular mechanisms as described by Favas et al. (2019).

Basically, the metal detoxification (As, Hg, Cd, Pb) process by such green methodology had started since early 1970s (Gogoi et al. 2015; Borah et al. 2018). Many plant species like water velvet, duckweeds, water hyacinth, etc., have been found to act as a biological filter and serve as a good metal accumulator from industrial effluents. The several species of macrophytes such as Pennywort, *Lemna minor*, *Eichhornia,* etc., are quite effective in treating run-off which is usually composed of cocktail of pollutants, sediments, organic chemicals, etc., and act as vegetated filter strips within a surface water body and pollutant sources. Many researchers (Rosal et al. 2010; Kim et al. 2005) have reported that removal through biological means happened through vegetated drainage system and multiple biochemical processes. Bacteria, fungi, and other extracellular enzyme producers through their biofilm and other physiological/morphological changes form polymeric cohesive stable matrices surrounding the particulate/granular form of activated carbon. These can be served as a biologically active matrix for C-filtration. Biodegradation and adsorption of dissolved contaminants occur on the surface of C-active medium. Physical adsorption onto the cellular matrices, biodegradation, and bacterial regeneration is the effective biologically mediated source filtration processes which are employed to harness the potential of nature biotechnology in the area of contaminant bioremediation.

15.2.3 Sustainable Natural Attenuation Techniques

Natural attenuation can be defined as a natural process which involves several contaminant removal techniques through sorption, dilution, dispersion, and volatilization, different physico-chemical stabilization techniques which happen in streams, sediments, and water of environmental compartments. Different chemical, physical, and biochemical processes help in the immobilization of different natural contaminants. The processes are summarized as below and are shown in Fig. 15.3, where phytovolatilization/stabilization, bioleaching, biomethylationrhizodegradation, and or abiotic/biotic dissipation processes build up the foundation stone for noxious metal removal.

a) A strong co-ordination with Fe/Mn oxides and hydroxides may lead to the precipitation and transformation metal (loids).
b) Oxidation and hydrolysis of minerals can lead to the formation of insoluble carbonates, oxides, and sulfides of stable complexes.
c) Bacterial reduction can lead to non-mobile forms of metals through changes in different physico-chemical factors which are particularly true for some metals like Cr, U, Se, Cu, Pb, Fe, Cd, etc (Kumari et al. 2018a, b; Kumar et al. 2017).
d) Organic matter plays a big role in metal sequestration/chelation properties by converting them to metallic/non-metallic forms.
e) Plant uptake and biological filtration of suspended solids can lead to conversion of toxic elements into non-toxic forms. Sometimes, aerobic/anaerobic biogenic decontamination processes (such as biomethylation, phytostimulation, and rhizodegradation) which are facilitated through involvement of plant root exudates, plant metabolic enzymes, and several microbial metabolic processes lead to attenuation of pollutants in constructed wetlands and aquatic ecosystems, where translocations and bio augmentation play a big role along with above fundamental processes. Many researchers (Lasat 2002; McGrath and Zhao 2003) have studied and critically analyzed the usefulness of phytostimulation and phytoextraction for rare earth elements decontamination study (such as U, La, Gd,

Nd, Lu, Ce, and Eu.), where speciation of metals plays a big role in natural attenuation of contaminated soils. Transfer factors and bioaccumulation factors are important for ecological engineers as bioconcentration factors govern the mineral processing activities through different stages of water treatment.

f) Biological solutions as natural remediation strategies gain much popularity in the last decades due to the involvement of genetic and geochemical transformations, which helps in metabolic regulation of metals decontamination through chelation, rhizofiltration, and genetic transformations. Usually, in the natural aquatic environment, several microbial populations lead to have potential reclamation actions which tend to sequestrate heavy metals and metalloids in their guts.

Therefore, a wide range of metal-biocomplexes are formed due to their structural rigidity and their binding energy differences show a great variation in stability and solubility indices. These will finally help in management of passive longterm less environmentally disruptive geogenic processes.

15.2.4 Hybrid and New Generation Clean up Technologies

There are many conventional techniques which are commonly used as promising technologies for water treatment since centuries, and among them, membrane-based reverse osmosis is the one which works under pressure/concentration-driven system and operated by thermodynamic functions. The combination of ion exchange methods with low cost ion exchangers is quite important to direct passive metal uptake process. Biomass through several hyper-bioaccumulation process converts unwanted salts and organic contaminants along with chemical toxins.

15.3 Reconnaissance Surveys at Different Levels of Sociological Structures

In the community, there are number of people whom may directly affected by the contaminated site includes the workers at site, local business owners, and people who live near site area. Although, most of the contaminated sites like gas stations and hydrocarbon spill sites which is been leaking through underground fuel tank and the community is not aware of the situation. This is a major concern as it may cause health as well as environmental risk. There are some major concerns about natural attenuation which panelists talk about like

a) Expansion of plume: There might be possibility of failure for the approved method of natural contamination and as a result plume may expand.
b) Unavailability of standard documents: Literature shows that other than dispersion, dilution, and volatilization, there are no other standard methods which show the mechanism behind the reduction of contaminant level.

c) Long-time line: Natural attenuation is a time-taking process, it may take several years to clean the site and hence, reuse of that site is prohibited.
d) Breakdown of chemical into hazardous by-product: During the process of natural attenuation like biodegradation, trichloroethene gets converted into vinyl chloride which is more toxic in nature.
e) Insufficient monitoring: There should be a specific process by which toxic concentration reduces by biological, chemical, or physical processes and this needed an extensive monitoring to get a unique end product.

Health impacts
The report of possible health effects due to contaminated site plays a major role for the approval of natural attenuation method by any community. If the report shows some adverse environmental and health impact, then many communities agree for the controlled contamination process as quickly as possible. In addition, evaluating the degree up to which pollutants at the contaminated site affect the nearby population is very uncertain and complex practice. Some previous investigations shows that there are many symptoms found for ill health of surrounding population which include neurological problems, eye and skin burning issues, and cardiac disease. A study of New York, states that those children whose parents were born at Love canal (contaminated landfill) faces the problem like skin rashes, hypertension, learning problems, and delay in growth (Paigen et al. 1987; Bhattacharya 2006). Another study of Europe shows that a mother who lived near hazardous landfill gives birth to babies with congenital disorder (Berry and Bove 1997) Some environmental contaminations are also have been reported like Bhopal gas tragedy in which methyl isocyanate released into air through carbide plant (Mishra et al. 2009).

15.4 Conceptual Framework of Groundwater Contaminants as Geochemical Tracers

Implementation of any groundwater remediation technique requires a valid data set that shows and verifies the source of contamination. The contamination can be derived from many sources which have a distinct "fingerprint." In the case of hydraulic fracturing, there can be two types of contamination indirect and direct contaminations. Direct contaminations are those fluids and gases which are migrating toward groundwater and degrading its water quality. On the other hand, the indirect contaminations are due to increase in concentration of already present natural species beyond a threshold value in ground water, for example, migrating fluids via biogeochemical processes.

Ground water consists of natural fluid and injected fluids. The major ion for both types of fluid may not identify the sources which are present in ground water. Isotopic tracers are used for the identification of surface water, subsurface water, groundwater mixing pattern, and sources of natural gas present in ground water (Harclerode et al. 2016). In recent years, isotopes have been used to address various environmental issues. Only those isotopes can be used as tracer which shows large mass difference between common isotopes to rare isotopes of particular element. There are various approaches to detect groundwater pollution like use of geochemical markers/tracers and use of stable isotopes. Generally, isotopes of carbon and hydrogen are used for evaluating natural attenuation of volatile compounds like BTEX, chlorinated solvents, or MTBE (Mulligan and Yong 2004). On the other side, larger molecules like PAHs or PCBs, which shows minimal effects of biodegradation, correlation can be develop by using individual isotopic fingerprint. Sources of contamination may include natural seepage of supertankers crude oil, leaking pipelines, dioxins, hydrocarbon polychlorinated biphenyles (PCBs), pesticides and many different types of chemical from various sources. In some cases, traditional techniques for characterization of spill/contaminants sources such as gas chromatography (GC) and gas chromatography—mass spectrometry (GCMS), may be obscure and inconclusive. The reason behind such ambiguous GCMS or GC data set is change in the distribution of components of original samples and spilled material due to weathering processes like biodegradation, evaporation and photooxidation. Depending on the environmental conditions, after the spill, evaporation may lead to remove volatile compounds, and water washing may lead to remove soluble components like hydrocarbons in aquatic environment. Simultaneously, biodegradation may change the distribution of compounds. Therefore, correlation of sources and spilled material requires selective parameters that should be insensitive to environmental conditions (Lu et al. 2015). Chlorine isotopes are widely used for the study of chlorinated contaminants like PCBs, dichloro-diphenyl-tricholoroetane (DDT), and dioxins in the environment. Hunkeler et al. (2005), discussed plume study data of chlorinated hydrocarbon. The dehydrochlorination of 1,1,2,2,PCE to TCE was found to be predominant pathway. Some studies showed enrichments of ^{13}C in VCE and *cis*-DCE are indication of dechlorination and compound-specific isotopes analyses (CSIA) data permitted to determine the rate of bioaugmentation. Hence, we conclude that stable isotopes are useful to monitor natural attenuation.

15.5 Sustainable Risk Assessment and Groundwater Impact/Status

Water security is a considerable concern, especially in countries facing remarkable population growth and vulnerable climate. There can be many reasons to consider sustainable water management as an important environmental assessment tool like less groundwater recharge, deterioration of groundwater quality due to seawater intrusion, high rainwater runoff, and increased wastewater generation by growing population. Water recycling through aquifers is an important study for sustainable water management. Managed aquifer recharge (MAR), to replenish groundwater in urban environment plays a major role worldwide. It depends on natural treatment processes which take place within the aquifer like infiltration, sorption, degradation, and filtration (Islam et al. 2016). There are various methods for recharging water like infiltration process and well injection method useful for unconfined and confined (deeper) aquifer, respectively. The various types of MAR include aquifer storage and recovery (ASR), where water is injected into a well and then recovered from same well. This method is useful for brackish aquifer, where water storage is more important rather than its treatment. In northeast region of India, this type of technique is used for rainwater harvesting (Philp 2007; Islam et al. 2015).

Infiltration gallery and infiltration ponds or basin are also used for aquifer recharge where urban runoff and treated waste water diverted into a pond and soaked under the unconfined aquifer. Such type of arrangement is made near the treatment site so as to reduce the pumping cost. Similarly rain water harvesting is also a beneficial technique as roof runoff is stored in ground via well or caisson and hence it avoids evaporation loss. This helps to reduce surface runoff which in turn enhances the groundwater recharge. RWH along with infiltration gallery can help to change the urban climate and lessen the heat island effect.

The quality of recharge water can ameliorate or improve through aquifers via natural processes: redox transformation (nitrification, denitrification etc.), sorption, filtration, and degradation. The aquifer matrix conditions should be such that it should be able to predict the natural attenuation rates for specific site condition. There are several studies which are related to check the aquifer matrix based upon nutrient content, total organic carbon (TOC), microbial pathogens, trace organic chemicals, and antibiotic resistant genes. An infiltration gallery site in Western Australia shows significant reduction in the concentration of phosphorous (P) and total organic carbon (TOC) as 30% and 51%, respectively, in unsaturated zone (Bekele et al. 2011). It is also stated that removal efficiencies are clearly defined for the particular infiltration rate of recycled water and aquifer conditions. Carbonate configuration of aquifer plays a major role to show the sorption mechanism of phosphate.

15.6 Challenges and Opportunities of Water Management

Some of the key issues which we are facing and which needs to be considered and are evolving with time include:

Climate change: Previous studies and analysis show that there was not much fluctuations on hydrological management through climate change; but now, due to severe drying and warm climate, there is lesser water availability. Initially observed data are now not suitable to plan for variability in climate. It is mandatory to have information about how probability is affected by climate change so as to carry out risk-cost analysis of alternative outlay in infrastructure required in the future.

Growth in urban demand: The population in urban areas is continuously growing with the spread in urban areas thus placing pressure on water supply system to avail the water for them. In recent decade, on globalscale, increase in percentage in water use has reached twice that of population growth. This has led to water stress in larger regions in the world leading the current restrictions on rates of water use and increase in consumption

Unlimited extraction: In many areas, it has been seen that no management plans have been developed on extraction of water such as pumping from rivers and groundwater extractions These have resulted in availability of less water and some case have led to mining of the resource. Moreover, the farm dams' expansion in some areas has also reduced the supply of water entering rivers.

Change in land use: Felling, expansion of plantations, and coming up of new areas in agriculture all have an impact on water resource. Events such as bushfires lead to reduction in availability of water and water quality issues. Changes to land use, even in the agricultural areas have effects on both water availability and water usage.

15.7 Conclusion

Natural attenuation is low cost remediation method for the treatment of contaminated soil and water. This technique can be used as pre- or post- treatment at contaminated site along with other remediation method. Many researchers have analyzed that the decontamination processes like phytoextraction, phytostimulation, and rhizodegradation are eco-friendly and cost-effective methods. However, there are various disadvantages to natural attenuation like longer remediation time, production of more hazardous by-product than parent compounds, significant monitoring, and moderate public acknowledgement.

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Chapter 16
Fantastic Floating Weeds and How to Use Them

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16.1 Introduction

Water hyacinth (*Eichhornia crassipes*) had originated in Brazil, Latin America, and is a common floating weed with purple flowers. It spreads in lakes, ponds, rivers, and paddy fields in many parts of the world and is commonly known as the greatest irksome freshwater weed (Holmes et al. 1997). It is known to be a floating or surface aquatic weed and is considered as one of the most obnoxious weeds. The growth of the water hyacinth plant as an ornamental plant around the world is because of its beautiful flowers. Wherever it has found favorable environmental ambience, it grows with prodigious swiftness to form huge single stranded branches from a common submerged root. As a result, it is detrimental to biodiversity and human ventures (e.g., navigation, fishing, boating, etc.) (https://www.cabi.org/) due to its resistance to all the efforts of destroying it by several methods such as physical, chemical, biological, and/or combination of methods (Rai 2009; Chauhan and Joshi 2010). It is difficult to eradicate, and often only an integrated management strategy, inclusive of biological control, can provide a long-term solution to this pest.

Intrusive aquatic weed control is considered as one of the difficult and enormous tasks in the area of solid waste management. Composting, as a solution for weed management, is one of the beneficial methods for the conversion of organic solid

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wastes into value-added substance, i.e., compost for utilization in the agricultural sector. This chapter compiles the available literature on the uses of water hyacinth for the benefit of mankind. The focus has been given on composting of water hyacinth and its application.

16.2 Water Hyacinth Application

16.2.1 Phytoremediation

Phytoremediation is considered as a spontaneously happening natural process, reported by men about >3 centuries ago (Lasat 2000). Ever since then, human exploited different plant's abilities to thrive in the heavily polluted regions and to remove various pollutants from the soil and water environment. Since the 1980s, research and development for the engineering of those unique plants' characteristics had been practiced (Paz-Alberto and Sigua 2013). Phytoremediation is defined by Kösesakal et al. (2016) as a technique where rhizospheric microbes and plants are used for the removal of pollutants from soil, groundwater, surface water, sediment, or even from the atmosphere. Similarly, Placek et al. (2016), described phytoremediation as the exploitation of plants and leguminous microbes to phytoextract/remove, phytostabilize/immobilize, phytodegrade contaminants from soil and water. Water hyacinth is contemplated competent for phytoremediation because of its capability to regenerate expeditiously, high nutrient/contaminants absorption capability, and acclimatization to harsh surroundings and natural conditions (Rezania et al. 2015).

16.2.1.1 In the Removal of Arsenic from Water

Arsenic (As) is a pernicious pollutant in water sources. It is recognized as carcinogenic (group A) by United States Environmental Protection Agency (USEPA). Availability of arsenic in water beyond its maximum permissible limit, i.e., 0.05 mg/L has affected many countries in the world (USEPA 2008). Water contaminated by agricultural and industrial effluents is considered as major cause for occurrence of As. Goswami et al. 2014, reported the ability of water hyacinth and lesser duckweed (*Lemna minor*) for the removal of As from contaminated sources up to a concentration of 0.15 mg/L. This study was conducted with plant density of 4 kg/m^2 water hyacinth and 1 kg/m^2 lesser duckweed (wet basis). Determination method of arsenic in foliar tissue of water hyacinth plant and in water samples used in the study was by hydride generation atomic absorption spectroscopy after 21 days of sampling. The authors had reported that there was no notable variance found in the As accumulation capacity (bioaccumulation) in these two aquatic plants. Furthermore, provided the conditions of the experimental design, removal efficiency for *E. crassipes* was 600 mg As/ha d and that of *L. minor* was 140 mg As/ha d. Removal rate of water hyacinth is greater with removal recovery of 18% mainly pertaining to its higher biomass production than the lesser duckweed with removal recovery of only 5%. However, the climate condition during the course of study was appropriate for water hyacinth and influenced positively in its removal capacity. The author also concluded that the growth and survival of water hyacinth is not influenced even at As contamination level of 0.15 mg/L. In similar studies conducted by Alvarado et al. (2008), Misbahuddin and Fariduddinin (2010), and Taleei et al. (2019) support the conclusion that the water hyacinth signifies as a reliable option for arsenic bioremediation in water.

16.2.2 Fired Brick Production

Many attempts are employed by engineers and researchers for the construction activities to be sustainable. In consequence, industries have explored strategies to not only to lessen the waste generation, energy expenditure, and carbon cost but also to subdue the misuse of scarce natural resources (Salas-Ruiz et al. 2019). Highly productive soil is among the valuable raw material utilized for manufacturing of bricks for many decades. The brick manufacturing industry requires economic transformations to utilize maximum amount of waste and for making brick production a sustainable one. There have been many reports that attempted the utilization of solid wastes for manufacturing bricks and thereby recycling the waste materials. Goel and Kalamdhad (2017) looked for the experimental feasibility to illustrate the utilization of organic wastes (water hyacinth and water hyacinth compost) for fired brick production. The bricks produced were subjected to physical, chemical/mineralogical characterization to find the quantity of the weed to be added in the bricks without compromising with its compressive strength, minimization of water adsorption, etc., according to the Indian (IS codes) and American society for testing and materials (ASTM) standards. X-ray powder diffraction (XRD) further confirmed that the composition of the bricks was not altered by the addition of water hyacinth but it only made the material porous. A maximum of 10% water hyacinth (at 900 °C) as a partial replacement to the soil was recommended to apply for brick production. During firing of the bricks, CO_2 emission was found to be significant and an approximately 7% net saving in the fuel consumption was calculated for every 10% addition of water hyacinth to the soil (Goel and Kalamdhad 2018).

16.2.2.1 As a Cement Composite

Water hyacinth, considered as an aquatic weed worldwide, has very low density petioles which on blending with cement proves to be a novel insulation building material. The low density of water hyacinth petiole (WHP) pertains to its anatomy/structure and turns out to be a principle characteristic in terms of thermal properties of water hyacinth. Among plants fiber reported so far WHP is known to have a very low density. Although the water hyacinth plant fiber has less lignin and sugar content that affects cement hydration (Jacktron and Jiajitsawat 2014). The appropriate WHP-to-cement ratio can result in formation of self-supporting WHP-cement boards which can be a substitute to thermal insulation materials. The ideal WHP-cement ratio reported ranges from 40:60 to 100:0 with various treatments for various WHPs particle sizes. This cement composite is energy efficient for buildings, especially in the areas, such as tropical countries of the world where, water hyacinth as an aquatic weed is still a problem. WHP cells have large size aerenchyma cells (can retain air). Thermal conductivity of 0.047–0.065 W/mK was reported by Salas-Ruiz and Barrera (2019) by employing staples and pulp. Hence, this simple production method of cement composite from the water hyacinth petiole supports sustainable advancement in construction and encourages several sustainable developments from water hyacinth.

16.2.3 Production/Extraction of Useful Compounds

16.2.3.1 In the Production of Greaseproof Paper

The proximate analysis of water hyacinth shows significant amount of hemicellulose and pentosan in it. Studies based on this fact report the application of water hyacinth in pulp, paper and paperboard production. The long fibers in water hyacinth, with low runkel number and high ash content have characteristic properties of fiber suspension and natural hydration capacity. Hence, water hyacinth proves to be an ideal source of greaseproof paper production on mixing with bamboo pulp (Knoshaug et al. 2013). Water hyacinth comprises of a significant amount of hemicellulose. A relative analysis of the drainage characteristics and pulp freeness (°SR) confirmed that drainage time elevates if the pulp freeness is increased. Mixing bamboo pulps with water hyacinth in appropriate proportions increases the strength of the material. Paper sheets produced with a blend of bamboo pulp (80°SR) and water hyacinth pulp (75°SR) in the ratio 25:75 yielded tensile index of 51 ‘10 N m/g and burst index of 7’ 25 kPa m^2/g (Goswami and Saikia 1994). These values were comparatively more than that produced in the ratio 10:90 and 20:80 of bamboo and water hyacinth pulp.

16.2.3.2 Bioethanol Production

Bioethanol (C_2H_5OH) in the liquid form is manufactured from numerous biomass substrates/waste products with the use of different techniques. It is a replacement for traditional non-renewable fuels as it is a biofuel and 35% enriched with oxygen. Being renewable, it limits the potential hazard of particulate matter and nitrogen oxides emission from combustion engines (Guragain et al. 2011). Bioethanol generated from *Saccharum officinarum* is often used along with gasoline for fuel and is known as gasohol. In the USA E10 is popularly used, which is a mixture of ~10% bioethanol by volume and gasoline. Other countries using bioethanol are India (E5), China (E10), Thailand (E10), Brazil (E20, E25), Paraguay (E7), Australia (E10), Columbia (E10), and Peru (E10) (Nair et al. 2007). Masami et al. (2008) saccharified water hyacinth by H_2SO_4 to form ethanol with yeast. A total of 624 strains was obtained out of which one strain was able to produce 22.4 ml of ethanol per kg of dry *E. crassipes*. Yet, in another study, *Saccharomyces cerevisiae* was used for saccharification (enzymatically) of *E. crassipes* on top of pre-treatment (alkaline oxidative) for a yield of 0.35 g ethanol per gram of biomass (Ahn et al. 2012). Guragain et al. (2011) compared various treatment techniques for wheat straw and water hyacinth for highest yield of bioethanol.

16.2.3.3 For the Extraction of Potassium

Water hyacinth plants have a tremendous ability to absorb nutrients and trace metals from its environment. Thirteen different treatments were performed on the stems and leaves of the water hyacinth plant for the study of potassium extraction by Zhou et al. (2007). The highest rate at which potassium was removed followed by a strong acid treatment (hydrochloric acid) was found to be 69.7%. The greatest efficient for the removal of the cations, Mg^{2+} and Ca^{2+} were at the alkaline pH of ~13 with 88.0% of potassium present in the infiltrate. The highest removal of potassium was achieved in precipitated form was obtained after the addition of tartaric acid, which lead to 72.3% removal of potassium from the media. Throughout the whole process, around 44.3% of potassium from the water hyacinth shoot was extracted with the help of $KC_4H_5O_6$. This technique represented the ideal application of water hyacinth as a source of potassium and can be utilized in the production of potassium salts and other value-added end products from the profoundly noxious aquatic weed.

16.2.3.4 High-Quality Cellulose Nanoparticles and Cellulase

Cellulose is used in a number of fields being a biopolymer and can be also extracted as nanoparticles, further widening its area of application. Cellulose nanoparticles (CNP) have low thermal expansion coefficient (10^{-7} K^{-1}), lighter density (1.6 g cm^{-3}), higher Young's modulus (138 GPa), and an even larger tensile strength making it one of the most robust biopolymers. These characteristics of CNPs make them an absolute applicant for innovative implications, e.g., as filtration units/membranes, nanocomposites, in biomedical field, as adsorbents, coating material, etc. Greener alternatives for isolation of cellulose nanoparticles are required. Water hyacinth, because of its appropriate properties, proved to be a good alternative for isolation of nanoparticles. Luna et al. (2019) isolated CNP from cellulose obtained from water hyacinth stem by thermochemical, alkaline, and enzymatic treatments. Therefore, if subjected to proper treatment high-quality CNP can be produced from water hyacinth stems which can be used in nanopharmaceuticals.

One of the various other ways to control water hyacinth is to use it as a substrate for cellulose production. Amriani et al. (2016) employed the cellulase-producing fungal strains viz., *Aspergillus niger* and *Trichoderma reesei*. The water hyacinth was treated biophysically and was pretreated with *Ganoderma boninense*, a white rot fungi. *G. boninense* was mainly used to delignify the substrate and expose the cellulose and hemicellulose in it. The treatment was carried out for 7 day and after the biological degradation supplementary nutrients were added and the moisture was maintained to 70% at pH 5. Finally, the sample was cleaned, dried and analyzed for cellulose content. The highest cellulase enzyme activity in this study was determined to be 1.035 IU mL^{-1}.

16.2.3.5 As Leaf Protein Concentrate

Water hyacinth along with other aquatic plants has been utilized extensively in production of food and also as coastal area protection (Ajayi and Ogunbayo 2012). Time and again the benefits of this plant evinced to be valuable to eradicate. Therefore, collective attempt has been made by many researchers to find useful application for food production. The plant is a very rich source of protein content in its leaves and can be extracted for consumption. Water hyacinth leaf protein concentrate (WHLPC) extraction was done and its composition such as alkaloids and phenols were analyzed by Adeyemi and Osubor (2016). WHLPC has been proven to be having high nutrient value by proximate analysis. Hence, WHLPC can serve as an edible direct raw food or as additives in food industry. In WHLPC, half of the nutrient is protein (50%), and rest parts are ash, fat, fiber and carbohydrate (33%). Amino acid profiling in WHLPC determined mainly Phe (3.67%) and Leu (5.01%) and 15 other common amino acids out of the 20 known ones. However, asparagine, tryptophan, and glutamine were not found to be present. Although lead, cadmium, iron, chromium, platinum, silver, antimony, nickel, zinc, etc., were found in the WHLPC but the concentrations of Pb, Cd, Hg, and Cr were less than 0.01. All the trace elements were present within the permissible limit. The concentrations of alkaloids and phenols in the WHLPC were 16.6 and 6.0 mg/kg, respectively. The above study, thus, shows that WHLPC is a rich source of protein and has many other health benefits. Also, it is non-toxic in nature and can be eaten as a raw food.

16.2.4 As Animal Feed

The need of animal protein with the hike in price of food is related to the continuous population growth whose need for quest to find alternate source such as WHLPC is on. The availability of good quantity of moisture and mineral in water hyacinth makes it suitable as feed and fodder for many animals. Water hyacinth can be shredded, boiled before feeding and when mixed with other vegetables or rice bran and salt can be used as a fodder for pigs. In China, Philippines, Malaysia, Thailand,

and Indonesia water hyacinth was reported to be used as feedstock for pigs, fishes, ducks, and other non-ruminants after sun drying. Oguniade et al. (1988), reported that after drying the protein mineral and vitamin content in water hyacinth increases and the dry matter had less fiber (33%) and elevated crude protein (18%). Healthy weight is seen to be retained when water hyacinth is mixed with fodder crops, e.g., *Ctenopharyngodon idella* grass up to 100%. It further decreased the protein efficiency ratio. Water hyacinth is also extensively used as fish feed. It has been used after removing moisture to feed channel catfish fingerlings to improve their production. When chemical control was used to eradicate the weed, the dead decayed matter released compounds in the water that were beneficial for both fishes and phytoplanktons (Jianbo et al. 2008). Water hyacinth is also enriched with calcium (~2%) and can strengthen the egg shells and increased total weight of the egg when used as duck feed. Furthermore, the digestion rate and absorption of other nutrients were found to have improved in ducks.

16.2.5 As Biosorbent

Water hyacinth comprises certain binding sites and functional groups that can bind cationic metals and anionic complexes to its matrix. The root portion of the plant acts as an excellent metal sorbent and the overall plant is considered as a better sorbent than yeast *Candida parapsilosis*, bacterium *Mycobacterium phlei*, and fungus *Rhizopusoryzae* strains or even better than the acacia bark (Priya and Selvan 2017). Zheng et al. (2009) utilized dried water hyacinth roots for Cu (II) bio sorption from aqueous media. Water hyacinth was converted to ash and then used as a sorbent and hyper accumulator for uptake of Pb^{2+}, Zn^{2+}, Cr^{6+}, Zn^{2+}, and Ni^{2+} (Mahmood et al. 2010). In most of the cases, metal absorbed by the plant could be desorbed and recovered after subjecting to proper treatment. A significant concern for water hyacinth to be commercially used as biosorbent is the regeneration capacity of its biomass and ability to recover the heavy metals uptake. Metal recovery is very essential, mainly if precious trace metals are involved in the process and cheaper desorption techniques are also crucial because formation of the biomass matrix is expensive (Mahamadi 2011). The more the sorbent efficiency and greater the absorption capacity with multiple reuse, more is its economic value. The absorption depends on many criteria viz., pH, dose, contact time, and temperature. Analysis of the rapid spread of water hyacinth and problems related to it can be compensated by involving them in biosorption.

16.2.6 Biogas Production

Biogas constitutes various gases mainly comprising of methane (CH_4) and trace amounts of carbon dioxide (CO_2), carbon monoxide (CO), hydrogen (H_2) and nitrogen (N_2) that are produced after the disintegration of organic substances that occurs naturally in the lack of oxygen. The occurrence of lignin with cellulose and hemicellulose fragments in water hyacinth makes it recalcitrant to treatments to some extent. This may slow down the hydrolysis process and affects biogas generation and also the rate. Erroneous depletion of fossil fuels and emission of greenhouse gases (GHG's) such as CO_2 has led to enormous research on clean and green or sustainable energy options from natural sources and mainly from waste. Anaerobic digestion (AD) is a widely applied efficient sustainable technique that uses wastes to convert into biogas in the absence of oxygen combining dual benefits of biofuel generation with sustainable waste management (Achinas et al. 2017). Several researches have crisply studied the generation of biogas from water hyacinth as the weed is abundant in all regions. Many researchers nowaday's focus on the pre-treatment of water hyacinth to solubilize the cellulose that leads to higher yields of gas (Barua et al. 2019; Sarto et al. 2019).

16.2.6.1 In the Production of Biohydrogen

Biohydrogen assures a replacement biofuel to substitute fossil fuels because of the expansion of inexhaustible energy source, addressing climate change, and depletion of petroleum and crude oil. Production of biohydrogen by the dark fermentation process is reliable because it is sustainable and requires minimum energy in comparison to the electrochemical techniques or thermochemical processes. While biohydrogen production from a stratum consisting of a major portion as carbohydrates like corn, sugar, starch, etc., increases the price of biohydrogen production significantly. Hence, the emerging research in the field is primarily on the usage of lignocellulosic wastes such as wheat straw, sugarcane bagasses, corn silage, etc., that are also known as second-generation processes. Water hyacinth comprises mainly of three major components, viz., lignin, hemicellulose and cellulose out of which the hemicellulose content is as high as 55% (dry weight basis). This hemicellulose gets converted into sugar as by-products. On treatment with dilute acid, two forms of sugars, mainly xylose and glucose are produced from hemicellulose (Pattraa and Sittijundab 2015). Glucose and xylose obtained during the process are converted into hydrogen by biohydrogen producing microorganisms in the culture.

16.2.7 Manure

Studies show the vast usage of water hyacinth as manure for organic farming. It has been reported to be used both as mulch and compost because of the rise in demand for chemical fertilizer free crops, especially in the western world. This aquatic plant is known to hold moisture in the soil predominantly in dry conditions and also recycle/replenish soil nutrients. Water hyacinth application as compost has been studied extensively. The minimum time needed to form water hyacinth compost has been reported to be 20–30 days. On the other hand, rest of the plants/weeds/wastes requires up to 2–3 months to form mature compost.

16.2.7.1 Mulch

Water hyacinth is known for its use on agricultural land and/or kitchen gardens after forming mulch. It has been reported that mulching water hyacinth on fields with crops led to higher yield of potato (14%), ladyfinger (67%), and tomato (90%) as compared to fields with no addition of water hyacinth mulch (Sannigrahi et al. 2002). While, it has been seen that when additional treatments like 2,4-*D* herbicides and glyphosate is given along with water hyacinth mulch then there is significant reduction in the production and growth of tomato as compared to the only water hyacinth mulch applied tomato crops (Tesi and Lenzi 1988). Therefore, it can be commenced that herbicide or fertilizer addition should be prohibited in fields aided with water hyacinth mulch and extreme care needs to be taken in this regard for better crop health (Table 16.1).

16.2.7.2 Compost

Since the Industrial Revolution generation of large quantities of waste has continuously increased across the globe. Concerning the management of this generated waste, recycling comes out to be the most reliable strategy to deal with this problem (Bendak and Attili 2016). Composting is a natural process of degrading organic wastes and their conversion into soil like, odorless, fertile manure called as compost. Apart from the reduction of waste, the process of composting also provides a valuable product. The final compost usually termed as humus, which is nutrient-rich and can be used to improve poor soils and fertilize gardens rather than using chemical fertilizers. The application of compost can also help in the soil to retain water and thereby promoting the growing conditions of the soil. Composting is an entirely aerobic process (Fig. 16.1).

A study by Gajalakshmi et al. (2002) was carried out on *Crossandra* plants (nine varieties) with the application of water hyacinth vermicompost and compost. The treatment of the plants with water hyacinth vermicompost had positive effect on the plant growth and flowering as compared to the untreated crops. However, water hyacinth compost did not improve *Crossandra* plant health that significantly like vermicompost but still was comparable to the control plants. Also, five kitchen garden sites were tested for the effect of the compost on their growth. Three of these five sites were treated with water hyacinth vermicompost and the rest two with water hyacinth compost. In the absence of any other chemical fertilizer or manure, it was observed that there were no harmful effects on the crops. The plots that had water hyacinth compost added to them had yielded better crops than the rest. Shoot and root length, number of leaves and flowers, biomass and crop yield index had increased in those

Table 16.1 Water hyacinth composting followed by its land application

Year and author	Type of compost	inference
Abdel-Sabour and El-Seoud (1996)	• 8% shale deposits (Tefla) (T) • 4%, 6%, 8% Biosolids (BS) and 8%BS + T 4%, 6%, 8% BS and 5% W + BS • 4%, 6%, 8% Municipal solid waste (MSW) and 8% MSW + T • 1%, 5%, 10% Water hyacinth compost (W) and 8%W + T	• Field experiments were carried out with sesame seeds • BS + W was most effective • Accumulation of heavy metals were within permissible limits but should be monitored regularly
Gajalakshmi and Abbasi (2002)	• Water hyacinth pile compost (WHC) • Water hyacinth vermicompost (WHV)	• Effect seen on C. undulaefolia (firecracker flower) • Compost:soil (1:2) • WHV produced more flower yields • Ladies finger, brinjal, cluster bean, chilli and tomatoes grown in kitchen garden were better with compost
Rakshit et al. (2008)	• Vermicompost • Farmyard manure (FYM) • WHC • Chemical fertilizers	• Field experiments were carried out with two varieties of rice • Plants showed more tillering in vermicompost > FYM > WHC > CF More pest resistance in vermicompost > FYM > WHC > CF
Chukwuka and Omotaya (2009)	• *T. diversifolia* (Hemsley) and WHC	• Nutrient depleted top soil (0-30 cm) and sub-soil (45-60 cm) from Nigeria • Pot expt. Compost:soil in various ratios • Maize plants grown • Compost addition improved nutrient content and increased crop yield
Singh and Kalamdhad (2013)	• Water hyacinth vermicompost (WHV)	• Speciation of HMs during WH vermicomposting • Exchangeable Mn fraction changed to less mobile fraction • Exchangeable fraction of Cd was reduced 100%

(continued)

Table 16.1 (continued)

Year and author	Type of compost	inference
Balasubramanian et al. (2013)	• Water hyacinth mulch (WHM) • Water hyacinth pile compost (WHC) • Water hyacinth vermicompost (WHV)	• Plants grown in field (randomized block design) for 3 years • Effect seen on rice field • C, total N, available P and K increased in WHM than others
Singh and Kalamdhad (2014)	• Water hyacinth pile compost	• Effect of carbide sludge (lime) in bioavailability and speciation during composting • Addition of 2% lime reduced water soluble, DTPA extractible and leachable metals
Singh and Kalamdhad (2014)	• Water hyacinth pile compost	• Effect of natural zeolite reduced water soluble, DTPA extractible and leachable metals Increased N, K, Ca conc. in compost
Singh and Kalamdhad (2016)	• Water hyacinth pile compost	• Lime reduced the bioavailability factor of Zn, Cu, Fe, Ni, Pb, Cd and Cr • Couldn't effect bioavailability of Mn • The total concentration of Pb was higher than Zn, Cu, Mn, Ni, Cd and Cr but its BF was lowest among the all
Goswami et al. (2017)	• Water hyacinth drum compost (DC) • Vermicompost (VC) • Farm yard manure (FYM) $(NPK)_{100}$ • FYM + NPK • DC + NPK • VC + NPK	• Effect seen on soil quality and growth of tomato and cabbage plants • Plants grown in field (randomized block design) • Soil pH neutral after DC • More yield in tomato and increased foliage size in DC + NPK and VC + NPK

plots. However, statistically significant results were shown by plants in the plots receiving vermicompost treatment. Harvest index and number of flowers had gone up in those crops. Similar study by (Paul and Bhattacharya 2012) also concluded that water hyacinth vermicompost shows best plant growth and flowering for *Crossandra* plants.

Singh and Kalamdhad (2015) had attempted to produce huge quantity of water hyacinth vermicompost in a more economic and time efficient way. For this, the whole plant was chopped into <1 cm pieces and composted by a 'high-rate' technique followed by adding to vermireactors and rotary drum vessel reactors. For vermicomposting, higher densities of efficient earthworms were added to the reactors. The entire process with final mature compost was over by the 20th day. Throughout the

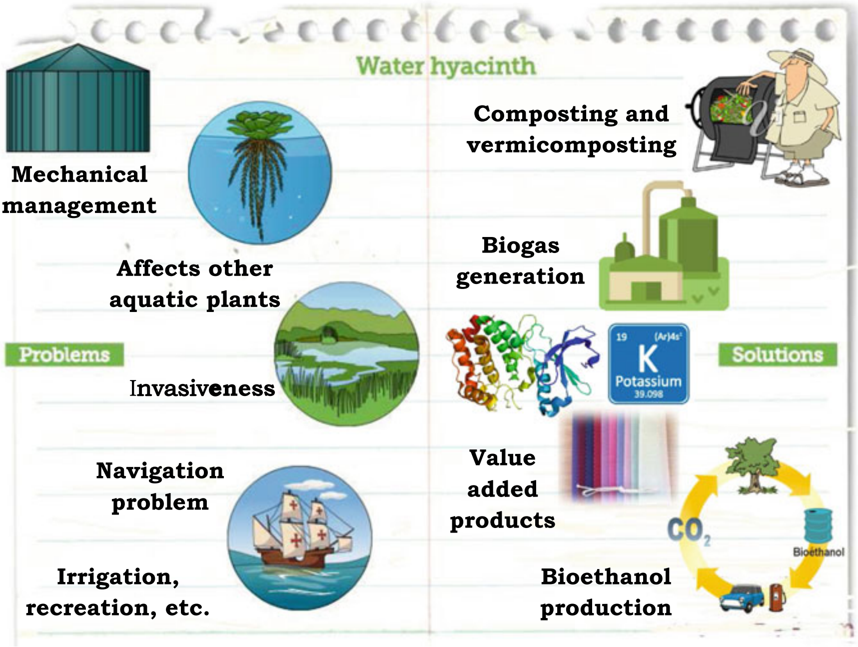

Fig. 16.1 Problems associated with water hyacinth and its management

operation time of seven months, vermicast was produced which confirmed the feasibility of the composting–vermicomposting systems. Their experiment results showed that the composting was enhanced on increasing the surface-to-volume ratio of the reactors. These studies showed the advantageous effect of vermicomposted water hyacinth on the availability of different nutrients in alluvial soils of Assam. Vermicomposted water hyacinth at 5 t ha^{-1} was prepared to replace chemical fertilization to a substantial extent.

16.3 Conclusions

Aquatic weed like water hyacinth is a menace and possesses many harmful impacts on aquatic life and is problematic to manage. However, appropriate techniques shall be used for extracting useful compounds from them and also can be used for the generation of fuel. A majority of the studies are based on composting of water hyacinth whose fate is almost always to soil. However, water hyacinth contains toxic metals which they take up from water bodies and these may end up in soil when such unchecked compost is added to the agricultural land. Metals from its compost can further be taken up by crop plants and get bio accumulated and biomagnified gradually. Therefore, toxicity analysis is important before soil application of water hyacinth compost.

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Chapter 17
Scope of Conventional Versus Advanced Technologies for the Control and Prevention of Emerging Contamination

Anjana Srivastava

Owing to on-going demographic shifts, urbanization and changing life styles supported by rapid industrialization, pollution by so-called emerging contaminants (ECs) is a rising environmental and public health concern globally. Some items that we use in our everyday lives like pharmaceuticals, pesticides, industrial chemicals, surfactants, and personal care products are collectively referred as "contaminants of emerging concern," These contaminants also include endocrine-disrupting compounds, analgesics, antibiotics, hormones and a whole range of other pharmaceutical compounds including anti-inflammatory, anti-diabetic, and anti-epileptic drugs that are also a cause of increasing antibiotic resistance and endocrine disruption in aquatic animals and possibly humans too. The list of compounds and chemicals in this group is significantly large and is ever expanding with the introduction of new commercial chemicals, changes in use and disposal of chemicals currently in widespread use and further identification of new molecules that form part of this classification (Rodriguez-Narvaez et al. 2017).

ECs may be synthetic or naturally occurring or any microorganisms that are not commonly monitored in the environment but possess the potential to enter the environment and cause known or suspected adverse ecological and/or human health effects. ECs are usually associated with various sources such as municipal wastewater treatment plants, runoff from agricultural, and urban land surfaces, septic systems, etc., and hence are consistently being found in groundwater, surface water, municipal wastewater, drinking water, and food sources. Despite strict regulations, significant amount of pharmaceutical compounds find their way in the environment causing detrimental impacts. There are several reports that, even at a lower dose, these compounds can have severe health impacts as well as drug resistance. Alternately, unused and expired drugs are another concerning factor responsible for increasing ECs in

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water, and this is due to lack of protocol to dispose off or to return such drugs to the pharmacist/concerned agency. All these have led to increased concentration of pharmaceutical compounds in water bodies and wastewater streams. Among the potential sources of entry of pharmaceuticals and personal care products (PPCPs) in the environment, municipal sewage treatment plants (STPs) contribute a major part (Deegan et al. 2011). These compounds have the tendency to a mass in living tissues and thus enter the food chain. The threat lies in the fact that the environmental and human toxicology of most of these compounds have not been studied much, although now this group of chemicals is receiving more attention. Effective treatment of wastewater is essential for public health and sanitation, water reclamation, preventing environmental pollution, and protecting water resources from contaminants getting introduced into the water systems. Furthermore, the treated wastewater is a potential resource, and its reuse will partially offset supply and demand in water-stressed areas (Nancharaiah et al. 2019). It is, therefore, an urgent need not only to develop reliable and cost-effective methods to analyze wide range of pharmaceutical compounds but also to find techno-economically feasible options for their efficient removal from water.

17.1 Conventional Methods of Water Treatment

Mainly four common conventional methods are there to treat wastewater. These include physical, biological, chemical, and sludge treatment.

Physical Water Treatment (PWT) The main practice involved in physical wastewater treatment is sedimentation, in which insoluble/heavy particles suspended in wastewater get settled down due to gravity. When the insoluble material settles down at the base, pure water can be decanted. Physical processes like screening, sedimentation, and skimming for removing the solids are also included under PWT.

Aeration is another useful technique of PWT. The process consists of circulating air through water to supply excessive oxygen to it. Filtration is also a widely accepted method of PWT and is used for filtering the contaminants by the use of special filters that can separate the contaminants and insoluble particles present in wastewaters. Sand filters are most commonly used filters as they are readily affordable. Even the grease found present on the surface of some wastewaters can be removed through this method.

Biological Water Treatment (BWT) In this method of water treatment, various biological processes are carried out to break down the organic matter like soap, human waste, oils and food, etc., which are present in wastewater. In BWT, microorganisms metabolize the organic matter present in wastewater. BWT can be carried out by three ways:

- Aerobic processes: Organic matter of wastewater is decomposed by bacteria in the presence of oxygen, whereby it is converted to carbon dioxide that can be used by plants.

- Anaerobic processes: In this process, fermentation of the waste in wastewater at a specific temperature is carried out without any oxygen supply.
- Composting: This is an aerobic process in which wastewater is treated by mixing it with sawdust or other sources of carbon.

Chemical Water Treatment (CWT) CWT involves the use of chemicals in water for purification. Chlorine is an oxidizing agent and forms hypochlorous acid (HOCl) with water. This HOCl is highly effective in killing the disease causing microorganisms.

$$\mathrm{Cl_2} + \mathrm{H_2O} \rightarrow \underset{\text{Hypochlorous acid}}{\mathrm{HOCl}} + \mathrm{HCl}$$

Ozone and potassium permanganate are also utilized as oxidizing agents for purifying the wastewaters.

If the pH of wastewaters is low or high (depending upon impurities), neutralization is done by adding acid or base to bring the water to its neutral pH of 7. The chemicals added to wastewater prevent the bacteria from reproducing in water, thus preventing water contamination. There are several other chemical processes, like chemical coagulation, chemical precipitation, chemical oxidation, advanced oxidation, ion exchange and chemical neutralization, and stabilization which are also applied to wastewater during the cleaning process.

Sludge treatment It is a type of secondary management for removal of most of the undesired solids present in wastewaters, leaving aside, nitrogen and phosphorous which may remain as dissolved nutrients. It is focused on dewatering of sludge from industrial wastewater or sewage plants whereby the disposal costs are reduced and potential health risks of disposal options are also reduced. It can be performed by two ways.

Activated sludge treatment This is the most commonly used modern process for the biological treatment of sewage. In this process, the sewage having organic matter with microorganisms is aerated in an aeration tanks using a mechanical aerator. The reactor contents are referred to as mixed liquor. Under aerobic conditions, the microorganisms metabolize the soluble and suspended organic matter. The generalized metabolic reaction is as follows.

$$\underset{\text{(Organic matter)}}{\mathrm{CONHS}} + \mathrm{O_2} + \text{Nutrients} \xrightarrow{\text{Bacteria}} \mathrm{CO_2} + \mathrm{NH_3} + \mathrm{H_2O}$$

In conventional activated sludge treatment process, the activated sludge is first processed in primary sedimentation tank. The system consists of a separation, settling or sedimentation tank, and sludge removal line (Fig. 17.1). The sewage after the primary treatment is introduced at the head of the tank where O_2 is supplied uniformly throughout the tank.

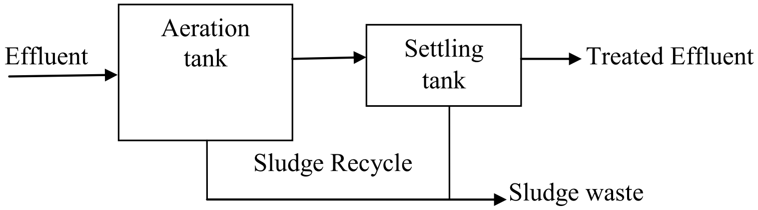

Fig. 17.1 Aerobic sludge treatment process

It then reaches the settling tank where the contaminants are metabolized and get settled below. The treated water effluent is then collected. In an array to enhance the performance of activated sludge system, modifications have also been done from time to time. These efficient aeration techniques include the use of aerated lagoons or aerated ponds, sequencing batch reactors, and aerobic digestion.

Apart from aerobic treatment, there are anaerobic sludge treatment processes too (Fig. 17.2) like anaerobic digestion which is mostly used for the stabilization of concentrated sludge that is produced during treatment of industrial sewage. Hydrolysis is used for high molecular weight compounds in enzyme-based catalyzed reactions, acidogenesis for converting low molecular weight compounds to acidic products, and methanogenesis for production of methane and carbon dioxide, from the intermediates formed in acidogenesis.

In common anaerobic treatment process, wastewater is made to pass through screen and grit chamber to the bioreactor which contains a thick, semisolid substance known as sludge. This sludge contains anaerobic bacteria, other anaerobes, and microorganisms which digest the biodegradable matter present in the contaminated water. This results in lowering the total suspended solids (TSS), biological oxygen demand (BOD), and chemical oxygen demand (COD) of water. It also helps in reducing the biogas byproducts formed during treatment process.

Granular Sludge treatment (GST) GST is yet another novel alternative for wastewater treatment and offers numerous operational and economic advantages over the conventional sludge treatment systems. GST focuses on optimization of

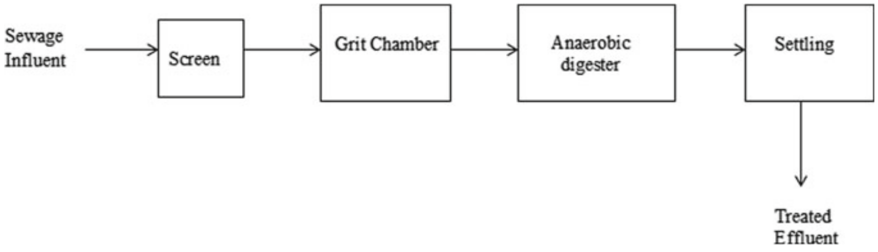

Fig. 17.2 Anaerobic sludge treatment process

engineering aspects relating to reactor operation with only little emphasis on fundamentals of microbiology. Granules making up aerobic granular activated sludge are understood to be aggregates of microbial origin, which do not coagulate under reduced hydrodynamic shear and which subsequently settle significantly faster than activated sludge. Aerobic activated sludge granules are opaque, impermeable, and globular biofilms which enhance purification efficiency and sludge settling process in wastewater treatment. Thus, the treatment allows excellent settleability, high biomass retention, simultaneous nutrient removal, and tolerance to toxicity.

Research has shown that GST performs better than activated sludge treatment (AST) in removing contaminants from the wastewater (Thwaites et al. 2018). GST has been demonstrated to degrade a variety of toxic and recalcitrant organic compounds such as azo dyes, phenols, metal-chelating agents, organophosphorus compounds, nitroaromatic compounds, anilines, and pharmaceuticals in laboratory-scale bioreactors (Sarvajith et al. 2017; Nancharaiah et al. 2006; Nancharaiah et al. 2015; Ramos et al. 2015; Zhao et al. 2015). However, studies on full-scale GST plants reported long start-up periods of up to 10 months for achieving reasonable granulation (80% of biomass in the form of granules). It is to be noted that these full-scale plants are used for treating wastewater consisting of significant proportion (30–70%) of industrial effluents.

Granular sludge treatment is done by the use of both aerobic as well as anaerobic granular sludge.

Aerobic granular sludge is developed under aerobic conditions and is mainly used for the aerobic degradation of organics (Fig. 17.3) as well as for nitrogen removal under aerobic and anoxic conditions (Liu and Tay 2004).

Anaerobic granular sludge treatment (Fig. 17.4) mainly consists of methanogenic, syntrophic acetogenic, and various hydrolytical fermentative bacteria and is widely applied in full-scale anaerobic reactors for wastewater treatment (Hickey et al. 1991).

Aerobic degradation is mainly a single species phenomenon, whereas in anaerobic degradation, numerous organisms are involved and hence proceed through a chain process. In general during anaerobic conversion of complex substrates, an interactive action of the microorganisms is besmeared.

Anaerobic treatment of organic compounds has several advantages over the aerobic treatment process because it requires less energy, low macro/micronutrients and

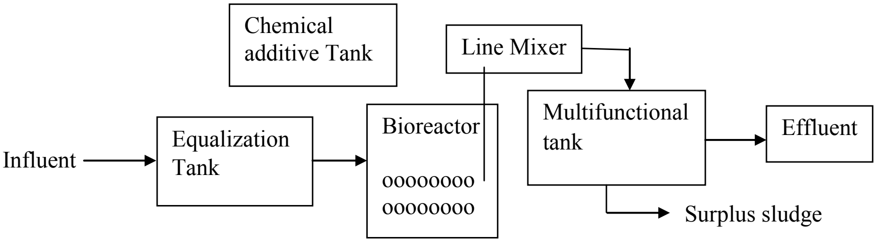

Fig. 17.3 Aerobic granular sludge treatment process

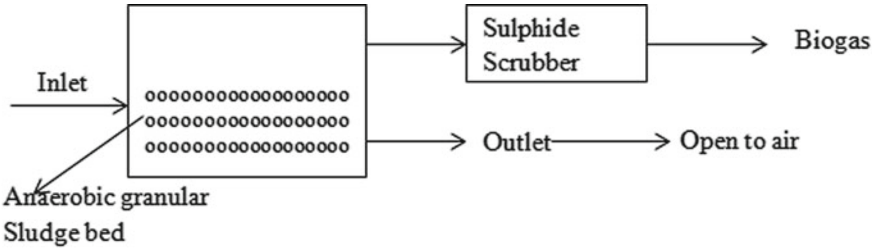

Fig. 17.4 Anaerobic granular sludge treatment process

generates low waste natal solids. In addition, anaerobic treatment is also used for generating biogas. In spite of all these advantages, there are some disadvantages too of anaerobic treatment such as sensitivity of procedure, susceptibility, stink smell problems, long start-up periods, and post treatments of standards discharged. However, there is a better control and regulation requirement both in aerobic and anaerobic treatment processes.

Considering the scope of the conventional processes, AST is no more considered sustainable for wastewater treatment due to large land footprint, higher costs, and complex process designs for achieving nutrient (nitrogen and phosphorous) removal. GST is on the other hand, a sustainable biological wastewater treatment method for meeting stringent effluent discharge limits. Though this process is advantageous over the AST for effective removal of contaminants, tolerability changes in influent/environmental perturbations and lower sludge production (Nancharaiah et al. 2019) but it has not yet been applied to full-scale wastewater treatment plants (WWTP), probably because of lack of fundamental knowledge of microbiology that is associated with the granulation process. Moreover, the complex ecological mechanisms involved in transformation of activated sludge into granules are also largely less known.

Thus, WWTPs have a mixed performance in dealing with ECs. There are also evidences that WWTPs can act as reservoirs of antibiotic resistant pathogenic bacteria (Xu et al. 2007; Amos et al. 2014; Schlüter et al. 2007). WTPs' wastewater contains a large number of bacteria, which are conducive to the bonding between bacteria, and this promotes transfer of multiple antibiotic resistance genes carried by movable elements. Due to limited availability of data, the fate of ECs in the environment and wastewater treatment remains under-investigated, limiting our ability to provide targeted cost-effective treatment (Thwaites et al. 2018).

In general, a conventional treatment is enough only to remove suspended solids and organic matter in urban wastewater treatment plants, but unfortunately, many emerging contaminants (ECs) remain in water. The usual treatment processes of removing the micropollutants are incapable as they are reported to bioaccummulate in macroinvertebrates (Rodriguez-Narvaez et al. 2017). It is extremely essential to identify the technical trend and information lacunae in relation to deletion of ECs in water. The reports must be addressed to the scientific community to inform it regarding the adoption of best practices so that the use of safe drinking water is ensured. The chemical structure of quite a lot of compounds which are included in the ECs are such that they can be easily solubilized in water and then transported through the water cycle causing threat to aquatic organisms as well as humans (Agüera et al. 2013). The ECs list of compounds has grown significantly in the current years leading to an unidentified numbers of parent compounds and transformation products (Nikolaou 2013).

Advanced technologies for the control and prevention of emerging contamination.

The occurrence of ECs in STP effluents, both industrial and domestic as well as hospitals, despite the treatment through conventional methods, makes it inevitable to adopt advanced treatment systems. The conventional wastewater treatment methods vary greatly in their ability to remove drug or personal care product residues from wastewaters. Some extra treatment ways need to be used at the effluent discharge location or prior to the entry point of the drinking water delivery systems. Thus, before wastewater disposal or reuse, some advanced wastewater treatments are essential to effectively remove ECs possessing chronic toxicity, endocrine-disrupting effects, and the capability of inducing the proliferation of highly resistant microbial strains in water. Membrane processes like microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) are some pressure-driven filtration processes that are considered as highly effective processes (Adams et al. 2002; Strathmann 2001) for removing huge amounts of organic micropollutants including ECs.

The organic precursor matter as well as other ECs can be effectively removed by use of membranes. Though there are several mechanisms through which ECs removal by membranes is feasible, size exclusion is an effective way that can be used to decontaminate water from these contaminants.

Microfiltration (MF) MF is the process in which impure or contaminated fluid is made to pass through a special pore-sized membrane for separating microorganisms and other suspended particles from the liquid (Fig. 17.5). It is mostly used along with other separation processes like ultrafiltration and reverse osmosis to get the polluted liquid free of undesired contaminants. MF in fact serves to be a pretreatment for other separation processes like granular media filtration, ultrafiltration, etc. The characteristic pore size is present in membranes used for microfiltration process

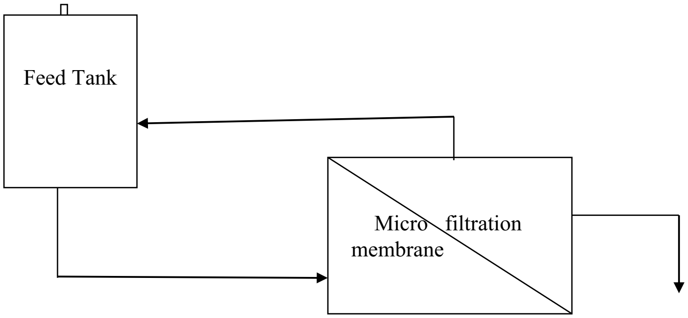

Fig. 17.5 Microfiltration membrane process of wastewater treatment

ranges between 0.1 and 10 μm (Baker 2012). The fairly accurate molecular weight of macromolecules, these membranes can separate, is usually less than 100,000 g/mol. The filters which are used in the MF process are specifically designed to avert particles such as algae, protozoa or large bacteria, and sediment from passing through the specially contemplated filters. Extra microscopic, ionic, or atomic materials as water (H_2O), sodium (Na^+) or chloride (Cl^-) ions, dissolved or natural organic matter, minute colloids and viruses, etc., can still pass through the filter. The suspended liquid is made to pass through at a moderately high velocity of about 1–3 m/s and at low-to-moderate pressures, ranging between 100 and 400 kPa, parallel or tangential to the semipermeable membrane in a sheet or tubular form. After treatment through the microfilter exit, process stream has a recovery rate usually in a range of about 90–98% (Kenna and Zander 2000). MF is an extensively process as it is capable of being used at normal atmospheric pressure. Most abundantly microfiltration membranes are utilized in beverage, water, and bioprocessing industries. However, inspite of having several advantages, since the use of MF is limited to the removal of contaminants of size <1 μm (i.e., dissolved solids), it is not useful for the removal of most of the ECs.

17.1.1 Feed Permeate

Ultrafiltration (UF) UF is another variety of membrane filtration in which forces like pressure or concentration gradients lead to a separation through a semipermeable membrane (Fig. 17.6). In this process, the wastewater is dispensed in an ultrafiltration vessel. The bottom of the vessel has a membrane generally made up regenerated cellulose. The pore size in these membranes is about 0.1 μm. On being kept in the centrifuge, the centrifugal force pushes the solvent and small molecules to pass through the membrane, whereas suspended solids and solutes of high molecular weight are

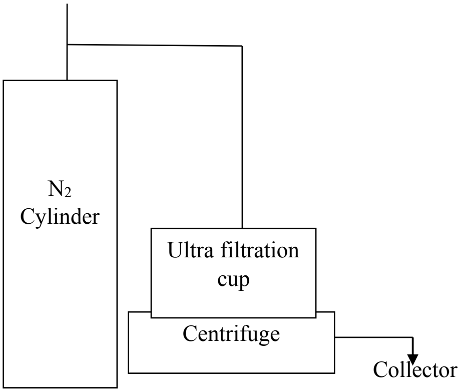

Fig. 17.6 Ultrafiltration membrane process of wastewater treatment

retained in the so-called retentate. Both the macromolecules and the solution containing the small molecules may be used for further analysis. UF membranes can be utilized for removal of micron-sized pathogens from drinking water. They can also be utilized to remove particulates and macromolecules from untreated water, to produce drinkable water. UF processes are preferred over traditional treatment methods because (i) no chemicals are required aside from cleaning and (ii) constant product quality is attained regardless of feed quality.

Those industries which consume huge volumes of water or release highly toxic effluents make use of ultrafiltration to reclaim water. Such industries are the chemicals, steel, plastics and resins, paper and pulp, and pharmaceutical industries. Food and beverage, including soft drinks and canned foods, industries also use UF process of reclaiming the effluent water from their industries.

In many cases, UF is used as prefiltration process, for example, in reverse-osmosis plants, ultra filtration is done prior to reverse osmosis in order to protect the reverse-osmosis process. UF is also frequently used to pretreat surface water, seawater, and biologically treated municipal water before directing the water to reverse-osmosis unit. UF is an efficient way of reducing the silt density index of water and remove such particulates that can taint the reverse-osmosis membranes.

Reverse Osmosis (RO) It is membrane desalination process which utilizes high stress such that water molecules are forced to pass through very small pores (holes) while preventing salts and other large molecules (Fig. 17.7). RO is the most widely used membrane desalination technology and represents 46% of global desalination capacity. The name of the process stems from the fact that high pressure is required to drive water molecules across the membrane in an opposite direction to that they would naturally move due to osmotic pressure. Since osmotic pressure needs to be overcome, the energy required to drive water molecules across the membrane is directly related to the concentration of the salt. Therefore, RO has been most often used for brackish waters that are lower in salt concentration. However, the energy efficiency and economics of RO have improved noticeably with the development of durable polymer membranes, improvement of pretreatment steps and execution of energy recovery devices. RO is now considered to be more economical than thermal methods used for treating seawater (Miller 2003; Greenlee et al. 2009).

Nanofiltration (NF) Nanofiltration is a comparatively new development in membrane technology (Fig. 17.8) which has characteristics that lie between UF and RO. While RO membranes are mostly used in the seawater desalination industries, NF

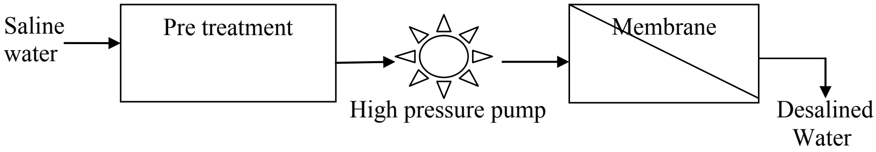

Fig. 17.7 Reverse-osmosis treatment of wastewater treatment

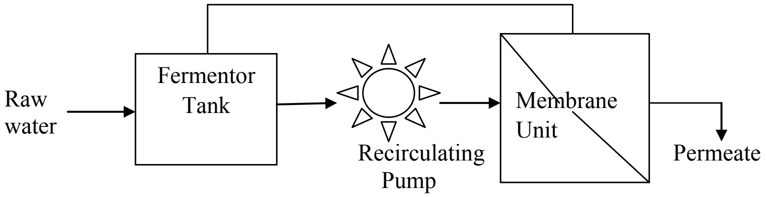

Fig. 17.8 Nanofiltration process of wastewater treatment

membranes are utilized in a number of water and wastewater treatment process and industrial applications. NF process selectively removes ions and organic substances and finds use in certain niche seawater desalination applications. The holes of nanofiltration membranes have pore sizes ranging between 1 and 10 nm. The materials which are mostly used in membrane making are polyethylene terephthalate or metals like aluminum, etc. (Baker and Martin 2007). The pore dimensions of the NF membranes are controlled by temperature, pH, and time of pores development. The pore densities range from 1 to 106 pores/cm^2. The membranes made are tracked for pore number and density after formation. “Tracking” involves bombarding the polymer thin film with high energy particles. This results in making the tracks that are chemically developed into the membrane or “etched” into the membrane, in the form of pores. “Track-etch” membranes refer to the way the pores are made on membranes (Apel et al. 2006). The solvent-stable NF membranes have found application in new areas like fragrance industries, pharmaceuticals, flavor and fine chemicals, etc. (Rahimpour et al. 2010). One of the major advantages of NF is that during the filtration process, calcium and magnesium ions are retained while small hydrated monovalent ions pass through the membranes. So, the filtration is achieved without adding any sodium salt for generating Na^+ ions, as needed in ion exchangers (Labban et al. 2017). A gentle molecular separation is also linked with NF separation processes (centrifugation). These are two of the main benefits that are associated with NF. Nanofiltration has a positive benefit of being the process that can purify large volumes of untreated waters and also constantly produce streams of product.

In spite of several benefits, NF is not a much used method of membrane filtration in industries probably because pores sizes in the membranes are limited to few nanometers only. For every minute particles, RO is used, and for bigger-sized particles, UF becomes the first choice. The main disadvantage of nanotechnology, as with other membrane filter technologies too, is the membrane cost and its maintenance (Baker and Martin 2007). NF membranes are quite expensive, and their repairs and replacement is dependent upon the total dissolved solids, other components of the feed, and flow rate. However, NF which is being used in various industries is only an estimation of replacement frequency. Nanofilters are required to be replaced at short intervals or just after their prime usage are complete.

Some major advantages and disadvantages of membrane technologies are as below.

17.2 Advantages

1. Separations are flexible and can be used for concentration and purification of a large number of contaminants.
2. The MF and UF processes can separate particle species as per their size and thus serve as highly efficient "sieves."
3. There is no phase change involved as both feed and product streams remain in the same physical phase, i.e., liquid form.
4. All the processes can function efficiently at low or room temperatures.
5. The energy required in these processes is low and hence are comparatively simple to scale up.
6. Membranes needed for different filtration processes can be manufactured through a highly precise and uniform approach.

17.3 Disadvantages

1. All the filtration processes are susceptible to membrane contamination effects that lead to the reduction in infused flux.
2. The cleaning and regeneration schemes which are usually expensive are essential.
3. Flow rates used in filtration processes are high and this can damage sensitive materials.
4. The cost of the equipment is also high.

The membrane manufacturing process has to be precisely controlled or else wide pore size distribution may result in membranes, leading to poor separation performance.

Nanotechnology Since the water industry is required to produce drinking water of high quality, there is a need for the development of cost-effective and stable materials for meeting the challenges of providing the freshwater in sufficient amounts. Nanotechnology is recently considered to be effective in solving water contamination problems related to water quality and quantity parameters. Nanoscale research has made it possible to develop economically feasible and environmentally stable treatment technologies for treating wastewater and meeting the increasing water quality standards. It has been found that nanotechnology can effectively address many water quality issues by the use of varying types of nanoparticles (NPs) and/or also nanofibers (Savage and Diallo 2005). In nanotechnology, materials of size smaller than 100 nm are used in a single dimension which means at the levels of atoms and molecules in comparison with other disciplines like engineering, materials science, and chemistry, etc. (Masciangialo and Zhang 2003), Eijkel and Berg 2005). NPs possess remarkably different physical, chemical, and biological properties mainly because of their structure, high surface area-to-volume ratio that provides treatment

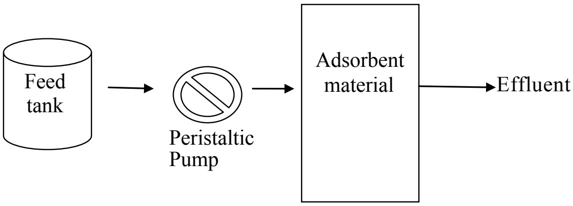

Fig. 17.9 Adsorption process of wastewater treatment

and remediation, sensing, detection, and prevention of pollution (Rickerby and Morrison 2007). These exceptional properties of nanomaterials are explored for their application in water or wastewater treatment.

TiO_2 crystals are effectively used nanoparticles for the treatment of water that has organic pollutants like benzenes, polychlorinated biphenyls (PCBs), and chlorinated alkanes as contaminants (Kabra et al. 2004). They are also used in "falling film" reactors for microcystins degradation, present in contaminated waters (Shephard et al. 2002). Nanocatalysts including semiconductor materials, zero-valence metal, and bimetallic nanoparticles have been used for degradation of environmental contaminants such as PCBs, pesticides, and azo dyes due to their higher surface area and shape-dependent properties (Zhao et al. 2011).

Phase Changing Technology Technologies that allow the movement of contaminants from one phase into another, that is from liquids to solids or vice versa, have been widely reported for removal of ECs. Adsorption processes are covered in such areas.

Several different types of pollutants can be removed from contaminated waters by adsorption processes. A general method to carry out any adsorption process is depicted in Fig. 17.9. Some of the different adsorbents utilized for removal of ECs in water are discussed below.

17.3.1 Activated Carbon (AC)

AC is one of the most commonly used adsorbent materials. It possesses high specific surface area and porosity. Such features make AC a highly effective adsorbent for removing a lot number of contaminants which also include ECs. The source from which the raw material of activated carbon (AC) is obtained plays an important role in determining its adsorption capacity, as ACs with different sources generate notably different removal rates. Some major sources of AC are wood activated with phosphoric acid, coconut shell sugar beet pulp, and peanut hulls. AC obtained from sugar beet pulp and peanut hulls can remove high amount of tetracycline antibiotic (>90%), whereas the AC obtained from activated wood removed 75% of tetracycline and that from coconut shell removed only 30% of the antibiotic (Torres-Pérez et al. 2012). This difference in the removal efficiency is attributed to the carbon structure of the raw material obtained from various sources (Rivera-Utrilla et al. 2013; Al-Othman et al. 2012). However, in general, AC has shown good results in the removal of ECs from water. The use of granular activated carbon (GAC) in an advanced wastewater reclamation plants showed that it can remove some more different types of ECs like diclofenac, ibuprofen, levofloxacin, ciprofloxacin, trimethoprim, carbamazepine, caffeine, erythromycin, N,N-diethyl-m-toluamide (DEET), and primidone drugs from water (Yang et al. 2011).

17.3.2 Biochar

Biochar is obtained from charcoal and is commonly used as a soil amendment. Unlike other carbon-based materials, biochar is prepared by heating the biomass at high temperature by the process known as pyrolysis without any oxygen (Xie et al. 2014; Ahmad et al. 2012). In the recent years and days, biochar has been utilized for adsorption of ECs (Karakoyun et al. 2011; Ji et al. 2011; Teixidó et al. 2011). Pyrolysis condition is one of the necessary features of biochar production because the process affects the capability of biochar for ECs adsorption. For instance a species classified as Arundodonax L which is used as feedstock for biochar production is used for the removal of sulfamethoxazole. Under similar reaction conditions, the biochar that was not thermally activated removed 35% of ECs, while by using thermally activated biochar, <16% of ECs removal could be achieved (Zheng et al. 2013). Such type of results can be correlated with the changes caused in acid–base and hydrophilic–hydrophobic properties of biochar. Such changes can transform the biomass of feedstock in terms of particle size and porosity which ultimately influences its capability to remove ECs. The feedstock which is used for biochar making, considerably influences its treatment effectiveness and selectivity in relation to removal of ECs. A key information in the use of biochar is related to the sustainability of its making process. The feedstock utilized for biochar production may be from agricultural waste. However, life cycle examination is essential to confirm that the waste feedstock is only used for conversion to biochar and does not have any other commendable application. In several cases, biochar production is done in incapable small-scale kilns which require an input of high energy. A precise evaluation of the carbon footprint linked to biochar production process and recognition of cleaner production processes is necessary to make sure of its sustainable use.

Inspite of having comparable characteristics, biochar does not perform similar to AC when used for coupled systems. It may be due to the type of contaminants that have to be removed by this process and also due to the material which has been used for biochar production. As biochar possesses different selectivities, it may be more competent in removal of some of the ECs that are not removed by AC (Mitchell et al. 2015). Hence, the application of biochar in sequentially coupled treatment systems requires more investigation.

17.3.3 Carbon Nanotubes (CNT)

CNTs are the allotropes of carbon having structure similar to graphite but exhibit different adsorption features that vary on the extent of whorl, the diameter, internal geometry, physical and chemical properties, the making of the original sheet, and the treatment process which has been used for synthesis (Ahmed and Theydan 2012; Ji et al. 2010a, b, Wu et al. 2012a, b and Zhang et al. 2010). Usually, these tubes are classified on the basis of their internal diameter (i.d.) as single-walled nanotubes (SWNT), if the i.d. is 1 nm (Lara et al. 2014 and Ren et al. 2011) and multi-walled nanotubes (MWNT), if numerous concentric tubes or laminated graphene layers are present together (Ren et al. 2011 and Kim et al 2014). The carbon materials differ according to their treatment for production, which is apparent by comparing the performance of CNTs, AC, and biochar. The surface area of CNTs also has an important role in their performance for removing of ECs. Single- or multi-walled CNTs structures result in different removal rates when used for the same contaminant. For instance, despite the same experimental conditions being adopted, Ji et al. (2010a, b), were able to achieve to remove 92% of tetracycline using SWNT but only 16% with MWNT. However, in the removal of other ECs, MWNT worked fairly well. For example, amoxicillin (>90%) and ibuprofen/triclosan (100%) were effectively removed by the use of MWNT (Teixidó et al. 2011; Mitchell et al. 2015 and Zheng et al. 2013). In the same way, 100% of norfloxacin was removed by using single-walled CNTs (Peng et al. 2012), but only 35% of norfloxacin could be removed by the use of MWCNTs (Yang et al. 2012). MWCNTs can be made from single-walled CNTs by the use of some extra chemical processes that enhance the contact region by several folds and the number of active sites for adsorption which results in better contaminant removal efficiency. Though these chemical treatments result in increasing the adsorption power of CNTS, it has been reported that all these features may not essentially improve the performance of CNTs because of the molecular sieving effects that occur in MWNTs (Cho et al. 2011 and Zhang et al. 2011). The removal of ECs by the use of CNTS is a vital area for advanced research because studies currently available are only limited, and therefore, more experimental support is needed to express the previously reported trends. On comparing the performance of single- and multi-walled CNTs, it has been found that the former show better performance than the latter and quite often ambiguous results are given by the use of the similar type of CNTs, in the removal of the same contaminant. The adsorptive nature of CNTs can be utilized in combination with other reactive nanomaterials for effective removal of ECs. It is an area of great importance and requires further research.

17.3.4 Clay Minerals

Clay is another material which has found application as an adsorbent in removal of ECs. The characteristics of clay as an adsorbent material govern the efficiency of the removal process, through adsorption. Similar types of clays have different removal efficiencies, and this depends on the presence of specific amount of iron or other minerals and nitrogen content (Rahardjo et al. 2011). The above fact has been proven by the studies undertaken by Wu et al. (2010 and 2012a, b), in which 35% and 100% removal of ciprofloxacin has been reported by the use of montmorillonite (MMT) clay as an adsorbent. This difference in removal efficiency was attributed to the source of the clay material. The cation exchange capacity (CEC) of adsorbent materials also plays an important role in their adsorption capacity, and these (CEC) values can be modified by impregnating with different ions to enhance the performance and selectivity of the clays (Parolo et al. 2012 and Zhao et al. 2012). The use of such approaches can demonstrate promising results, but need further thorough investigations as the fate of the contaminants and mechanisms involved in their remains is largely unknown.

17.3.5 New Adsorbents

Several other new adsorbent materials have been developed for removing of ECs from contaminated waters. These include microporous materials, resins, oxides of metals, zeolites, etc. (Ahmed et al. 2015 and Hou et al. 2010). The structure of these adsorbent materials produces a significant effect on the adsorption/removal efficiency of the adsorbents. An example of this is the study conducted by Liu et al. 2012 for the removal of tetracycline antibiotic by the use of binary oxides of Fe–Mn. Both the metal oxides were tested individually, and it was found that Mn oxide could remove >98% of the tetracycline, whereas Fe oxide could remove only 30% of the antibiotic. However, by increasing the content of Mn in the binary oxide formulation, there was a considerable decrease in removal of EC. In a similar manner, the combination of CNTs with aluminum oxide in a ratio of 1:1 increased the removal of carbamazepine EC from 0 to 70%. The chemical nature of the pollutant also plays a significant role on the efficiency of the adsorbent material. Some other examples are of pumice or zeolite which have been utilized for removal of ciprofloxacin (Ji et al. 2010a, b), use of alum oxide for adsorption of different antibiotics gave different removal results ranging from 43 to 90% (Rahardjo et al. 2011). The application of varied nature of adsorbents and molecularly imprinted polymer materials has been utilized for the removal of a variety of pharmaceuticals of (Genç and Dogan 2015; Avisar et al. 2010).

Besides the above technologies, some more recent technologies have been proposed for removal of ECs.

1. **Sonication**: Ultrasound technology has been proposed as a recent, environment-friendly process in a rising number of processes and chemical industry applications for removal of ECs. The practice of this technology is in chemistry, biotechnology, pharmacy, and environmental engineering. Ultrasound applications make use of the different effects of ultrasound for the processing of solid, liquid, and gaseous media. The process covers a unique method for the activation and quickening of several processes. Some of the water scavenging plants use the ultrasound process for disintegrating sludge. Aspirin is widely used analgesic in many countries as a life saving drug. However, it occurs in pharmaceutical wastewater as waste from pharmaceutical industry. Aspirin in the normal course takes very long to degrade in the environment but when treated in water by sonication method can degrade very fast than in the normal course. (Khedkar and Ingole 2017). The combined ozonation and sonolysis process has been reported to eliminate 90–94% diclofenac (DCF) from pharmaceuticals laden water according to the applied ultrasonic amplitude (Fraiese et al. 2019). Some other applications from the aspect of environmental engineering are in the use of ultrasound in potable water treatment.
2. **UV Irradiation/Photocatalytic Oxidation processes**: All the organic micropollutants cannot be removed only by conventional drinking water treatment. Some chemical oxidants like ozone (O_3) are capable of oxidizing a large number of ECs; however, such oxidants are ineffective in removing a large number of emerging contaminants. Some advanced oxidation processes (AOPs) like UV/H_2O_2, UV/O_3, and O_3/H_2O_2 can also be used for removal of persistent organic contaminants during treatment of drinking water. Some of these contaminants include pesticides, gasoline additives, taste and odor compounds, and pharmaceutical compounds. The removal of ECs like diclofenac (DCF), sulfamethoxazole (SMX), and carbamazepine (CBZ) in synthetically prepared aqueous solutions has been achieved by photocatalysis. More than 20% of degradation of DCF, SX, and CBZ has been achieved through oxidation by photocatalytic method (Fraiese et al. 2019).

It has been confirmed that AOPs in combination with reactive oxidants are highly effective in the removal of ECs (Oller et al. 2011; Kunkel and Radke 2008). The efficacy of AOPs is dependent upon the production of exceptionally reactive species such as hydroxyl radicals ($^{\bullet}OH$), which can degrade obstinate molecules into products that are biodegradable and ultimately get converted to CO_2, H_2O, and some inorganic ions.

17.4 Conclusion

A considerable amount of research has been undertaken in the current years for the developing technologies for removal of rising environmental pollutants like ECs in water. However, a universal method for removal of all pollutants from wastewaters is a difficult and tricky task. The conventional methods of treating wastewater are based upon preliminary, primary, secondary, and tertiary treatment technologies which involve the biological, physical, and chemical processes. The most frequently used biological process of treating wastewater is by means of activated sludge. Although the usual method of biological treatment is greatly efficient as it uses lesser space in comparison with the non-conventional methods of treatment and its performance is also independent of outdoor conditions, there are some drawbacks of these treatments as well. These include constant high electrical energy requirements, the design and maintenance, supervision, and overall the general cost of production that requires extremely skilled workers. Similarly, the membranes which are used for the removal of organic precursor matter are highly effective for the treatment of other emerging contaminants as well but here too; size exclusion is very significant and determines membrane capability. Both MF and UF are useful in removing pathogens from wastewater but they are limited only to the removal of bacteria and allow viruses and mycoplasms to pass through them. The membranes are highly sensitive to oxidative chemicals like nitric and sulfuric acids and also to peroxides and persulphates. The processes of RO and NF have the broadest range of treatment ability and have proved to be a good substitute of conventional treatment technologies. However, both are diffusion and size exclusion controlled processes and require high degree of pretreatment. NF removes harmful contaminates like pesticides and other organic macromolecules but retains minerals that have to be removed through RO. Different studies have revealed that the process of adsorption can be used as effective method for removing the emerging contaminates from the water (Simeonov and Sargsyan 2008). These water wastes can be removed by using the techniques of adsorption. Nanoparticles which have attracted a great deal of research interest in removal of ECs release persistent free radicals (PFRs) with a half life of hours and days and induce toxicity in microbes and plants. Hence, it can be concluded that,

- A single treatment technology cannot be the best strategy for the removal of ECs from contaminated waters. It is imperative to examine the use of such coupled systems that can bridge the dearth in a single technology for the removal of the complex EC from the contaminated waters.
- Though phase-change processes are effective in wastewater treatment but are not altogether successful in cases where low concentrations of EC are present in water. Besides this, these procedures also do not have any permanent solution to the problem due to generation of a concentrated phase after application of one type of phase. Hence, these procedures can be used for concentration or pretreatment and then successively coupled with further treatment(s) that are capable of degrading ECs in aqueous phase.
- The biological processes utilized for scaling-up degradation of ECs do not identify the microorganisms responsible for degradation; rather they only report their use in the form of activated sludge which is capable of removing the contaminants. Additionally, though these type of processes have been presented in the form of well-organized treatment technologies but scaling-up studies do not confirm to the experimental developments or detailed description of the processes tested.

Hence, it has resulted in a significant number of queries about the elementary processes that occur within the system.

- In research and literature, it has been mentioned that advanced oxidation processes are efficient for the degradation of ECs, but here too there is a major knowledge gap related to the industrial development or scaling-up process. A limited number of studies in this regard have been undertaken so far.

Most of the research till date is focused on industrial wastewater treatment processes. Unfortunately, neither water treatment plants (WTPs) nor STPs are designed to specifically remove PPCPs using conventional treatment methods (Hu et al. 2015). This may be due to the fact that no legislative limits exist for these micropollutants. Hence, it is imperative to adopt some recently introduced advanced treatment methods such as advanced oxidation processes (AOPs), namely ozonation, photocatalysis, ultraviolet (UV) treatment, etc., for removal of ECs. A comparison of the available technologies can then be done to account for effective in situ treatment of these contaminants.

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Chapter 18
Perfluorooctanesulfonate (PFOS), Its Occurrence, Fate, Transport and Removal in Various Environmental Media: A Review

Kiran Dhangar and Manish Kumar

18.1 Introduction

The widely used group of chemicals, perfluorinated compounds (PFCs), was first manufactured during the 1950s. The robust carbon–fluorine bond in PFCs results in distinctive physicochemical properties like high radiation, thermal, chemical, biological stability, water and oil repellence and high surface activity (Lindstrom et al. 2011; Giesy and Kannan 2001, 2002; 3M 1999; Key et al. 1997). These properties reflected its use in various household, commercial and industrial applications like upholsteries, carpets, leathers, oil-resistant coatings, paper and packaging for food contact, firefighting foams, surfactants, emulsifiers, shampoos, large polymers, pesticides, insecticides, metal plating, electronics production, photography, non-stick cookware, etc. (Baduel et al. 2015; Kostov et al. 2009; de Voogt and Sáez 2006; Begley et al. 2005; Lehmler 2005; Kissa 2001). Due to its extensive usage, careless disposal and direct-indirect discharge from manufacturing industries, it has been detected worldwide in the environment consisting of water bodies (Ahrens et al. 2010; Rayne and Forest 2009; Berger et al. 2004; Saito et al. 2004; Sinclair et al. 2006), air (Dreyer and Ebinghaus 2009; Barber et al. 2007; Kim and Kannan 2007), indoor dust (Björklund et al. 2009), human blood and serum samples (Bao et al. 2014; Kannan et al. 2004) as well as in various animals such as birds, fishes and marine animals (Murakami et al. 2011; Yeung et al. 2009; Houde et al. 2006; Giesy and Kannan 2001).

Various studies discuss the vunlnerability of the urban water to micropollutants (Kumar et al. 2019) and chemicals in the PFC family including perfluorooctane alkyl acids (PFOA) and perfluorooctanesulfonate (PFOS). However, PFOS has been one of the most focused PFC during research due to its common occurrence at global

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level. The concern regarding PFOS started to rise in the 2000s, when the renowned PFC manufacturer, 3M Company, USA, decided to phase out the production of PFOS related products. Since then, several research works and review papers started to be documented regarding the occurrence of PFOS in different environmental media such as surface water, wastewater, sludge/biosolids, groundwater, human and other biota. Some review papers summarized the fate and transport of PFOS in WWTPs, surface water and groundwater (Xiao et al. 2015; Arvaniti and Stasinakis 2015; Prevedouros et al. 2006). Limited studies are available reviewing occurrence and effect of PFOS on biota (Giesy and Kannan 2001). However, most of the review literature have been associated with particular media of occurrence or the domain of PFOS.

Based on the above, the main objective of this study is to review and summarize the currently available literature regarding the worldwide occurrence, fate and transport of PFOS in different environmental media. This study also discusses the removal technologies available for remediation of PFOS. The literature gaps are identified, and future directions are suggested accordingly.

18.2 PFOS and Its Characteristics

PFOS is one of the perfluorinated surfactant anions. Its chemical formula is $C_8F_{17}SO_3$, and its structure is shown in Fig. 18.1. Table 18.1 shows other chemical characteristics of PFOS. Its commercially important salts are potassium salt, diethanolamine salt, ammonium salt and lithium salt. PFOS has high solubility in water; hence, it is highly mobile in aqueous medium. Also, it has very negligible vapor pressure, which indicates its chances of presence in atmosphere. Under favorable conditions, PFOS possesses moderate sorption capacity toward solids (sediments/soil). Sometimes, PFOS is intentionally produced for certain purposes, but in some cases, it is unintentionally get produced due to degradation of PFOS-related substances usually referred as PFOS precursors. Some of the identified precursors of PSOF are listed in Table 18.2. Like other PFCs, PFOS also shows the strong PBT

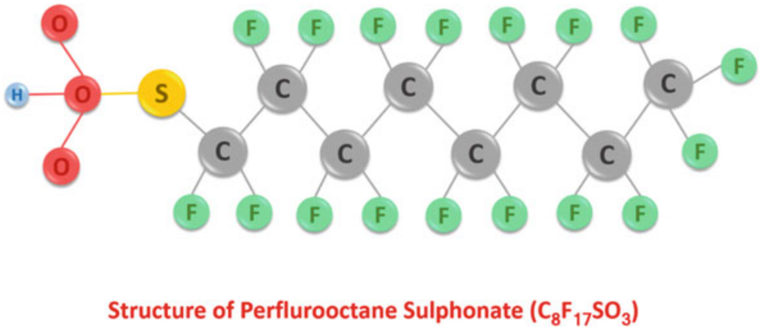

Fig. 18.1 Structure of PFOS

Table 18.1 Physical and chemical characteristics of PFOS

Characteristics	PFOS (acidic form)	References
Chemical Abstracts Service Registry No. (CASRN)	1763-23-1	
Chemical abstracts index name	1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro1-octanesulfonic acid	
Synonyms	Perfluorooctane sulfonic acid; heptadecafluoro1-octane sulfonic acid; PFOS acid	
Chemical formula	$C_8HF_{17}O_3S$	
Molecular weight (g/mol)	500.13	HSDB (2012), Lewis (2004), SRC (2016)
Color/physical state	White powder (potassium salt)	OECD (2002)
Boiling point	258–260 °C	SRC (2016)
Melting point	No data available	
Vapor pressure	2.0×10^{-3} mm Hg at 25 °C (estimate)	HSDB (2012)
Henry's law constant	Not measureable	ATSDR (2015)
pKa	<1.0	
K_{ow}	Not measureable	ATSDR (2015), EFSA (2008)
Log K_{aw}	$<2 \times 10^{-6}$	
K_{oc}	2.57	Higgins and Luthy (2006)
Solubility in water	680 mg/L	OECD (2002)
Half-life in water	Stable	UNEP (2006)
Half-life in air	Stable	UNEP (2006)

K_{ow} octanol-water partition co-efficient; K_{aw} air-water partition co-efficient; K_{oc} organic carbon-water partitioning coefficient

Table 18.2 PFOS precursors/derivatives

Chemical name	Acronym	CAS number
Potassium perfluorooctane sulfonate		2795-39-3
Lithium perfluorooctane sulfonate		29457-72-5
Ammonium perfluorooctane sulfonate		29081-56-9
Diethanolammonium perfluorooctane sulfonate		70225-14-8
Perfluorooctane sulfonyl fluoride	PFOSF	307-35-7
Tetraethylammonium perfluorooctane sulfonate		56773-42-3
Di(decyl)di(methyl)ammonium perfluorooctane sulfonate		2551099-16-8
Perfluorooctane sulfonamide	PFOSA	754-91-6
N-Methyl perfluorooctane sulfonamide	MeFOSA	31506-32-8
N-Methyl perfluorooctane sulfonamidoethanol	MeFOSE	2448-09-7
N-Methyl perfluorooctane sulfonamidoethyl acrylate	MeFOSEA	25268-77-3
Ammonium bis[2-*N*-ethyl perfluorooctane sulfonamidoethyl phosphate		30381-98-7
N-Ethyl perfluorooctane sulfonamide (sulfluramid)	EtFOSA	4151-50-2
N-Ethyl perfluorooctane sulfonamidoethanol	EtFOSE	1691-99-2
N-Ethyl perfluorooctane sulfonamidoethyl acrylate	EtFOSEA	432-82-5
Di[*N*-ethyl perfluorooctane sulfonamidoethyl] phosphate	EtFOSEP	67969-69-1
3-[(Heptadecafluorooctyl)-sulfonyl]amino]-*N*,*N*,*N*-trimethyl-1-propanaminium iodide/perfluorooctyl sulfonyl quaternary ammonium iodide	Fluorotenside-134	1652-63-7
Potassium *N*-ethyl-*N*-[(heptadecafluorooctyl) sulfonyl] glycinate		2991-51-7
N-Ethyl-*N*-[3-(trimethoxysilyl)propyl] perfluorooctane sulfonamide		61660-12-6

nature. It persists for several years in environment and travels long distances without breaking. Higher PFOS was observed in the animals in higher food chain (eagles, mink, etc.), which represents its bioaccumulative characteristics (Giesy and Kannan 2001).

18.3 Pathway (Life Cycle) of PFOS

From the current knowledge, it has been generally accepted that PFOS enters into the environment either by its direct (anthropogenic) production, usage in various applications and disposal of the products containing PFOS or by indirect sources such as degradation or transformation of its precursors (Prevedouros et al. 2006).

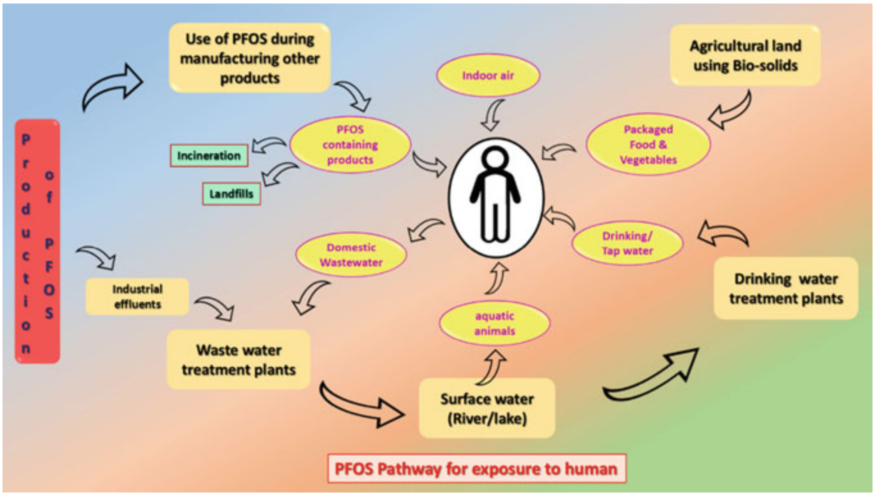

Fig. 18.2 PFOS pathway for exposure to human

Due to its high mobility in aqueous medium, it travels from industrial, commercial and domestic discharge systems to sources of natural water such as rivers and lakes (Sinclair and Kannan 2006). The wide range of applications of PFOS compounds complicates the portrayal of its pathway in the environment. Hence, based on the current literature, this review work estimates the pathway of PFOS and its routes toward exposure to human (Fig. 18.2).

After the use of PFOS containing consumer products, they are either recycled or dumped into solid waste. The solid waste is dumped into landfills either directly or after incineration in the form of ash. The landfills leachates promote entry of PFOS in soil and hence in groundwater (Cheng et al. 2010). Many studies detected PFOS in groundwater samples due to leaching from landfills or the past use of PFOS contain products (e.g. firefighting foams) (Moody et al. 2003). The conventional wastewater treatment plant is referred as a point source of PFOS emission as higher concentrations of PFOS are found than that of in raw influents (Lam et al. 2016; Sun et al. 2011; Möller et al. 2010; Ahrens et al. 2009; Huset et al. 2008). Many studies detected that the PFOS concentration increases after secondary biological treatments which is attributed to the degradation or transformation of PFOS precursors (Guerra et al. 2014; Campo et al. 2014; Arvaniti et al. 2012; Thompson et al. 2011a, b, c; Yu et al. 2009; Loganathan et al. 2007). Significant concentrations of PFOS are observed in sludge produced from such WWTPs as the result of moderate sorption mechanism (Guerra et al. 2014; Campo et al. 2014; Kim et al. 2012; Arvaniti et al. 2012). Such PFOS contaminated sludge/biosolids when used in agriculture land; they pollute the surrounding soil and groundwater too (Sepulvado et al. 2011; Washington et al. 2010). Through soil, the PFOS is bioaccumulated into the plant species and ultimately in the terrestrial food chains (Navarro et al. 2017; Wen et al. 2014; Rich et al. 2015). Due to high mobility of PFOS in aqueous medium, it travels long distance in river water without further degradation (Sinclair and Kannan 2006). Due to the presence of PFOS in the river water, PFOS was also detected in various aquatic organisms such as fishes, river minks, river otters and birds (Murakami et al. 2011; Yeung et al. 2009; Houde et al. 2006; Giesy and Kannan 2001).

18.4 Potential Hazards to Human Health and Biota

From various studies of PFOS, it is clear that PFOS is present almost everywhere which includes water, air, soil and sediments. It is not only limited to abiotic things but also found in significant concentrations in human blood samples, seminal plasma, breast milk, aquatic organisms (fishes, water birds, marine mammals, etc.), some wildlife species too (polar bears, pigs, cynomolgus monkeys, rabbits, etc.) (Bao et al. 2014; Murakami et al. 2011; Yeung et al. 2009; Houde et al. 2006; Kannan et al. 2004; Giesy and Kannan 2001). PFOS's inexplicable concentration prevents it from degradation in ecological system. PFOS has various modes of exposure to humans such as food ingestion (packed food, contaminated edible crops, contaminated fishes, etc.), drinking water and inhalation of indoor or outdoor dust (Weiss et al. 2012; Hoffman et al. 2011; Post et al. 2009; Emmett et al. 2006) (Fig. 18.2). Its bioaccumulation can cause potential risk to human health and other animals. Mostly animal studies are conducted to check the toxicity of PFOS and relate those studies to humans (Calafat et al. 2006). Such studies have been conducted on various species like monkeys, rats, rabbits, livestock, etc., for both short and subchronic durations (Seacat et al. 2002; Case et al. 2001). Such studies showed adverse effects on these animals in terms of immune effects, developmental neurotoxicity, developmental effects (survival, implications in body weight and elevated serum glucose levels and insulin resistance in adults), liver toxicity (hepatotoxicity), reproduction (mate behaviors) and cancer (liver and thyroid) (Rahman et al. 2014; Butenhoff et al. 2012; Corsini et al. 2012; Brieger et al. 2011).

Many studies detected PFOS concentrations in human blood, serum, plasma and tissues (Maestri et al. 2006). From available human epidemiology data during various studies, the health risks were associated with suppressed immune response, attention deficit in children, thyroid diseases, liver and bladder damage, high cholesterol level, low birth weights, reproductive parameters (low semen quality in men and early menopause in women), etc. (Vieira et al. 2013; Barry et al. 2013; Grandjean et al. 2012; Knox et al. 2011; Melzer et al. 2010; Hoffman et al. 2010; Joensen et al. 2009; Fei et al. 2007).

Considering the risk to human health, in May 2009, PFOS has been listed under the United Nations Stockholm Convention on Persistent Organic Pollutants (POPs) and is subjected to strict restrictions as an Annex B substance (UNEP 2010). European Chemicals Agency had also listed PFOS as a "Substance of Very High Concern" and is subject to restriction under Annex XVII, entry 53, of Registration, Evaluation, Authorization and Restriction of Chemicals (REACH), a European Union regulation

Table 18.3 International guidelines for PFOS

Country/agency	Guideline value (μg/L)		References
	Health based	Administrative	
US EPA	0.2	–	USEPA (2009)
German Ministry of Health	0.3	Composite precautionary guidance value for PFOA + PFOS is 0.1	German Ministry of Health (2006)
United Kingdom (UK) Drinking Water Inspectorate	1.0	Action levels: Tier 1: potential hazard Tier 2: >0.3 Tier 3: >1.0 Tier 4: >9	UK Drinking Water Inspectorate (2009)
Danish Ministry of the Environment	0.1	Composite drinking water criteria are based on relative toxicity of PFOS, PFOA, and PFOSA	Danish Ministry of the Environment (2015)
Dutch National Institute for Public Health and the Environment	0.53	Negligible concentration: 0.0065	RIVM (2010)
Swedish National Food Agency	0.09	Also 0.09 for the mixture of: PFOS, PFOA, PFHxS; PFBS; PFHpA, PFHsA, PFPeA (total PFASs) 0.9: Pregnant women, women trying to get pregnant, and infants should not consume if total PFASs exceed	Livsmedelsverket (2014), cited in Danish Ministry of the Environment (2015)

(European Commission Proposal 2012). It has been listed as a priority action chemical in the list of OSPAR (UNEP 2010). Apart from all these regulations, the lifetime drinking water health advisory for PFOS of 0.07 μg/L is recommended by USEPA which is applied to both short-term scenarios and lifetime long scenarios (USEPA 2016). Table 18.3 summarizes the guidelines values for PFOS established by several countries and agencies.

18.5 Worldwide Occurrence of PFOS

The worldwide occurrence of PFOS in various environmental media such as air, water, soil, wildlife as well as human tissues is an emerging concern for the environment. Its wide occurrence is attributed to the resistance for degradation in the ecological systems, which results in its bioaccumulation in various trophic levels of ecosystems. PFOS's potential hazards to human health inspired various studies for its detection in various media in order to develop mitigation and management strategies. High-performance liquid chromatography (HPLC) coupled with tandem mass spectrometry (MS/MS) was the primary detection method for PFOS (ATSDR 2015; de Voogt and Sáez 2006).

18.5.1 Occurrence of PFOS in Surface Waters

Table 18.4 gives the concentration range of PFOS detected in the surface waters from around 25 countries including the developed and developing ones. From these studies of the past two decades, it is observed that the natural surface water has higher concentration of PFOS in developed and more industrialized countries which include USA, Coastal China, England and Italy. This indicates the connection link with the production and use of PFOS-contained products in these countries. The concentration in these countries ranged from non-detection level (NDL) to some hundreds of ng/L. Some limited studies detected significantly high concentration of PFOS in countries like Spain (31–119 ng/L) (Flores et al. 2013) and South Korea (2.24–651 ng/L) (Rostkowski et al. 2006). Maximum concentration of PFOS in coastal and estuarine water of South Korea (730 ng/L) supports the fact of higher concentration in estuarine/marine water (Pan and You 2010; So et al. 2004).

Among all the studies reported, higher concentration of PFOS was detected in Spanish water. The Llobregat River and Besós River water had mean concentrations of 254 ng/L and 275 ng/L, respectively (Loos et al. 2009). Flores et al. (2013) reported average concentration range in Spanish water as 31–119 ng/L. Various studies at different locations in USA shows higher concentration of PFOS ranging from <1 to 190 ng/L (Quinones and Snyder 2009; Plumlee et al. 2008; Loganathan et al. 2007; Nakayama et al. 2007; Hansen et al. 2002) except Georgia region where maximum concentration was 22 ng/L (Loganathan et al. 2007). The high concentration areas of USA includes California, Kentucky, North Carolina and Tennessee River where the concentration value reported beyond 100 ng/L. Lake Erie and Lake Ontario in Canada (USA) reported PFOS concentration as 11–39 ng/L and 6–121 ng/L, respectively (Boulanger et al. 2004). Enormous studies have been conducted on Japanese river waters. Zushi et al. (2008) report highest concentration of Japan as 180 ng/L in Tsurumi River. The author reports that the higher concentration is attributed to the PFOS load coming from various nonpoint sources as well as discharge from nearby sewage treatment plants. The Yodo River basin also showed significant concentration up to 123 ng/L, whereas other areas such as Chubu, Chugoku, Hokkaido–Tohoku, Kanto, Kinki, Kyoto, Kyushu-Shikoku and Osaka has concentration <40 ng/L (Takagi et al. 2008; Lein et al. 2008; Senthilkumar et al. 2007; Saito et al. 2004). Taniyasu et al. (2002) conducted detection studies on bay waters of Ariake Bay, Osaka Bay and Tokyo Bay and reported their concentration as < 9–11 ng/L, <4–21 ng/L and 8.0–59 ng/L, respectively. So et al. (2007) reported concentration up to 99 ng/L in

Table 18.4 Occurrence of PFOS (ng/L) in worldwide surface waters

Country	Location	PFOS concentration (ng/L)	References
River water			
Australia	–	0–16	Thompson et al. (2011b)
Brazil	–	0.58–6.7	Quinete et al. (2009)
China	–	1.7	Kunacheva et al. (2012)
	–	<0.1–14.8	Jin et al. (2009)
	Guangzhou	0.90–99	So et al. (2007)
	Liao River	n.d.–6.6	Yang et al. (2011)
	Pearl River Delta	0.02–12	So et al. (2004)
	Yangtze River	<0.01–14	So et al. (2007)
England	–	14.4	Kunacheva et al. (2012)
France	Orge River	4.0–4.6	Labadie and Chevreuil (2011)
Germany	–	<10	Wilhelm et al. (2008)
	Rhine River	2.0–26	Skutlarek et al. (2006)
	River Elbe	<0.01–2.9	Ahrens et al. (2009)
India	–	<0.03–8.4	Mak et al. (2009)
	Indian Rivers	<0.1–3.91	Yeung et al. (2009)
	Tamilnadu	3–29	Sunantha and Vasudevan (2016)
Italy	River Olona	30.0	Castiglioni et al. (2015)
	River Po	10.0	Loos et al. (2008)
Japan	–	2.0	Kunacheva et al. (2012)
	–	<0.1–6.9	Takagi et al. (2008)
	Chubu	0.24–3.88	Saito et al. (2004)
	Chugoku	0.45–25.10	
	Hokkaido-Tohuku	0.25–4.62	
	Kanto	0.33–31.42	
	Kinki	0.78–37.32	
	Kyoto	<5.2–10	Senthilkumar et al. (2007)
	Kyushu-Shikoku	0.29–14.86	Saito et al. (2004)
	Osaka	0.26–22	Takagi et al. (2008)
	–	0.24–37.3	Saito et al. (2004)
	Tsurumi River	180.0	Zushi et al. (2008)
	Yodo River	0.4–123	Lein et al. (2008)
Laos	–	1.3	Kunacheva et al. (2012)

(continued)

Table 18.4 (continued)

Country	Location	PFOS concentration (ng/L)	References
Malaysia	–	1.5	Kunacheva et al. (2012)
	Kota Kinabalu	<0.1–3.4	Lien et al. (2006a, b)
Nepal	–	2.6	Kunacheva et al. (2012)
Sri Lanka	–	1.1	
Singapore	–	5.5	
Spain	Spanish surface water	31–119	Flores et al. (2013)
	Llobregat River	254	Loos et al. (2009)
	Besós River	275	
	Catalan Rivers	1.09–9.56	Sánchez-Avila et al. (2010)
Sweden	–	1.2	Kunacheva et al. (2012)
Taiwan	–	3.5	
Thailand	–	0.8	Kunacheva et al. (2012)
	Phong River	<0.1–1.1	Lien et al. (2006a, b)
Turkey	–	1.0	Kunacheva et al. (2012)
U.K.	–	<11–208	Atkinson et al. (2008)
USA	–	<1–57	Quinones and Snyder (2009)
	California	20–190	Plumlee et al. (2008)
	Georgia	1.8–22	Loganathan et al. (2007)
	Kentucky	7.0–149	
	North Carolina	132.0	Nakayama et al. (2007)
	Tennessee River	16.8–114	Hansen et al. (2002)
Vietnam	Hanoi, Danang, Hue and Ho Chi Minh City	0.18–5.3	Duong et al. (2015)
	Red River	0.21	
Lake water			
Africa	Lake Victoria	<0.1–2.5	Orata et al. (2009)
Canada/USA	Lake Erie	11–39	Boulanger et al. (2004)
	Lake Ontario	6–121	
China	Taihu Lake	3.6–394	Yang et al. (2011)
Italy	Lake Maggiore	9.0	Loos et al. (2007)
South Korea	Shihwa and Banweol	2.24–651	Rostkowski et al. (2006)
Coastal and Bay water			
Australia	Moreton Bay	0.64–2.3	Gallen et al. (2014)

(continued)

Table 18.4 (continued)

Country	Location	PFOS concentration (ng/L)	References
	Sydney Harbour/Parramatta River	7.5–21	Thompson et al. (2011a)
China	East to South China Sea	<0.02–0.07	Cai et al. (2012)
	Hong Kong	0.73–5.5	So et al. (2004)
	South China Sea	0.24–16	
Germany	German Bight	0.69–3.95	Ahrens et al. (2009)
Japan	Ariake Bay	<9–11	Taniyasu et al. (2002)
	Osaka Bay	<4–21	
	Tokyo Bay	8.0–59	
Korea	Estuarine and coastal of Korea	4.11–450	Naile et al. (2013)
South Korea	–	0.04–730	So et al. (2004)

Guangzhou region of China, whereas other areas such as Liao River, Pearl River Delta and Yangtze River reported concentration below 15 ng/L. As per the study of Yang et al. (2011) on Taihu Lake of China, PFOS found at higher concentration up to 394 ng/L. In one of the limited studies in United Kingdom, higher concentration (208 ng/L) was reported at one of the 15 risk sites (Atkinson et al. 2008). The reason stated was nearby pollution load caused by oil depot and nearby airfields. On the other side, studies in some countries such as Australia, Germany, India and Italy reported PFOS concentration below 30 ng/L (Sunantha and Vasudevan 2016; Castiglioni et al. 2015; Thompson et al. 2011b; Skutlarek et al. 2006). On one side, many countries are reporting higher concentrations which can cause potential hazards to human and ecological systems, whereas on another verge, some countries have very low or negligible PFOS contamination in their river waters. Studies conducted in the countries like France, Laos, Malaysia, Nepal, Sri Lanka, Singapore, Sweden, Taiwan, Thailand, Turkey and Vietnam reported very low concentration of PFOS (Duong et al. 2015; Kunacheva et al. 2012; Labadie and Chevreuil 2011; Lien et al. 2006a, b).

18.5.2 Occurrence of PFOS in Wastewater Treatment Plants (WWTPs)

PFOS has been detected in wastewater influents from both domestic and industrial sources. The occurrence of PFOS in WWTPs in 14 countries across the continents is summarized in Table 18.5. As PFOS is resistant to biodegradation, its removal

Table 18.5 Occurrence of PFOS in sludge, influents and effluents of wastewater treatment plants (ng/L) in various countries

Country	Location/description	PFOS concentration			References
		Influent (ng/L)	Effluent (ng/L)	Sludge (ng/g dw)	
Australia	Plant with advanced treatments (UF, RO)	23–39	0.2–0.5	–	Thompson et al. (2011c)
	Plant having several stages of ozonation	2.2–3.7	0.3–0.7	–	
Canada	Influents and effluents of 20 WWTPS	2–1100	1–1300	9.7–8200	Guerra et al. (2014)
China	Beijing	0.03–12	0.04–7.3	0.69–16.7	Pan and You (2010)
	Hong Kong	29.4–49.9	19–28.8	3.1–157.9	Ma and Shih (2010)
Denmark	Domestic and commercial waste water	<1.5–10.1	<1.5–18.1	4.8–74.1	Bossi et al. (2008)
Germany	Bayreuth, Northern Bavaria	44.0	86.0	80–120	Becker et al. (2008)
Greece	Athens	5–61.8	7.5–25.3	4.6–11.3	Stasinakis et al. (2013)
	Athens (80% domestic + 20% industrial effluent)	2.4–26.3	5.2–21.0	1.8–16.7	Arvaniti et al. (2012)
	Mytilene (100% domestic effluent)	1.0–6.3	<0.18–0.45	0.58–3.8	
Japan	Kanto	14–336	42–635	–	Murakami et al. (2009)
	Tsurumi River basin	–	79–640	–	Zushi et al. (2008)
Korea	Domestic plant	0.9–40	0.9–8.9	3.3–54.1	Guo et al. (2010)
Singapore	40% domestic + 60% industrial effluent	56.30–374.5	95.6–461.7	291.6–390.1	Yu et al. (2009)
	95% domestic + 5% industrial effluent	7.9–25.3	7.3–16.7	28.2–35.2	
Spain	Ebro, Guadalquivir, Jucar and Llobregat Rivers	78.1–118	76.7–91.0	41.4–229	Campo et al. (2014)

(continued)

Table 18.5 (continued)

Country	Location/description	PFOS concentration			References
		Influent (ng/L)	Effluent (ng/L)	Sludge (ng/g dw)	
Switzerland	Bellinzona and Geneva	–	–	49–130	Alder and van der Voet (2015)
	WWTPs of the Glatt Valley	18–449	16–303	–	Huset et al. (2008)
	Zurich (Digested sludge)	–	–	20–600	Sun et al. (2011)
Taiwan	Hsinchu	175–216.7	162.7–264.7	–	Lin et al. (2010)
Thailand	Central Thailand	465.4	190.1	82.3	Kunacheva et al. (2011)
	Eastern Thailand	381.3	552.8	683.7	
USA	10 WWTPs	1.0–429	0.5–141	–	Schultz et al. (2006)
	California (4 WWTPs)	–	20–187	–	Plumlee et al. (2008)
	Georgia	2.5–7.9	1.80–13	22–70	Loganathan et al. (2007)
	Kentucky	7.0–16	8–28	133–993	
	Lowa	–	26.0	–	Boulanger et al. (2005)
	New York (6 WWTPs)	–	3–68	<10–65	Sinclair and Kannan (2006)

efficiency in conventional WWTPs with biological treatments is very low or negligible, and sometimes it gives negative removal efficiency (Campo et al. 2014; Guerra et al. 2014; Arvaniti et al. 2012; Thompson et al. 2011c; Yu et al. 2009; Loganathan et al. 2007). Hence, WWTPs are also referred as point sources for releasing PFOS in surface water streams (Lam et al. 2016; Sun et al. 2011; Möller et al. 2010; Ahrens et al. 2009; Huset et al. 2008). Various studies detected PFOS concentrations in influents, effluents as well as sludge of several WWTPs. Higher PFOS load was observed from industrial sources than that of the commercial and domestic wastewater sources (Arvaniti et al. 2012; Yu et al. 2009)

Higher concentration was observed in developed and industrialized countries such as USA and Japan. Schultz et al. (2006) detected higher concentration of PFOS in both influent (1.0–429 ng/L) and effluent (0.5–141 ng/L) samples of 10 WWTPs of USA. However, the opposite case was observed in the study done by Loganathan et al. (2007) in WWTPs of Georgia and Kentucky region of USA. In both regions, higher concentration is detected in effluents than that of influents which results in negative removal efficiency. High range of PFOS concentration was observed in the sludge from Kentucky (133–993 ng/g dw), whereas the concentration detected in the sludge of WWTPs of Georgia was 22–70 ng/g dw. In the reported study of Canada, wide concentration range of PFOS was observed in the influent stream (2–1100 ng/L), effluent stream (1–1300 ng/L) and effluent sludge (9.7–8200 ng/g dw) (Guerra et al. 2014). From the reported study by Murakami et al. (2009) in Kanto area of Japan, the maximum concentration in the effluent (42–635 ng/L) was found to be double than the maximum of influent water samples (42–635 ng/L). Whereas in WWTPs of the Tsurumi River basin of Japan, PFOS concentration in the range of 79–640 ng/L was found in the effluent streams (Zushi et al. 2008). Kunacheva et al. (2011) report removal efficiency around 50% for PFOS in WWTPs of Central Thailand and negative removal efficiency in WWTPs of Eastern Thailand. In case of WWTPs of some countries such as Singapore, Spain, Switzerland and Taiwan, removal efficiency <10% was observed during the biological treatments of the wastewater influents (Alder and van der Voet 2015; Campo et al. 2014; Sun et al. 2011; Yu et al. 2009; Huset et al. 2008). Some countries like Denmark, Greece and Korea reported relatively less PFOS concentrations in influent stream, effluent stream as well as in the sludge (Stasinakis et al. 2013; Arvaniti et al. 2012; Guo et al. 2010; Bossi et al. 2008). Thompson et al. (2011a, b, c) traced the concentration of PFOS in the wastewater during its journey in WWTPs having two different advanced treatment technologies. Plant with treatments like ultrafiltration (UF) and reverse osmosis (RO) showed more than 98% removal efficiency, whereas plant having several stages of ozonation gave around 90% efficiency.

18.5.3 Occurrence of PFOS in Drinking/Tap Water

The occurrence of PFOS in drinking or tap water is the effect of its pre-presence in surface water systems and less effective drinking water treatments. Some advanced treatments like ultrafiltration, reverse osmosis, etc., found effective for PFOS removal from water, but many municipal water treatments facilities do not have these treatments due its high installation and maintenance cost. Table 18.6 summarizes the occurrence of PFOS in drinking/tap water samples tested across various countries. The Spanish drinking water showed highest PFOS concentration (<0.12–58.12 ng/L) among the reported studies (Ericson et al. 2009). This indicates the direct correlation between high surface water or raw water concentration and drinking water concentration. Other countries such as Japan (0.16–51 ng/L) and United Kingdom (<11–45 ng/L) also showed higher concentrations in some samples (Takagi et al. 2008; Atkinson et al. 2008; Fujii et al. 2007). Concentration between the range of 11–25 ng/L was reported in some countries such as China, Germany and USA (DWHA, US EPA 2016; Ullah et al. 2011; Mak et al. 2009; Fujii et al. 2007; Skutlarek et al. 2006). Concentration level was below concern level in countries such as Belgium,

Table 18.6 Occurrence of PFOS (ng/L) in worldwide drinking/tap water

Country	Location	PFOS concentration (ng/L)	References
Belgium	University of Antwerp	2.71	Ullah et al. (2011)
China	–	1.5–13.2	Fujii et al. (2007)
	Shanghai and Shenzhen	7.6–11	Mak et al. (2009)
Germany	Fraunhofer Institute, Schmallenberg	0.847	Ullah et al. (2011)
	Rhine-Ruhr	0–22	Skutlarek et al. (2006)
India	Goa, Coimbatore, Chennai, Patana	<0.04–8.4	Mak et al. (2009)
Italy	IES, ISPRA	6.92	Ullah et al. (2011)
	Lake Maggiore	8.1	Loos et al. (2007)
Japan	Osaka	0.16–51	Takagi et al. (2008), Fujii et al. (2007)
	WWPs near Yodo river Basin	3.9–9.4	Shivakoti et al. (2010)
Malaysia	–	0.1	Fujii et al. (2007)
Netherland	University of Amsterdam	0.861	Ullah et al. (2011)
	VU University, Amsterdam	0.397	
Norway	NIAR, Tromsø	0.573	Ullah et al. (2011), Haug et al. (2010)
Spain	Catalonia	<0.12–58.12	Ericson et al. (2009)
Sweden	–	0.3–0.8	Fujii et al. (2007)
	Stockholm University	8.81	Ullah et al. (2011)
Thailand	–	0.1–1.9	Fujii et al. (2007)
UK	–	<11–45	Atkinson et al. (2008)
USA	Albany	1.4	Mak et al. (2009)
	New Jersey	4.2–19	DWHA, US EPA (2016)

India, Italy, Malaysia, Netherland, Norway, Sweden and Thailand (Ullah et al. 2011; Haug et al. 2010; Mak et al. 2009; Loos et al. 2007; Fujii et al. 2007). However, the increasing concentration of PFOS in surface water systems is critical for future directions regarding the drinking water facilities and treatments.

18.5.4 Occurrence of PFOS in Human and Biota

The manufacturing of PFOS and its extensive use in various industrial activities and domestic products has not only affected the abiotic components but also increased its exposure to various biotic components including human. PFOS has been detected in humans, fishes, birds and mammals throughout the world (Bao et al. 2014; Murakami et al. 2011; Yeung et al. 2009; Houde et al. 2006; Kannan et al. 2004; Giesy and Kannan 2001). As PFOS is robust to biodegradation, it is persistent in environment and hence shows bioaccumulative nature among the ecological trophic levels via food chain. Giesy and Kannan (2001) have reported the global distribution of PFOS in the tissues of wildlife. The species selected for this study were from urbanized areas, coastal and marine waters, lake areas and remote areas like Arctic and Pacific Ocean areas. The species having traces of PFOS concentration included aquatic mammals (ringed seals and other species of seals, otters, mink, dolphins, polar bears and sea lions), birds (double crested cormorant, gull, albatrosses and bald eagle), fishes (whitefish, salmon, brown trout and tuna), turtles and frogs (Giesy and Kannan 2001). Houde et al. (2006) have done excellent review discussing biological monitoring of PFOS and other PFCs in human and wildlife, comparison of concentrations profiles among various species and their locations, evaluation of bioaccumulation in the ecosystems and various possible sources of exposure to wildlife.

Various studies have reported PFOS concentration in human tissues such as serum, plasma and blood. Higher concentrations were detected in blood and serum samples of people from USA and Canada as compared to those from Southern Hemisphere Europe and Asia (Houde et al. 2008). Table 18.7 shows reported concentrations of PFOS in human blood, serum and plasma from various countries. The results indicate that many people from developed and industrialized countries are exposed to PFOS significantly, whereas less exposure has happened to people from developing nations.

18.6 PFOS Removal Using Advanced Technologies

Several emerging contaminants and heavy metals has shown promising removal by many sustainable and economic treatment technologies (Mukherjee et al. 2020; Shim et al. 2018, 2019a, b; Borah et al. 2018; Kumari et al. 2018a, b; Ahmed et al. 2017; Kumar et al. 2017; Matamoros et al. 2016; Gogoi et al. 2015). But for PFOS, From the available literature, it is widely accepted that PFOS does not degrade during conventional biological wastewater treatment processes. There was no evidence of biodegradation of PFOS compounds (Schultz et al. 2006; Key et al. 1998). It is inert/recalcitrant to most of the conventional treatment too. Instead its concentration found to be increasing in such treatments due to the degradation of its precursors (Guerra et al. 2014; Campo et al. 2014; Arvaniti et al. 2012; Yu et al.

Table 18.7 Concentration of PFOS (ng/ml), mean (range) in human blood samples from different countries

Sample details	Country	No. of samples	PFOS concentration (ng/ml)	References
Plasma	Belgium	20	13.9 (4.5–27)	Kannan et al. (2004)
	Northern Canada	NA	36.9 (2.8–57.9)	Tittlemier et al. (2004)
Serum	Brazil	27	12.1 (4.3–35)	Kannan et al. (2004)
	Colombia	56	8.2 (4.6–14)	
	India	45	2.0 (< 1–10.3)	
	Italy	50	4.3 (< 1–10.3)	
	Japan	38	17.1 (4.1–40.3)	
	Japan (Yodo river Basin)	100	NA (16.3–57.7)	Harada et al. (2007)
	Korea	50	21.1 (3.0–92)	Kannan et al. (2004)
	Malaysia	23	12.4 (6.2–18.8)	
	Poland	25	44.3 (16–116)	
	USA	645	34.9 (<4.3–1656)	Olsen et al. (2003)
	USA (Michigan, Kentucky and New York)	175	49.5 (<1.3–164)	Kannan et al. (2004)
	USA, Atlanta	20	NA (3.6–164)	Kuklenyik et al. (2004)
Whole blood	Japan	10	9.0 (2.4–14)	Taniyasu et al. (2003)
		26	8.1 (2.0–20.2)	Masunaga et al. (2002)
	Sweden	66	18.2 (1.7–37)	Karrman et al. (2006)

2009; Loganathan et al. 2007). PFOS reacts slowly with OH radicals which makes advance oxidation processes (AOPs) ineffective to treat PFOS (Hori et al. 2004). As biodegradation of PFOS is associated with slow kinetics profile, advanced degradation and treatment processes were explored. The recent promising advanced processes involved use of physical processes and certain redox processes (Fig. 18.3). The physical processes involve removal by adsorption and filtration processes. The redox processes consist of various oxidation and reduction processes such as electrochemical (Lin et al. 2012; Niu et al. 2012; Zhuo et al. 2011), sonochemical (Lin et al. 2016; Vecitis et al. 2008, 2010; Cheng et al. 2008, 2010; Moriwaki et al. 2005), photochemical (Li et al. 2012; Qu et al. 2010; Cao et al. 2010; Hori et al. 2004), plasma (Obo et al. 2015) and subcritical processes (Hori et al. 2006, 2009; Yamamoto et al.

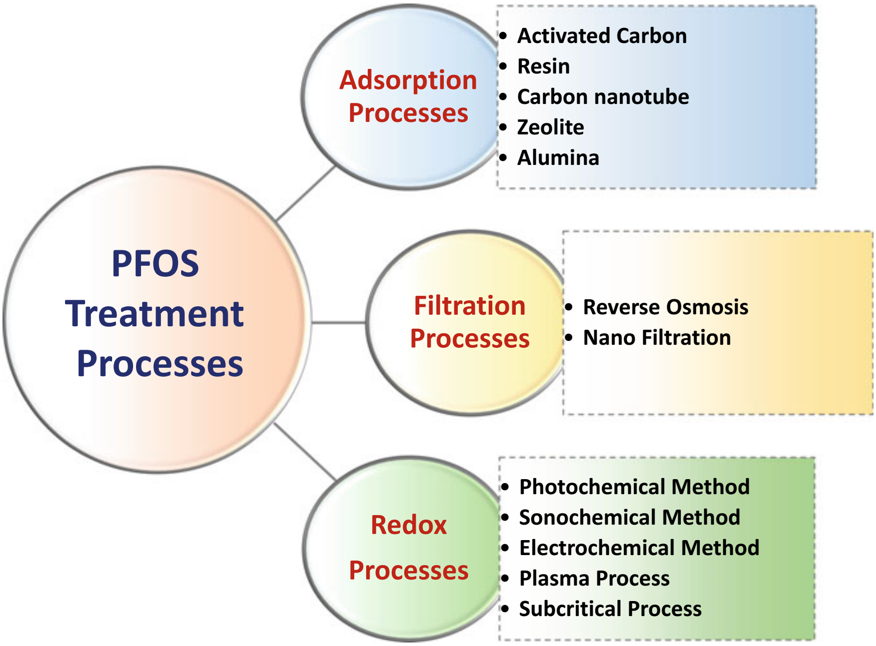

Fig. 18.3 Available treatment processes for PFOS removal

2007). Most of the mentioned methods were used on natural or pure water samples; hence, it should be noted when applying to wastewater samples.

18.6.1 Adsorption Processes

Table 18.8 summarizes several studies published on the removal of PFOS using adsorption processes. Various adsorbent materials used were chitosan, activated carbon (AC), zeolite, resin, goethite, carbon nanotubes and alumina. Out of two forms of AC used powdered activated carbon (PAC) showed faster and higher adsorption potential than that of the granular activated carbon (GAC). Less equilibrium time (6 h) was observed during PAC treatment (Rattanaoudom et al. 2012; Yu and Hu 2011; Liang et al. 2011; Qu et al. 2009; Yu et al. 2009), whereas GAC treatment required higher equilibrium time (up to 168 h) (Senevirathna et al. 2010; Yu et al. 2009; Ochoa-Herrera and Sierra-Alvarez 2008). The smaller pore size and particle diameter of the PAC result the higher surface area in comparison with GAC within the same volume of the carbon (Rahman et al. 2014; Du et al. 2014). Additionally, it provides more surface functional groups. The presence of the organic matter in the water reduces the efficiency of adsorbents as it creates competition in adsorption sites (Yu and Hu 2011). Various other factors affecting adsorption are pH, ionization state,

Table 18.8 PFOS removal by adsorption process

Matrix	Absorbent material	Dosage (g)	Equilibrium sorption capacity for PFOS	References
Water	Chitosan-based molecularly imprinted polymer	0.01	550 (μmol/g)	Yu et al. (2008)
	PAC	0.01	0.60–0.69 (mmol/g)	Yu et al. (2009)
	GAC		0.41–0.51 (mmol/g)	
	Resin		0.34–0.36 (mmol/g)	
	Resin	0.01	0.53–5.70 (mmol/g)	Deng et al. (2010)
	Goethite	NA	44 (μg/m)	Tang et al. (2010)
	Carbon nanotube	<0.03	149–237 (mg/g)	Chen et al. (2011)
	Carbon nanotube	0.001	0.75 (mmol/g)	Li et al. (2011)
	PAC	0.02	376.10–480.34 (mg/g)	Wang and Shih (2011)
	Alumina	0.2	0.252 (μg/m)	Yu and Hu (2011)
	Cross-linked chitosan beads	0.015	0.72–5.04 (mmol/g)	Zhang et al. (2011)
	PAC	NA	486.34 (mg/g)	Punyapalakul et al. (2013)
	Zeolite		38.96 (mg/g)	
	GAC	0.01	22.1 (mg/g)	Yao et al. (2014)
	Resin		22.0 (mg/g)	
	Carbon nanotube		21.3 (mg/g)	
Wastewater	PAC	0.1	0.128 (mmol/g)	Rattanaoudom et al. (2012)

temperatures and electrostatic interactions (Tang et al. 2010). Under low pH conditions, electrostatic interactions increase the sorption capacity (Higgins and Luthy 2006). In recent comparative studies, the sorption potential for PFOS was examined using various adsorbents such as double and multi-walled carbon nanotubes, non-ion and anion exchange resins, PAC, GAC, silica and alumina. With removal efficiency up to 98%, PAC and anion exchange resin were the most effective adsorbents.

18.6.2 Filtration Processes

As the conventional sand filters failed to remove PFOS from the water (Eschauzier et al. 2010; Takagi et al. 2011), advanced membrane filtration methods such as nanofiltration and reverse osmosis were examined for the same (Appleman et al. 2013; Schröder et al. 2010; Steinle-Darling and Reinhard 2008; Tang et al. 2007). Nanofiltration showed promising potential to remove PFOS from water/wastewater with the efficiency ranging from 90 to 99% (Schröder et al. 2010; Tang et al. 2007). According to the literature, due to smaller pore size and membrane selectivity, reverse osmosis is more effective as compared to nanofiltration (Tang et al. 2007). The membrane fouling in such filtration processes can be controlled by using pretreatments such as pre-oxidation and coagulation (Deka et al. 2020).

18.6.3 Redox Processes

The recent redox processes are very popular and promising for removal of PFOS, as it gives complete mineralization. Various energy sources have been used in redox processes for PFOS removal.

Photochemical Method: During photochemical processes, an inexhaustible energy source, solar energy, is used as photocatalytic force to degrade PFOS. PFOS degradation has been carried out using both photo-oxidation and photo-reduction technologies. Though photo-oxidation is commonly used, photo-reduction technology found more effective for PFOS degradation (Wang et al. 2017). Under mild conditions, higher defluorination and decomposition are obtained by photochemical methods. Till date, various photolytic methods such as photocatalysis (Hori et al. 2004), persulfate photolysis (Chen and Zhang 2006; Hori et al. 2005), hydrogen peroxide photolysis (Hori et al. 2004), persulfate photolysis (Chen and Zhang 2006; Hori et al. 2005), alkaline isopropanol photolysis (Yamamoto et al. 2007), direct photolysis (Yamamoto et al. 2007; Chen and Zhang 2006; Hori et al. 2004) and photo-Fenton (Tang et al. 2012; Wang et al. 2008; Hori et al. 2007) have been used to effectively degrade PFOS in water samples.

Sonochemical Method: Sonochemical treatment is effective to degrade PFOS in water over wide range of concentrations (Vecitis et al. 2008). Ultrasonic irradiation is used to induce acoustic cavitation, which produces high temperature enough for pyrolysis at the bubble–water interface (Vecitis et al. 2008). This in situ pyrolysis results faster and complete degradation of PFOS into fluoride (F^-), sulfate (SO_4^-), CO and CO_2. Half-life of 30 min has been reported for PFOS degradation via sonochemical method (Vecitis et al. 2008).

Electrochemical Method: Recently, PFOS has been treated via the first-order kinetics by electrochemical process using a divided electrochemical cell with Ti/RuO_2 anode and boron-doped diamond (BDD) anodes in undivided cells (Zhuo et al. 2011; Ochiai et al. 2011; Carter and Farrell 2008). During these experimental studies, fluorine was generated, which clearly indicates PFOS defluorination. As most of the studies have been conducted on synthetic groundwater samples, more future studies need to be conducted under relevant environmental conditions. Preliminary investigations should be carefully done as some studies noted the perchlorate formation in chloride-containing ground waters (100 mg/L of chloride resulted >1 mg/L increase in perchlorate) (Donaghue and Chaplin 2013; Pérez et al. 2012).

Plasma Process: According to a recent experimental study, generating plasmas generating within the bubbles in water, PFOS can be decomposed efficiently (Obo et al. 2015). High-voltage direct current of several kilovolts is applied across the bubbles to generate the plasmas. Due to high surface activity of PFOS, it adheres to air bubbles, and hence, plasmas within the bubble can selectively decompose PFOS. But, due to smaller contact surface area of plasmas (within 4 mm diameter bubble), the decomposition/degradation process is slower. Removal can be accelerated by generating multiple plasmas and increasing time as well as energy efficiencies (Obo et al. 2015).

Subcritical Process: Processes carried out in sub/supercritical water are the innovative and environment friendly reaction techniques (Jessop and Leitner 2008). A hot water with maintained pressure for liquid state is known as subcritical water. Subcritical water possesses various desirable reaction characteristics such as low viscosity, high diffusivity and hydrolyzing ability for many organic compounds (Hori et al. 2006). According to the reported study (Hori et al. 2006, 2009), pure subcritical water at ~350 °C was not able to degrade PFOS, but it can be decomposed by adding reducing agent, zero-valent iron (ZVI) powder, in the medium (water). Commercial nanoscale ZVI (nZVI) (coated and uncoated) was used to investigate removal of PFCs, where PFOS showed higher removal efficiency under high dosage of nZVI (1000 mg/L), acidic condition ($\text{pH} = 3$) and low temperature (20 °C) (Arvaniti et al. 2015). The mechanism behind PFOS removal was reported as sorption as well as degradation. No other byproducts were detected by LC–QTOF–MS during defluorination of PFOS.

18.7 Future Perspectives Toward Research

From the available literature, work regarding PFOS research or knowledge gap has been identified, and future directions have been proposed accordingly as follows:

1. Till date, PFOS has been studied mostly in its dissolved form; hence, detailed investigations should be conducted for PFOS in particular phase.
2. Factors causing negative removal efficiency (higher concentration in effluent than that of influent) of PFOS during biological treatments have not been well documented. Hence, detailed studies should be conducted for monitoring the PFOS concentration at various stages of treatment processes.
3. Detailed monitoring studies of advanced treatments on large scale and at normal conditions are needed.
4. Various factors responsible for solid/water partitioning regarding PFOS need to be conducted for understanding the fate of PFOS.

5. Factors governing the transport behavior of PFOS across various environmental media should be investigated in detail.
6. Ultimately, to avoid or minimize the potential hazards of PFOS, its alternative materials should be investigated.

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