Emerging Contaminants and Associated Treatment Technologies

Paromita Chakraborty
Daniel Snow *Editors*

Legacy and Emerging Contaminants in Water and Wastewater

Monitoring, Risk Assessment and Remediation Techniques

Springer

Emerging Contaminants and Associated Treatment Technologies

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Preface

Freshwater resources are under growing pressure from a rapidly increasing population with expanding needs for sustainable food supply and improved living standards. Pollution of rivers, lakes, and groundwater by legacy and emerging contaminants is an inevitable outcome of agricultural and economic development in every country. Persistent pesticides and other legacy contaminants continue to be released either through continued use or hydrospheric recycling of previous releases. Emerging contaminants, such as pharmaceuticals and hormones, are released in ever-greater quantities through wastewater discharge and can have lasting effects on organisms living in receiving waters. Societies everywhere need to understand how to accurately monitor and control releases of these pollutants to help conserve and protect water for drinking, irrigation, recreation, and habitat. Legacy and emerging contaminants in water and wastewater are widely dispersed throughout the environment, generally occurring at low concentrations in complex matrices which render them difficult to measure. To adequately protect freshwater, we need to measure and understand their occurrence, transformation, and potential effects on ecosystems and human health. Further, it is imperative to find possible remediation techniques to remove toxicants from water and wastewater. It is hoped that, with the knowledge and information presented here, readers will better understand the tools available to them to design better monitoring programs and improved treatment and remediation technologies and help prioritize these contaminants through risk assessment.

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About the Editors

Daniel Snow is a research professor at the University of Nebraska and director of the Water Sciences Laboratory, a part of the Nebraska Water Center and Robert B. Daugherty Water for Food Institute. Over the past more than 30 years, his research has focused on studying the environmental fate of emerging contaminants and agrichemicals in ground and surface water. He directs staff and students in the development of analytical methods using advanced mass spectrometry technologies to better understand and protect water resources. He has coauthored over 200 refereed journal articles, book chapters, and conference proceedings. He is an associate editor for the journals *Bulletin of Environmental Contamination and Toxicology* and *MDPI Water*. He has also served as a review panelist and consultant for the American Association of Analytical Chemists, Environmental Protection Agency, National Science Foundation, Department of Defense, Gulf of Mexico Research Initiative, CRDF Global, and several international research funding programs.

Paromita Chakraborty is an associate professor in the Department of Chemical Engineering at SRM Institute of Science and Technology, Kattankulathur, Tamil Nadu. Dr. Chakraborty leads the environmental science and technology research group and works on the multimedia transport of legacy and new persistent organic pollutants, bioavailability of organic contaminants, environmental chemistry, transformation and remediation of endocrine disrupting compounds, mismanagement of plastic and electronic waste, and conversion of waste into wealth. Dr. Chakraborty is the principal investigator for projects funded by national funding agencies like DST and MoEFCC, and international funding agencies like Research Council of Norway, Norwegian Embassy, and Swiss Development Cooperation. She has published over 100 peer-reviewed journal articles and book chapters. Her research has been used as the basis for the creation of several policy briefs that were important for decision makers. She is the recipient of the prestigious Water Advanced Research and Innovation (WARI) Fellowship 2016, awarded by the Indo-US Science and Technology Forum. Among numerous awards that Dr. Chakraborty received, Early-Career Chemist 2015 and Hiyoshi Environmental Award 2020 are the most prestigious. Dr. Chakraborty is the special mentor for the Association of Commonwealth Universities Blue Charter Fellowship. She is an associate editor in the *Arabian Journal of Geosciences* and is in the editorial board of the journal *Science of the Total Environment*.

Part I
State of the Science on Organic Micropollutants in Water and Wastewater

Source, Treatment, and Management Options of Contaminants of Emerging Concerns (CECs) in Water

Harikaranahalli Puttaiah Shivaraju, Yadav Sneha, Shivamurthy Ravindra Yashas, and B. Das Diganta

Abstract Contaminants of emerging concern (CECs) are defined as pollutants present in negligible amounts in the environment, which have not been detected previously and cause high-level environmental and health risks. These CECs include pharmaceutical and personal care products, endocrine-disrupting chemicals, persistent organic compounds, disinfection by-products, phthalate compounds, etc. The present chapter reveals the different contamination sources of CECs including point and non-point sources and types of contamination in the context of health and environmental problems. The existing water and wastewater treatment techniques and novel remediation approaches including merits and demerits are discussed in detail. Potential technologies in the treatment of CECs in water and wastewater such as adsorption, advanced oxidation processes, membrane processes, and hybrid techniques are also discussed in the perspective of resilience and implantation. Centralized and de-centralized treatment strategies including novel treatment approaches at point of entry and point of use are well explained with suitable illustration. Safe and sustainable management and treatment approaches including regulatory, citizen science, networking, technological, and other strategies, which have been demonstrated for real-time application, are well elucidated for sustainable management of CECs in different environments.

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Keywords Contaminants of emerging concern (CECs) · Health risks · Personal care products · Wastewater treatment · Safe and sustainable

1 Introduction

Over 70% of the earth's surface is covered with water. It is considered as one of the most valuable resources and is the primary support on the earth. Water acts as a requirement source for almost each and every species. Also, it acts as a carrier for various organic or inorganic chemicals, diseases, energy, etc. The modernized development of emerging new technologies has created advancement in the field of science. However, these resources have added up potential increases of chemicals and waste in the environment, which are creating serious threats to the living beings. The pharmaceuticals and personal care products (PPCPs) are one of the prominent bioactive pollutants, which stay in the environment for a long duration affecting aquatic and human life. Pharmaceuticals are emerging innovation in human scientific development, from curing many minute to very lethal diseases, in order to increase the quality of life as well. Recently, these pharmaceuticals and personal care products are coming out as a major source of pollution for the aquatic environment (Miller et al. 2018). A high measure of squanders is produced from medical clinics that have a prominent amount of synthetic waste as anti-toxins, disinfectants, and different medicine squanders, which at that point at last move into the aquatic source. In the event of pharmaceutical deposits, it has been seen that solitary 18–32% of the pharmaceutical buildups could be corrupted by the auxiliary treatment of these seven advancements, and it has been expanded to 30–65% by tertiary treatment. Undoubtedly, it has been seen that MBR evacuates the deposits with the productivity of 28–100%, fluctuating for every pharmaceutical (Khan et al. 2020).

Majority of current research is based on the industrial WWT process. PPCP removal from the aquatic environment is becoming very necessary in order to attain a sustainable environment and to create a balance in the aquatic nature. In that context, the chapter focuses on various treatment technologies covering conventional systems, advanced treatment methods, and advanced oxidation methods to eradicate PPCPs from the environment. Advanced oxidation methods in collaboration with membranes can be a futuristic advancement for removal of PPCPs.

2 Sources of PPCPs

The major route of dumping of PPCPs in the environment comes via wastewater treatment plants, sewage treatment plants, and medicine disposal (Patel et al. 2019). Essentially these PPCPs enter natural ecosystem post-use. For example, human drugs are either discharged or arranged off which at last advance toward sewage treatment plants and amasses in the surface water or as a sludge. Surface water makes its route to the drinking water bodies ultimately. Treatment of sewage water is further utilized by agricultural land as treated sludge. Another route of PPCPs to the environment is at the source manufacturing unit where they are dumped directly into the sewage treatment plants. After their treatment, they remain in the soil as sludge and may affect the surface water, which can also produce surface runoffs and contaminate freshwater sources. Direct leaching to the groundwater source additionally occurs, which is a danger to drinking water. Additionally, veterinary medications were discharged into the earth through creature squander and furthermore get an opportunity to enter the natural food chain. Further sources are applying cosmetic items, which legitimately goes into the sewage plants through shower squander, washing, swimming, and washing sinks. They can pass through WWTPs undegraded and harm the environment. Another source is that proper disposal of unused medicines is not done. They are straightforwardly dumped which stay tenacious over an extremely extensive stretch of time. Though there are conventional systems based in sustainable water treatment, there are certain PPCPs, which are not degraded, and they remain into the environment, pursuing bioaccumulation and bio-toxicity and ultimately hampering aquatic environments and human health (Fig. 1).

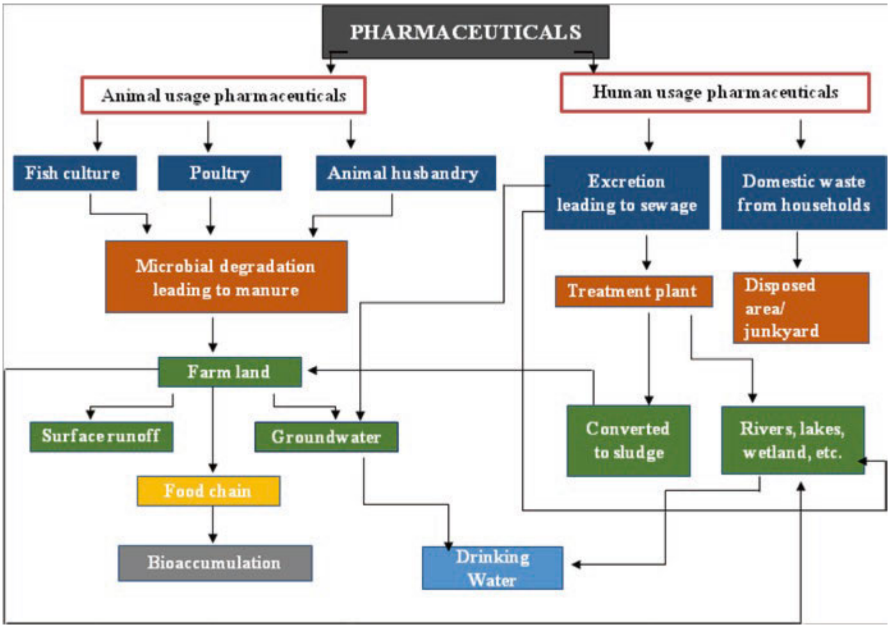

Fig. 1 Schematic showing sources of environmental pollution

3 PPCP Removal: Comparison of Different Methods

As we realized above, pharmaceuticals are essential to humans for different disease treatment strategies. However, they stay active in nature for an extended timeframe. These constant factors likewise change depending upon the motion occurring in the earth. These diligent elements are upgraded by explicit atomic structure containing chloro, nitro, and fluoro useful gathering connected to the aromatic ring. These structures do not experience oxidation because of electron withdrawal, which makes aromatic rings stable (Khetan and Collins 2007). This is more reflected in environment occurrence of antihyperglycemic drugs, for example, metformin, which are frequently found in high quantities in water sources far and wide (Badran et al. 2019). Due to the high occurrence of pharmaceuticals in wastewater, there is a current need for treatment execution plan. PPCP removal technique can be remediated by physical, chemical, thermal, and biological strategies. Physical treatment techniques incorporate adsorption (Ahmed et al. 2017), filtration (Homem and Santos 2011), electrodialysis (Homem and Santos 2011), dialysis (Homem and Santos 2011), evaporation, steam stripping, and reverse osmosis. Substance techniques incorporate ion exchange, reduction, precipitation, and calcination, while thermal strategy incorporates incineration and pyrolysis. Organic treatment techniques incorporate activated sludge treatment, anaerobic absorption, streaming filters, and waste adjustment lakes, which are the most generally utilized natural strategies. The removal technique of PPCPs is a complicated process leaving behind many restrictions, and it all depends on the nature of the pollutant, e.g., solubility, hydrophobicity (Evgenidou et al. 2015), absorption competency, etc.

3.1 Conventional Drinking Water System

The event of PPCP release in the water system is led by the main water source. Conventional treatment processes include biological systems of coagulation and flocculation, filtration, and sedimentation. The conventional treatment processes are further improved by various advanced treatments like membrane filtration technique, advanced oxidation processes (AOPs), etc. (Pallavi and Shivaraju 2019). By disinfection, only a limited number of pharmaceuticals can be possibly removed, mostly by chlorination or ozonation. There are processes like clarification in which the source water is chemically treated where the colloids are disrupted, facilitating flocculation and promoting their settlement along with suspended solids and sediments. In filtration, various suspended particles present in the wastewater are sieved out by passing through granulated media. But, this process does not degrade harmful wastes like PPCPs. Disinfecting water with a chlorination process is one of the major conventional techniques used all over the world. Removal of various microbes and contamination has been reported with usage of chlorination (Gibs et al. 2007).

3.2 Conventional Wastewater Treatment

Over many years, various conventional techniques have been used for the treatment and removal of harmful wastes. There are many techniques emerging to remove and degrade pharmaceuticals and personal care products, but they have not been installed at a large scale due to many constraints.

3.2.1 Primary Treatment Method

Primary systems cannot effectively adsorb PPCPs making them not capable of effectively removing harmful wastes, including PPCPs. Some xenobionts additionally ruin microbial colonies, adding to their deficient expulsion (Rivera-Utrilla et al. 2013). Hydrophobic versus hydrophilic subatomic structure assumes a significant job in pharmaceutical expulsion rates. Polar pharmaceuticals display low expulsion rates (7−10%) (Rivera-Utrilla et al. 2013), while compounds with medium extremity have higher normal evacuation rates (Ternes 1998). High polarity typically increases water solubility, lowering adsorption, which makes pharmaceutical decomposition in STPs and WWTPs. Biodegradation of pharmaceuticals happens when they start to dissolve, while adsorption requires having electrostatic interaction and presence of suspended particulate matter. The pH of the PPCPs additionally assumes a significant job alongside other physical properties with microorganisms for experiencing degradation. PPCP degradation is also dependent upon various climatic conditions. In summary, photodegradation becomes efficient due to high light intensity, whereas during winter, removal efficiencies drop (Table 1).

3.2.2 Secondary Treatment Method

Biological treatment methods or traditional strategies for water treatment have utilized organic treatment techniques to expel pharmaceuticals and individual PPCPs for accomplishing a sustainable environment. This basically happens with aerobic and anaerobic microbial degradation in WWT methods. Membrane bioreactor activated sludge methods, bioreactors, etc. fall under aerobic degradation; UASB reactors, anaerobic filter reactors, anaerobic sludge blanket reactors, etc. fall under anaerobic degradation processes. There are various biological methods like culture treatment, biocatalyst treatment, phytoremediation, constructed wetlands, etc.

Table 1 Treatment technologies for the removal of PPCPs from water

Treatment methodologies	Example	References
Conventional methodologies		
Primary method Simple filtration, coagulation and flocculation, and sedimentation	Treatment of laundry wastewater	Nascimento et al. (2019)
Secondary method 1. Biodegradation using microbial culture	Bisphenol A (BPA) and tetracycline (TCY) removal using *Chlamydomonas* sp.	Xie et al. (2019)
2. Biodegradation using biocatalysts	Degradation of persistent aromatic compounds using *P. chrysosporium*	Peralta-Zamora et al. (1998)
3. Phytoremediation	Antibiotic sulfadimethoxine degradation using *Salix fragilis L.*	Michelini et al. (2012)
4. Constructed wetlands	Treatment of paracetamol, salicylic acid, tetracycline, caffeine, and sulfa drugs	Li et al. (2014)
Advanced treatment methods		
1. Adsorption on activated carbon	Treatment of tetracycline, doxycycline hyclate (DXC), and chlortetracycline HCl (CTC) by GAC filtration	Choi et al. (2008)
Membrane filtration		
RO	Ketoprofen and diclofenac	Snyder et al. (2007)
Nanofiltration	Sulfamethoxazole and carbadox	Shah et al. (2012)
Ultrafiltration	DEET, 1H-benzotriazole, 3-methylindole, chlorophene, and nortriptyline HCl using PAC/UF	Rodriguez et al. (2016)
Advanced oxidation processes		
1. Ozonation	Acyclovir	Mascolo et al. (2010)
2. Fenton's reaction	Acetaminophen	Koottatep et al. (2017)
3. TiO_2 with UV	Caffeine, paracetamol, atenolol	Rimoldi et al. (2017)
4. O_3/UV	Hospital wastewater (HWW)	Mejía-Morales et al. (2020)

3.2.2.1 Biodegradation Using Microbial Culture

A major concern related to PPCPs is the probable occurrence of antibiotic resistance genes. The presence of antibiotics over a sustained period leads to stress which causes them to be resistant for a long time. Microbes are omnipresent in this ecosystem, and they play a very important role in balancing the ecosystem. They can degrade various types of organic compounds, including xenobiotics like PPCPs. Both aerobic and anaerobic microbes assume a significant role in biodegradation of these pharmaceuticals either by co-metabolic processes with other compounds or metabolic biodegradation (Barra Caracciolo et al. 2015). Most microscopic organisms are harmful to pharmaceuticals, but there are certain bacteria, which naturally occur, that have the ability to degrade them by co-metabolically utilizing them as N or C source. Certain microorganisms which tend to show the best biodegradable rate in terms of pharmaceuticals are *Trametes versicolor* and *Ganoderma lucidum* (Vasiliadou et al. 2016), algae like *Chlorella sorokiniana* (Escapa et al. 2015) and *Scenedesmus obliquus* (Chen et al. 2020), and fungal species like *Trichoderma* (Manasfi et al. 2020). Sulfamethazine, enrofloxacin, paracetamol, salicylic acid, diclofenac, and carbamazepine have been degraded using microbial, algal, and fungal cultures.

3.2.2.2 Biodegradation Using Biocatalysts

Biocatalyst has been an emerging biotreatment tool in the field of environmental enzymatic bioremediation for the past decade (Alcalde et al. 2006). Biocatalyst technique usage has been in practice for degrading many xenobiotics including PPCPs. The enzymes used here increase the capacity of biodegradation of aromatic compounds through oxidation and oxygenation (Abdelraheem et al. 2019). Evacuation of compounds like anilines, dyes, chlorophenols, and phenols can be the result of usage of these enzymes, parallel to their decontamination of Kraft effluents (Karam and Nicell 2010). As an example, *P. chrysosporium* produces lignin peroxidase which results in aromatic compound degradation and effluent. Fifty-five percent of total phenol removal, 15% of total organic carbon reduction, and 70% of de-colorization were attained in the treatment process (3 h) (Peralta-Zamora et al. 1998). There are few techniques that use fungal biofilms, which are less economical though. The biofilms are selected to produce particular enzymes, e.g., poly(1-methylethylene), polystyrene foam, and polypropylene. The water treatment can then be achieved by employing these bioactive films (Cornwell et al. 1990). Distinctive enzymatic features make biocatalysis more advantageous in application, allowing chemo-selectivity, regio-selectivity, and enantio-selective chemical reactions. Likewise, for a biocatalyst to be utilized in these techniques, it should be steady and dynamic under various conditions, like temperature, pH, salinity, and so forth.

3.2.2.3 Phytoremediation

Pollutant degradation mechanism using rhizobacteria to transform and remediate toxic materials in the environment present in ground or surface water, soil, or sediments has been regarded as a source of alternative secondary treatment method. It explicitly shows favorable application in the decentralized wastewater treatment systems (Li et al. 2014). Recent research focuses mainly on uptake of pharmaceuticals from plant root, thus terming phytoremediation. With economic attainability, environmental sustainability, low vitality, and innovative interest, demand for phytoremediation is worthy broadly (Iori et al. 2012). Macrophytes have also been reported for removing pharmaceuticals by usage of hydroponic technique with specific species of plant and specific pharmaceuticals. The study for removal of antibiotic sulfadimethoxine was done through accumulation by *Salix fragilis L.* species. The assimilation and plant resistance was built up for 25 days at concentration up to 2 mm. Decline rate in graphs of transpiration and photosynthesis proportion was accounted for, yet overall development accounted remained unaffected (Michelini et al. 2012). Vegetation species existing in wetlands also seem to account on the effect of factors of phytoremediation. The problem lies in the fact that particular species can degrade particular pharmaceutical. The plant species present can influence the nearness of the bacterial network present, along these lines influencing microbial prohibition process (Ruiz-Rueda et al. 2009).

3.2.2.4 Constructed Wetlands

Natural or constructed wetlands are often considered as a sustainable wastewater treatment system, considering its efficiency and reliability. Since this method is considered to be environment-friendly, cost-effective, and easy to maintain, they can serve well in wastewater treatment plants. These wetlands have a unique property to eradicate the BOD, SPM, and other contaminants including pesticides, PPCPs, etc. (Matamoros and Bayona 2006). The natural wetlands act as ecotones for the elimination of waste from water source. Constraint with wetland is it cannot eliminate the PPCPs completely, except for some specific cases where PPCPs under biodegradation or natural oxidation. For example, in constructed wetlands, 70% removal of paracetamol, salicylic acid, tetracycline, caffeine, and sulfa drugs was accomplished (Li et al. 2014). Sedimentation, sorption process, plant uptake, plant accumulation, volatilization, microbial degradation, and photodegradation are some of the biochemical processes which concurrently occur in the plant-built aquatic system like wetlands (D. Zhang et al. 2014). The system lacks in showcasing efficient biodegradability, sorption, photodegradation, and plant uptake mechanisms (Imfeld et al. 2009).

On the basis of data availability, the pharmaceutical removal efficiency was categorized under four divisions, namely, hardly, moderately, readily, and low. Lincomycin, erythromycin, and ampicillin display mean removal efficiencies <20% and were categorized as hardly removed. Carbamazepine, clarithromycin, diclofenac, and amoxicillin display low removal (20–50%). Naproxen, doxycycline, gemfibrozil, and ibuprofen displayed moderate removal (50–70%), while sulfa drugs, salicylic acid, tetracycline, metoprolol, trimethoprim, atenolol, furosemide, and acetaminophen were readily removed (>70%) (Li et al. 2014). Research studies have not been very much in the application of constructed wetlands as an alternative source of WWTPs for removing PPCPs from the aquatic environment.

4 Advanced Treatment Methods

Advanced treatments have been a very promising sustainable technique for clearing out pollutants for wastewater treatment as compared to conventional treatments. Methods like oxidation, membrane filteration methods, adsorption, etc. have been applied in advanced methods. Methods like use of carbon-based NT, activated carbon, or graphene, RO, etc. have been applicable for physical advanced treatment processes. Likewise, ultraviolet irradiation, photocatalysis, ozonation, and oxidation using ozone, UV/ozone, O_3/hydrogen peroxide, etc. have been applicable under chemical treatments.

4.1 Adsorption on Activated Carbon

Activated carbon as an adsorbent for tertiary WWT has been used widely, mostly from industrial waste sludge or surface water or groundwater. Activated treatment can be used either as granular (GAC) or powdered (PAC), the former being most ideal because of its low cost and due to suppleness quantity which lets the PAC concentration to be accustomed making it compact along with changing contaminant levels (Grassi et al. 2013).

As more of PPCP removal efficiency, GAC filters have a more wide response, though there are physiochemical factors which matter. Choi et al. (2008) examined that, using coagulation and GAC filtration, seven classes of tetracycline antibiotics (TAs) can be treated. Also, considering the fact that the removal efficiencies dependent upon the physiochemical properties of the TAs. Effective removal of tetracycline, doxycycline hyclate (DXC), and chlortetracycline HCl (CTC) by GAC filtration was seen rather than a coagulation process.

4.2 Graphene-Based Adsorption

Graphene is noted as a novel 2D sheet structure in parallel to being an allotrope of carbon. Along with its derivatives like graphene oxide, graphene nanoribbions, etc. are an emerging catalysts which aid in advanced treatment process, which cast-off as carbon nanotubes or graphite (Fan et al. 2011). Great surface area, electrical conductivity, capacity charge, and thermal capacity are the characteristics which make graphene applicable for effectual adsorption and also photocatalysis (Mangalam et al. 2019), all summed up for WWT.

4.3 Carbon Nanotubes

Carbon nanotubes, demarcated as cylindrical large molecules entailing hexagonal C atoms arranged which can be rolled into sheets of single-layer carbon atoms having a potential to treat PPCPs. They can be single-walled CNTs (diameter less than 1 nm) and multi-walled CNTs (several interlocked nanotubes). Naproxen (Heo et al. 2014) and ciprofloxacin (Li et al. 2014) were seen to be adsorbed by SWCNT, while oxytetracycline (Oleszczuk et al. 2009), acetaminophen, and 4-acetylaminoantipyrine (Wang et al. 2016) were adsorbed by MWCNT.

4.4 Reverse Osmosis (RO)

RO is characterized as a diffusion method for elimination of particles and huge atoms by a particular semipermeable layer under tension. RO technique helps in a high percentage removal of PPCPs. This procedure is reliant on membrane type and properties, its porosity, mechanical resistance, and chemical characteristics (Song et al. 2020). RO effectively destroys numerous pharmaceuticals (>90%), yet low expulsion has additionally been watched for diclofenac (55.2−60%) and ketoprofen (64.3%) (Snyder et al. 2003).

4.5 Removal Using Nanofiltration

Around >90% deduction levels of pharmaceuticals from water and wastewaters have been achieved by nanofiltration (Shen et al. 2011). Removal efficiency depends upon physiochemical properties, membrane properties, and operating conditions (Verlicchi et al. 2010). Elimination efficiencies of contrarily charged pharmaceuticals are higher than that of neutral pharmaceuticals (Zwiener 2007). Rejection efficiency rate was increased from 90% to 95% during sulfamethoxazole and carbadox nanofiltration because of membrane charge repugnance when the two antibiotics turned out to be adversely charged at $pH > 5.6$ (Shah et al. 2012).

4.6 Advanced Oxidation Processes (AOPs)

AOP has been very promising for clearing out pollutants for wastewater treatment as compared to conventional treatments. AOPs generate $O_2^{\bullet}$, $HO^{\bullet}$, and $HO_2^{\bullet}$ as dominant radicals which make them necessary for degradation purpose (Schwab et al. 2005). These radicals endorse oxidation of various organic and inorganic pollutants making AOP multipurpose (Schwab et al. 2005). The oxidation and degradation efficiency in the process of photocatalysis are administered by some of the parameters like concentration of organic pollutant, concentration, reaction temperature, pH, irradiation time, light intensity, etc. of photocatalyst. AOPs lately have accomplished high rate evacuation (99%) of assortment of PPCPs from the aquatic system. Past years, different techniques like photolysis, ozonation, or oxidation were in use however, AOPs lately, have accomplished high rate evacuation (99%) of assortment of PPCPs from the aquatic system.

a. *AOP Comprising Hydroxyl Radical*

Hydroxyl radicals are notably with high responsive classes and accordingly short-lived which mostly react with organic molecules. Hydroxyl radicals play an imperative role in oxidation degradation of organic noxious waste. The following equation shows how hydroxyl radicals are formed either by oxidation of water or hydroxide ions or by the combinations of various oxidation methods (Huang and Liu 2015), mentioned above.

$$H_2O \rightarrow OH\bullet + H^+ + e^- \tag{1}$$

b. *Ozonation*

Ozone particularly reacts to organic compounds, making itself a strong oxidizing agent. Ozone sets off strong hydroxyl radicals that terminate detrimental bacteria in water which degrades organic pollutants into small molecules. Recent research is interested in ozone oxidation treatment used for antibiotics, hormones, and other pollutant degradation. Reactions involved in generating strong hydroxyl radicals are as follows:

$$3O_3 + H_2O \rightarrow 2OH\bullet + 14O_2 \tag{2}$$

$$H_2O_2 \rightarrow HO_2^- + H^+ \tag{3}$$

$$HO_2^- + O_3 \rightarrow OH\bullet + O_2^- + O_2 \tag{4}$$

$$O_3 + H_2O + h\nu \rightarrow H_2O_2 + O_2 \tag{5}$$

$$H_2O_2 + h\nu \rightarrow 2OH\bullet \tag{6}$$

c. *Photolysis and Ultraviolet Irradiation*

Photolysis is the decomposition of organic pollutants/xenobiotics in the presence of natural or artificial light. Two kinds of transformations are introduced, direct and indirect photolysis. Direct photolysis leads to decomposition of organic compounds by direct absorption of UV light, while indirect photolysis encompasses radiant energy by formation of radicals, reactive species, etc. either by photosensitization or with the help of a catalyst. Indirect photolysis is obligatory to achieve photodegradation of many PPCPs. AOPs have shown effective results in degrading trace organic chemicals, which include PPCPs. Photocatalysis and ultrafiltration are considered as AOPs, but they are not suited for pharmaceutical retention (Rosman et al. 2018). Nevertheless, specific compounds which are hydrophobic tend to show adsorption efficiency onto ultra-filter membranes resulting in temporary diminution (Rosman et al. 2018).

Processes like H_2O_2/UV, UV photolysis, and UV/TiO_2 are based on UV irradiation aided radical production. Equation 7 shows H_2O_2/UV process generating hydroxyl radical.

$$H_2O_2 + h\nu \rightarrow OH\bullet + H^\bullet \tag{7}$$

AOP can be classified into two kinds, viz., homogeneous and heterogeneous. The heterogeneous photocatalysis claims significant application than homogeneous photocatalysis due to non-poisonous, modest, simple partition, and recyclable property (S. Zhang et al. 2013). Heterogeneous photocatalysis has shown efficient degradation of PPCPs in aquatic environments, adding to sustainability. The mechanism of generation of hydroxyl radical in the UV/TiO_2 process is shown below:

$$TiO_2 + h\nu \rightarrow e^-_{cb} + h^+_{vb} \tag{8}$$

$$e^-_{cb} + O_2 \rightarrow O^-_2 \tag{9}$$

$$h^+_{vb} + H_2O \rightarrow OH\bullet + H_2 \tag{10}$$

5 Management Strategies for CECs

There is a lack of field data revealing about the concentration of PPCPs released into the environment, which becomes a threat for the aquatic environment affecting the flora and fauna and also human health. The primary management can be viewed at the source itself. Wastewater and drinking water treatment methodologies at the source can be done as a technical priority. Apparently, these contaminants are not fully degraded by conventional sewage treatment plants. Despite the fact that the distinguished pharmaceuticals were screened based on their standard accessibility, it very well may be expected that numerous different pharmaceuticals are available in the aquatic environmental condition. Primary, secondary, and tertiary systems can be issued based on the concentrations of PPCPs detected. General methodologies may include practices like increasing awareness to the consumers, also that there is a dire need to create open mindfulness and notwithstanding the advancement of administering and removal strategies of drug squander, paying little heed to their gender, age, conjugal status or instructive foundation. This is on the grounds that the utilization of PPCPs is not constrained to gender, age, conjugal status, or instructive foundation. To minimize the PPCP contamination, quality utilization of medication through sensible recommending works on, administering and selling techniques, just as balanced use and removal of PPCPs ought to be incorporated. Besides, advancements through wastewater treatment plants ought to be utilized to screen, control, corrupt or wipe out PPCPs contaminations and execution of rules for the utilization of biosolids and reused water to guarantee PPCPs are not discharged into the environment. Also giving advisory and regulatory policies, etc. can be a non-technical measure. The information regarding technical and non-technical diminution can be given in the form of a list having detailed information of the compound, targeted group of compounds, its toxicity, mitigation methods, and proficiencies. This will help the user to get knowledge, maintain precautionary measures, and conduct research. Guidelines should be actualized and perceived so as to help these goals and this must be finished by the Government by methods for right off the bat, arranging PPCPs as unsafe waste and furthermore, deciding the most extreme contaminant levels (MCL). Furthermore, projects, for example, the medications can be arranged off as clinical waste utilizing appropriate removal strategies. Awareness can be interpreted like people should not dispose or throw the pharmaceuticals simply over land or in any drain areas; instead awareness should be given that the unused or expired medicines should be returned to the pharmacies. Also, policies regarding sustainable water management should be created like water quality limits for chemicals in surface water. Monitoring of the surface water and groundwater should be done by comparing drinking water quality with a universal standard. A global coordinated effort is important to oversee proficiently this exceptional issue dependent on a multi-logical methodology, water being the fundamental base forever, industry and improvement. It is just through joint endeavors from the makers of these PPCPs, the administration, private association and even people can carry the Green Pharmacy vision to a reality.

6 Conclusions and Future Prospects

There are various technologies taken from the traditional methodologies to the AOPs. Regardless of various advanced technologies in degradation of PPCPs, there is a need to upgrade the technologies to be more cost-effective and most sustained, including safe disposal techniques. Oxidizing agents like ozone, H_2O_2, TiO_2, etc. have been experimented in various chemical processes to degrade organic pollutants. Nevertheless, chemical oxidation techniques are expensive in terms of operating costs. A solution to these techniques can be amalgamation of biological and advanced techniques to treat organic pollutants in water sources. Biological treatment methods have shown to be more cost-effective than chemical oxidation process. One notable factor is that the quantity of water in addition to quality is important for pollution management. More research needs to be involved in knowing the characteristics of the system on how to enhance or limit the specific and global proficiencies and eventually the total treatment cost.

References

Abdelraheem EMM, Busch H, Hanefeld U, Tonin F (2019) Biocatalysis explained: from pharmaceutical to bulk chemical production. Reaction Chem Eng 4(11):1878–1894. https://doi.org/10.1039/c9re00301k

Ahmed MB, Zhou JL, Ngo HH, Guo W, Johir MAH, Belhaj D (2017) Competitive sorption affinity of sulfonamides and chloramphenicol antibiotics toward functionalized biochar for water and wastewater treatment. Bioresour Technol 238:306–312. https://doi.org/10.1016/j.biortech.2017.04.042

Alcalde M, Ferrer M, Plou FJ, Ballesteros A (2006) Environmental biocatalysis: from remediation with enzymes to novel green processes. Trends Biotechnol 24(6):281–287. https://doi.org/10.1016/j.tibtech.2006.04.002

Badran I, Manasrah AD, Nassar NN (2019) A combined experimental and density functional theory study of metformin oxy-cracking for pharmaceutical wastewater treatment. RSC Adv 9(24):13403–13413. https://doi.org/10.1039/c9ra01641d

Barra Caracciolo A, Topp E, Grenni P (2015) Pharmaceuticals in the environment: biodegradation and effects on natural microbial communities. A review. J Pharm Biomed Anal 106:25–36. https://doi.org/10.1016/j.jpba.2014.11.040

Chen Q, Zhang L, Han Y, Fang J, Wang H (2020) Degradation and metabolic pathways of sulfamethazine and enrofloxacin in Chlorella vulgaris and Scenedesmus obliquus treatment systems. Environ Sci Pollut Res 27. https://doi.org/10.1007/s11356-020-09008-4

Choi KJ, Kim SG, Kim SH (2008) Removal of antibiotics by coagulation and granular activated carbon filtration. J Hazard Mater 151(1):38–43. https://doi.org/10.1016/j.jhazmat.2007.05.059

Cornwell KL, Tinland-Butez MF, Tardone PJ, Cabasso I, Hammel KE (1990) Lignin degradation and lignin peroxidase production in cultures of Phanerochaete chrysosporium immobilized on porous ceramic supports. Enzym Microb Technol 12(12):916–920. https://doi.org/10.1016/0141-0229(90)90109-4

Escapa C, Coimbra RN, Paniagua S, García AI, Otero M (2015) Nutrients and pharmaceuticals removal from wastewater by culture and harvesting of Chlorella sorokiniana. Bioresour Technol 185:276–284. https://doi.org/10.1016/j.biortech.2015.03.004

Evgenidou EN, Konstantinou IK, Lambropoulou DA (2015) Occurrence and removal of transformation products of PPCPs and illicit drugs in wastewaters: a review. Sci Total Environ 505:905–926. https://doi.org/10.1016/j.scitotenv.2014.10.021

Fan ZJ, Kai W, Yan J, Wei T, Zhi LJ, Feng J et al (2011) Facile synthesis of graphene nanosheets via fe reduction of exfoliated graphite oxide. ACS Nano 5(1):191–198. https://doi.org/10.1021/nn102339t

Gibs J, Stackelberg PE, Furlong ET, Meyer M, Zaugg SD, Lippincott RL (2007) Persistence of pharmaceuticals and other organic compounds in chlorinated drinking water as a function of time. Sci Total Environ 373(1):240–249. https://doi.org/10.1016/j.scitotenv.2006.11.003

Grassi M, Rizzo L, Farina A (2013) Endocrine disruptors compounds, pharmaceuticals and personal care products in urban wastewater: implications for agricultural reuse and their removal by adsorption process. Environ Sci Pollut Res 20(6):3616–3628. https://doi.org/10.1007/s11356-013-1636-7

Heo J, Lee H, Han J, Son M, Her N (2014) An influence on EDC/PPCPs adsorption onto single-walled carbon nanotubes with cationic surfactant. J Korean Soc Water Wastewater 28(4):419–429. https://doi.org/10.11001/jksww.2014.28.4.419

Homem V, Santos L (2011) Degradation and removal methods of antibiotics from aqueous matrices - A review. J Environ Manag 92(10):2304–2347. https://doi.org/10.1016/j.jenvman.2011.05.023

Huang H, Liu G (2015) Ozone-oxidation products of ibuprofen and toxicity analysis in simulated drinking water. J Drug Metab Toxicol 6(3):1–5. https://doi.org/10.4172/2157-7609.1000181

Imfeld G, Braeckevelt M, Kuschk P, Richnow HH (2009) Monitoring and assessing processes of organic chemicals removal in constructed wetlands. Chemosphere 74(3):349–362. https://doi.org/10.1016/j.chemosphere.2008.09.062

Iori V, Pietrini F, Zacchini M (2012) Assessment of ibuprofen tolerance and removal capability in Populus nigra L. by in vitro culture. J Hazard Mater 229–230:217–223. https://doi.org/10.1016/j.jhazmat.2012.05.097

Karam J, Nicell JA (2010) ChemInform abstract: potential applications of enzymes in waste treatment. ChemInform 28(38). https://doi.org/10.1002/chin.199738345

Khan NA, Khan SU, Ahmed S, Farooqi IH, Yousefi M, Mohammadi AA, Changani F (2020) Recent trends in disposal and treatment technologies of emerging-pollutants- A critical review. TrAC - Trends Anal Chem 122:115744. https://doi.org/10.1016/j.trac.2019.115744

Khetan SK, Collins TJ (2007) Human pharmaceuticals in the aquatic environment: a challenge to green chemistry. Chem Rev 107(6):2319–2364. https://doi.org/10.1021/cr020441w

Koottatep T, Phong VHN, Chapagain SK, Panuvatvanich A, Polprasert C, Ahn KH (2017) Potential of laterite soil coupling fenton reaction in acetaminophen (ACT) removal in constructed wetlands. Water Air Soil Pollut 228(8). https://doi.org/10.1007/s11270-017-3454-x

Li Y, Zhu G, Ng WJ, Tan SK (2014) A review on removing pharmaceutical contaminants from wastewater by constructed wetlands: design, performance and mechanism. Sci Total Environ 468–469:908–932. https://doi.org/10.1016/j.scitotenv.2013.09.018

Manasfi R, Chiron S, Montemurro N, Perez S, Brienza M (2020) Biodegradation of fluoroquinolone antibiotics and the climbazole fungicide by Trichoderma species. Environ Sci Pollut Res 27(18):23331–23341. https://doi.org/10.1007/s11356-020-08442-8

Mangalam J, Kumar M, Sharma M, Joshi M (2019) High adsorptivity and visible light assisted photocatalytic activity of silver/reduced graphene oxide (Ag/rGO) nanocomposite for wastewater treatment. Nano-Struct Nano-Obj 17:58–66. https://doi.org/10.1016/j.nanoso.2018.11.003

Mascolo G, Laera G, Pollice A, Cassano D, Pinto A, Salerno C, Lopez A (2010) Effective organics degradation from pharmaceutical wastewater by an integrated process including membrane bioreactor and ozonation. Chemosphere 78(9):1100–1109. https://doi.org/10.1016/j.chemosphere.2009.12.042

Matamoros V, Bayona JM (2006) Elimination of pharmaceuticals and personal care products in subsurface flow constructed wetlands. Environ Sci Technol 40(18):5811–5816. https://doi.org/10.1021/es0607741

Mejía-Morales C, Hernández-Aldana F, Cortés-Hernández DM, Rivera-Tapia JA, Castañeda-Antonio D, Bonilla N (2020) Assessment of biological and persistent organic compounds in hospital wastewater after advanced oxidation process UV/H2O2/O3. Water Air Soil Pollut 231(2). https://doi.org/10.1007/s11270-020-4463-8

Michelini L, Meggio F, La Rocca N, Ferro S, Ghisi R (2012) Accumulation and effects of sulfadimethoxine in Salix fragilis L. plants: a preliminary study to phytoremediation purposes. Int J Phytoremed 14(4):388–402. https://doi.org/10.1080/15226514.2011.620654

Miller TH, Bury NR, Owen SF, MacRae JI, Barron LP (2018) A review of the pharmaceutical exposome in aquatic fauna. Environ Pollut 239:129–146. https://doi.org/10.1016/j.envpol.2018.04.012

Nascimento COC, Veit MT, Palácio SM, Gonçalves GC, Fagundes-Klen MR (2019) Combined application of coagulation/flocculation/sedimentation and membrane separation for the treatment of laundry wastewater. Int J Chem Eng 2019. https://doi.org/10.1155/2019/8324710

Oleszczuk P, Pan B, Xing B (2009) Adsorption and desorption of oxytetracycline and carbamazepine by multiwalled carbon nanotubes. Environ Sci Technol 43(24):9167–9173. https://doi.org/10.1021/es901928q

Pallavi N, Shivaraju H (2019) Photocatalytic degradation of bromobenzene using novel Fe-Mn-CeO2/TiO2 nano-composite under light emitting diodes. Int J Environ Health Technol 1(3):78–85. Retrieved from www.greenstrust.com/pub

Patel M, Kumar R, Kishor K, Mlsna T, Pittman CU, Mohan D (2019) Pharmaceuticals of emerging concern in aquatic systems: chemistry, occurrence, effects, and removal methods [Review-article]. Chem Rev 119(6):3510–3673. https://doi.org/10.1021/acs.chemrev.8b00299

Peralta-Zamora P, de Moraes SG, Esposito E, Antunes R, Reyes J, Durán N (1998) Decolorization of pulp mill effluents with immobilized lignin and manganese peroxidase from phanerochaete chrysosporium. Environ Technol (United Kingdom) 19(5):521–528. https://doi.org/10.1080/09593331908616708

Rimoldi L, Meroni D, Falletta E, Pifferi V, Falciola L, Cappelletti G, Ardizzone S (2017) Emerging pollutant mixture mineralization by TiO2 photocatalysts. The role of the water medium. Photochem Photobiol Sci 16(1):60–66. https://doi.org/10.1039/c6pp00214e

Rivera-Utrilla J, Sánchez-Polo M, Ferro-García MÁ, Prados-Joya G, Ocampo-Pérez R (2013) Pharmaceuticals as emerging contaminants and their removal from water. A review. Chemosphere *93*(7):1268–1287. https://doi.org/10.1016/j.chemosphere.2013.07.059

Rodriguez E, Campinas M, Acero JL, Rosa MJ (2016) Investigating PPCP removal from wastewater by powdered activated carbon/ultrafiltration. Water Air Soil Pollut 227(6). https://doi.org/10.1007/s11270-016-2870-7

Rosman N, Salleh WNW, Mohamed MA, Jaafar J, Ismail AF, Harun Z (2018) Hybrid membrane filtration-advanced oxidation processes for removal of pharmaceutical residue. J Colloid Interface Sci 532:236–260. https://doi.org/10.1016/j.jcis.2018.07.118

Ruiz-Rueda O, Hallin S, Bañeras L (2009) Structure and function of denitrifying and nitrifying bacterial communities in relation to the plant species in a constructed wetland. FEMS Microbiol Ecol 67(2):308–319. https://doi.org/10.1111/j.1574-6941.2008.00615.x

Schwab BW, Hayes EP, Fiori JM, Mastrocco FJ, Roden NM, Cragin D et al (2005) Human pharmaceuticals in US surface waters: a human health risk assessment. Regul Toxicol Pharmacol 42(3):296–312. https://doi.org/10.1016/j.yrtph.2005.05.005

Shah AD, Huang CH, Kim JH (2012) Mechanisms of antibiotic removal by nanofiltration membranes: model development and application. J Membr Sci 389:234–244. https://doi.org/10.1016/j.memsci.2011.10.034

Shen LQ, Beach ES, Xiang Y, Tshudy DJ, Khanina N, Horwitz CP et al (2011) Rapid, biomimetic degradation in water of the persistent drug sertraline by TAML catalysts and hydrogen peroxide. Environ Sci Technol 45(18):7882–7887. https://doi.org/10.1021/es201392k

Snyder S, Westerhoff P, Yoon Y, Sedlak D (2003) Disruptors in water: implications for the water industry. Environ Eng Sci 20(5):449–469. https://doi.org/10.1089/109287503768335931

Snyder SA, Adham S, Redding AM, Cannon FS, DeCarolis J, Oppenheimer J et al (2007) Role of membranes and activated carbon in the removal of endocrine disruptors and pharmaceuticals. Desalination 202(1–3):156–181. https://doi.org/10.1016/j.desal.2005.12.052

Song W, Lee LY, Ng HY (2020) Nanofiltration and reverse osmosis processes for the removal of micro-pollutants. Curr Dev Biotechnol Bioeng. https://doi.org/10.1016/b978-0-12-819594-9.00021-8

Ternes TA (1998) Occurrence of drugs in German sewage treatment plants and rivers. Water Res 32(11):3245–3260. https://doi.org/10.1016/S0043-1354(98)00099-2

Vasiliadou IA, Sánchez-Vázquez R, Molina R, Martínez F, Melero JA, Bautista LF et al (2016) Biological removal of pharmaceutical compounds using white-rot fungi with concomitant FAME production of the residual biomass. J Environ Manag 180:228–237. https://doi.org/10.1016/j.jenvman.2016.05.035

Verlicchi P, Galletti A, Petrovic M, BarcelÓ D (2010) Hospital effluents as a source of emerging pollutants: an overview of micropollutants and sustainable treatment options. J Hydrol 389(3–4):416–428. https://doi.org/10.1016/j.jhydrol.2010.06.005

Wang Y, Ma J, Zhu J, Ye N, Zhang X, Huang H (2016) Multi-walled carbon nanotubes with selected properties for dynamic filtration of pharmaceuticals and personal care products. Water Res 92:104–112. https://doi.org/10.1016/j.watres.2016.01.038

Xie P, Ho SH, Peng J, Xu XJ, Chen C, Zhang ZF et al (2019) Dual purpose microalgae-based biorefinery for treating pharmaceuticals and personal care products (PPCPs) residues and biodiesel production. Sci Total Environ 688:253–261. https://doi.org/10.1016/j.scitotenv.2019.06.062

Zhang S, Li J, Zeng M, Zhao G, Xu J, Hu W, Wang X (2013) In situ synthesis of water-soluble magnetic graphitic carbon nitride photocatalyst and its synergistic catalytic performance. ACS Appl Mater Interfaces 5(23):12735–12743. https://doi.org/10.1021/am404123z

Zhang D, Gersberg RM, Ng WJ, Tan SK (2014) Removal of pharmaceuticals and personal care products in aquatic plant-based systems: a review. Environ Pollut 184:620–639. https://doi.org/10.1016/j.envpol.2013.09.009

Zwiener C (2007) Occurrence and analysis of pharmaceuticals and their transformation products in drinking water treatment. Anal Bioanal Chem 387(4):1159–1162. https://doi.org/10.1007/s00216-006-0818-2

Nanomaterials and Heavy Metals: Environmental Risk Assessment and Remediation Strategies for Wastewater

Gagandeep Kour, Richa Kothari, Sunil Dhar, and Deepak Pathania

Abstract Emerging contaminants are the chemicals that either are produced synthetically or have natural occurrence or any microorganisms that are not commonly monitored but have the potential to cause adverse effects on humans and healthy functioning of an ecosystem. These include industrial chemicals, pharmaceuticals, microplastics, nanomaterials, narcotics and personal care products in addition to antibiotics, pesticides and toxins produced by certain blue-green algae, etc. These substances are collectively referred to as emerging contaminants of concern as these contaminants pass through the treatment system and finally find their way to soil with the help of water/wastewater and impede the normal functioning of an ecosystem. In general, trend of wastewater use is increased nowadays after several treatments and steps for multipurpose applications to avoid water crisis/freshwater use. This trend is good enough on the scale of water crisis, but use of chemicals to treat wastewater may always not turn into useful end product, or sometimes their interactions are responsible for production of harmful toxins as a by-product. Similarly, use of biological agents to treat the wastewater is also not a friendly step because the release of secretions from them is target specific; as a result, some of the contaminants get escaped from processing and get entered in ecosystem channel pathway. Some common emerging contaminants noticed and included here as a part of the chapter to study are nanomaterials and heavy metals (like metal oxides, nanosilver and nanoagrochemicals); their sources of generation and impacts on surroundings are also included in the sections. Because of unique chemical, physical and biological properties, nanomaterials find numerous applications which are

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intended for the betterment of the society and environment, discussed and reviewed in details in this chapter with associated risks, till date unseen on front of day-to-day life because they sometimes act as a double-edged sword, having side effects too. Therefore, keeping these as a base point, this chapter is formulated with an objective to assess the associated risk from these newly introduced contaminants in the wastewater/water environment and their approaches or sources of entering and possible remediation approaches to sort out these contaminants for the sustainable growth and economy.

Keywords Water contaminants · Nanomaterials · Heavy metals · Risk assessment · Remediation

1 Introduction

The universe of chemical pollutants is expanding day by day as a result of changing lifestyle, industrial development and advances in technology. The chemicals produced are released into waterways as the water bodies are considered as universal dumping sites, where they ultimately settle in soil, groundwater and other surface water reservoirs and enter the biological community through food chain. These chemicals present in water, wastewater, soil and sediments have a significant effect on humans and hence can be managed by adopting necessary strategies and regulated. But the concern has been raised by the introduction of a new class of contaminants that are non-regulated by environmental legislation or other policymakers. The reason for their non-regulation may be attributed due to the lack of available information about their existence or because of their poor traceability. This set of contaminants is designated as emerging contaminants (ECs). ECs are a set of newly discovered substances or chemicals that are produced either synthetically or naturally by certain microorganisms in traceable amounts that are unregulated. These include substances like flame retardants, pharmaceuticals, endocrine-disrupting compounds, organic wastewater contaminants, nanomaterials, persistent organic compounds and personal care products which are released by the processes or products used on a daily basis but cannot be determined earlier because of their poor traceability. With the recent advances in analytical techniques, the determination of traceable substances can be made possible. There is a scope for detection from micrograms per litre to nanograms per litre. These substances are collectively referred to as emerging contaminants of concern as these contaminants pass through the conventional treatment system and finally find their way to soil with the help of water or wastewater and impede the normal functioning of an ecosystem. Nowadays, the reuse of wastewater is increased after several treatments and steps for multipurpose applications to avoid water crisis or freshwater use. This trend is good enough to manage the water crisis, but the usage of chemicals to treat wastewater may turn into harmful end products which sometimes produce toxic materials as a by-product. Similarly, the application of biological agents to treat the wastewater is also not a friendly step because the release of secretions from them is target specific; as a result, some of the contaminants get escaped from processing and enter the ecosystem channel pathway. These substances are present in minute quantities that are non-persistent and removed from the environment by the natural process of self-restoration, but their continuous exposure in small amounts adds up to the existing concentration and results in deleterious effects on the ecosystem and human health. Hundreds of pharmaceuticals, daily care products and other industrial additives are found in river waters across the globe that are known to cause potential health risks to humans and other species like cancer, endocrine disruption, reproductive stress, etc., and also they are bioactive and bioaccumulative and have a widespread occurrence and persistence.

There has been very less published data in the literature about emerging contaminants because of flawed sampling strategies employed. ECs are found more commonly in developing countries as compared to developed nations, and their distribution varies according to geographical locations, climate, population density, topography, etc. (Tran et al. 2018). A huge number of ECs are not legalized by law; hence, there is an urgent need for continual monitoring and assessment of ECs in water and wastewater.

The present chapter entertains nanomaterials (NMs) and heavy metals which have emerged as contaminants of concern in the past few years. Nanosized materials find wide applications because of their unique physical and chemical characteristics and have been appreciated for their significant commercial impact, but at the same time, they have negative impacts too. Therefore, it becomes necessary to have a comprehensive understanding of the sources and pathways for the exposure of nanomaterials to continuously assess and evaluate the health risks to humans and the ecosystem and also to provide the necessary remediation techniques for sustainable growth and economy.

2 Nanomaterials and Heavy Metals

Nanomaterials (NMs) are a subset of emerging contaminants and can be defined as materials that have their internal structure or surface structure or external dimensions in nanoscale or submicroscale (Christian et al. 2008). These are processed in nanoscale and are too small to be seen by naked eyes and even with conventional lab microscopes. A human hair is 100,000 times bigger than the diameter of a nanosized particle. The nanoform of material encourages the larger surface area to volume as compared to their conventional forms (Alagarasi 2011). At the nanoscale, the quantum effect becomes a prominent property in determining the characteristics and material properties, thus making the material in possession of new and advanced electrical, optical and magnetic behaviour. The smaller size of the materials makes them both promising and challenging as the properties like their small size, shape and high reactivity make them a boon in product development and drug delivery; at the same time, they are the cause of concern because of their interaction with the biological systems and potential effects in the environment as they can easily enter the body even at the cellular level as compared to other larger particles. Fibrous nanomaterials especially made up of carbon are known to cause inflammation of the lungs: a similar condition exhibited by asbestos fibres. They might also evoke inflammatory responses and can even cause DNA damage. However, very little is yet known about the possible toxic properties of nanoparticles (Wiesner et al. 2009). They are used in almost every field, and hence, there is a possible chance of release or contamination by nanomaterials from the various activities which are performed in everyday life. As a result of their nanoscale dimensions, nanomaterials escape the conventional treatment processes and find their way into the environment where they accumulate or add up. They also find their way through wastewater treatment streams, landfills, recycling of metals and other recyclable products and combustion of products. Another possible entry to the environment is through weathering or degradation of products from nanoproducts and nanocomposites. Examples of nanomaterials include nanoplastics, nanopesticides, nanomedicines, nanosilver, nanoscale metal oxides, carbon nanotubes, fullerene, nanosilica, nanoclays, etc.

Heavy metals are elements with atomic weights between 63.5 and 200.6 and a specific gravity greater than 5.0 (Zare et al. 2018). Heavy metal pollution of water or wastewater is of growing concern now a days due to their mobility in natural water ecosystems and toxicity they cause to human life throughout the world. Heavy metals and their oxide in nanoform also constitute nanomaterials. Therefore, in this chapter, heavy metals and their oxides in nanoparticle form under the broader view of nanomaterials are studied. Nanoparticles of zinc oxide and copper oxides are also used for environmental remediation (Singh et al. 2018). It is a well-known fact that the decrease in the size of particles leads to remarkable variations in the properties of the materials. Figure 1 lists some of the major variations that take place in the properties of metals in the nanoscale dimension.

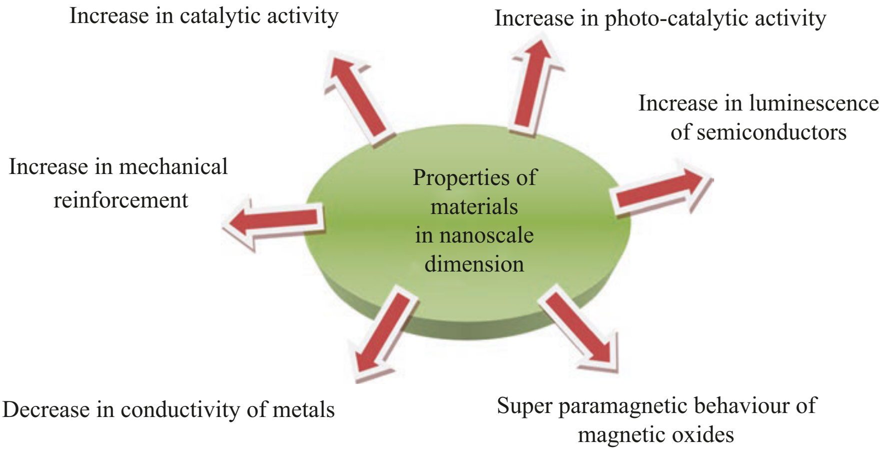

Fig. 1 Modifications in the properties of metals in nanoscale dimensions

2.1 Applications of Nanomaterials

The existence of nanomaterials on earth dates back to millions of years, and man has been using nanomaterials for hundreds of years. However, the usage has increased many folds in the past few years. Nanomaterials can occur naturally or are engineered to be used in commercial products and processes. Nanomaterials find applications in day-to-day life products ranging from daily care products to medicines and even medical applications (Alagarasi 2011). A broad overview of the applicability of nanomaterials in various fields is presented in Fig. 2. Nanocoatings are applied in windows and glass bottles for UV blockage, to prevent beverages from damage from sunlight, etc. Nowadays, nanomaterials are being applied in textiles to increase the strength and longevity of the material. An example of such application is the use of nanoclay composites for increasing the shelf-life or longevity of tennis ball. Nowadays, butyl rubber is also used for increasing the durability of tennis balls. Titanium dioxide in its nanoform has been widely used in cosmetics as well as in solar cells, paints and coatings because of its UV blocking properties (Klaine et al. 2008), and nanoscale silica acts as a filler in dental fillings as well as in cosmetics and drug delivery (Priyadarsini et al. 2018). Carbon nanotubes and their derivatives have a wide range of applications in electronics and medicines, avian and automobile industries, water purification, etc. (Klaine et al. 2008).

Iron oxide nanoparticles have superparamagnetic properties with proper surface chemistry can be used for various in vivo applications. These involve their use in detoxification of biological fluids, cell separation, tissue repair and immunoassay, drug delivery and MRI contrast enhancement. The nanomaterials required for these biomedical applications must include a narrow particle size distribution, a particle size less than 100 nm in diameter and a high magnetization value (Laurent et al.

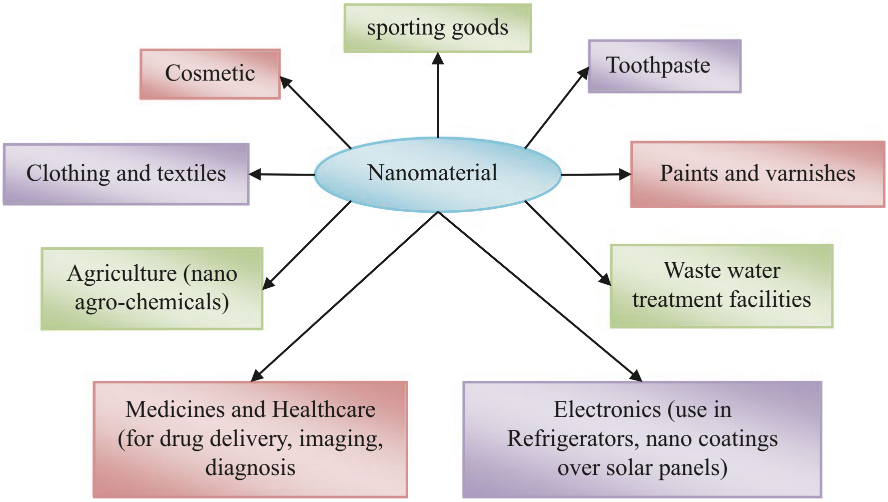

Fig. 2 Applicability of nanomaterials

2008). Cerium dioxide is widely used as a combustion catalyst in diesel fuels; in oxygen pumps; in metallurgical, glass or ceramic industry; and in solar cells (Corma et al. 2004; Lin et al. 2006). Manganese dioxide (MnO_2) finds applications for rechargeable batteries in cars and other vehicles. Nanostructures like ZnO are used as light-emitting diode, sensors as well as a template for phase separation (Alagarasi 2011). Nanomembrane for water purification and detoxification has been used. Nowadays, magnetic nanoparticles are used for water treatment and remediation. Nanoparticles of silver have been used in products such as wound dressings, socks, air filters, toothpaste, washing machines, etc. as an antimicrobial agent to kill microbes that cause odour or foul smell. Gold nanoparticles find applications in the medical field and can be used as a vector in tumour therapy and also used in the field of electronics in flexible conducting inks or films (Klaine et al. 2008). TiO_2 nanoparticles are employed for the catalytic degradation of water pollutants. The nanomaterial market projection as predicted by various market research bodies is very positive. To conclude, the various applications of nanomaterials that help in enhancing the economy of the countries especially the developing countries like India include sectors of energy storage, production and conversion, agricultural productivity enhancement, water treatment and remediation, disease diagnosis and screening, drug delivery systems, food processing and storage, air pollution and remediation and health monitoring and in pest detection and their control.

2.2 Types of Nanomaterials

Nanomaterials can be of different types based on their shape, size, structure and occurrence. These can be zero-dimensional (0D), one-dimensional (1D), two-dimensional (2D) and three-dimensional (3D) nanostructures depending on their structure, and the classical examples of these nanostructure are spheres and clusters; nanofibres, nanowires and nanorods; nanofilms, nanoplates and networks; and nanomaterials representing 0D, 1D, 2D and 3D, respectively (Alagarasi 2011). According to Klaine et al. (2008), nanomaterials can be of different types based on their occurrence. They can be carbon based (natural or engineered), metal oxides (natural or engineered), zerovalent metals (engineered), quantum dots (engineered) and nanosilver (engineered), and the details of these nanomaterials are shown in Table 1.

There is a rapid growth in the development of newly manufactured or engineered nanomaterials during the past couple of years. The rapidly developing market of engineered nanomaterials is being exploited by speedily growing nanotechnology industries. The assortment of nanotechnology products is very wide and can be divided into a number of different compound classes, including carbonaceous nanomaterials (carbon nanotubes), metal oxides, quantum dots, zerovalent metals and nanopolymers such as dendrimers (Klaine et al. 2008). The first class of nanomaterials called carbon nanotubes is widely used in fuel cell electrodes, batteries, components in electronics, aircraft, aerospace and plastics, as well as in medical

Table 1 Types of nanomaterials

Nanomaterials	Occurrence	Type of constituents	Examples	References
Nanoadsorbents	Natural or engineered	Carbon based, polymer based, metal oxide based or zerovalent metal based	Carbon nanotubes; dendrimers; nanocomposites; TiO_2; ZnO; CeO_2; metal catalyst like gold, nickel, platinum and silver; etc.	Klaine et al. (2008), Gupta et al. (2011), and Mehta et al. (2018)
Nanopesticides/ nanofertilizers	Engineered	Carbon based, zerovalent metal based, metal based	Carbon nanofibres, nanosilver, TiO_2 nanoparticles	Agarwal and Rathore (2014)
Nanomedicines	Engineered	Metal or metal oxide based, inorganic and organic based	Silica, lipid, iron oxide nanoparticles (Fe NPs)	Zhang et al. (2017)
Nanometals	Natural or engineered	Metal and their oxide based	Iron, gold, silver, copper oxide, zinc oxide nanoparticles	Singh et al. (2018)

application like orthopaedic implants. Metal oxides which form the second class of nanomaterials are widely used in cosmetics, sunscreens and bottle coatings and other ceramic or glass applications because of their UV blocking ability. The third class of nanomaterials includes quantum dots also known as semiconductor nanocrystals. These are used because of their optical properties. Semiconductor nanocrystals are widely used in medical applications such as medical imaging as well as in solar cells, photovoltaics, security inks and telecommunication (Alivisatos et al. 2005). Nanozerovalent metals like iron designed as the fourth class of nanomaterials are being used for the remediation of water, sediment and soil. The fifth class of nanomaterials is dendrimers having numerous applications in diverse fields like material sciences for surface modifications, biology, etc., including their use for making nanolatex, macrocapsules, DNA chips, uncoloured glasses, chemical sensors, modified electrodes, drug delivery, etc.

2.3 *Sources of Nanomaterials in the Environment*

Nanoparticles exist in the environment and their existence can be natural, incidental or engineered. Natural sources include nanoparticles or nanostructures present in living organisms. The genetic materials like DNA and RNA are the nanostructures which are present in every living organism. A wide variety of nanoparticles are produced naturally and are present in the biological sphere ranging from simpler forms of life such as bacteria, viruses, algae, fungi and yeast to complex and higher-order organisms such as insects, birds, animals and plants and including humans

(Jeevanandam et al. 2018). Some nanomaterials or nanoparticles are engineered or artificially made to be used for commercial purpose like in medicines, paints, fibre, other products, etc. Such artificially manufactured nanoparticles have certain properties meant for the desired purpose. Another source of nanomaterials is incidental whereby nanomaterials are produced incidentally as a by-product of the industrial process. Nanomaterials enter the environment intentionally and unintentionally. Because of their ability to remediate contaminated water and wastewater, engineered nanomaterials are introduced deliberately. An example of the deliberate introduction of engineered nanomaterials is the introduction of nanoparticles of iron and silver for environmental remediation. The unintentional entry of nanomaterials or nanoparticles occurs through the solid and liquid waste stream from production facilities and stack emissions as a result of combustion processes and from municipal waste incineration. Examples of unintentional nanoparticles also include particles or compounds from forest fires, volcanic eruptions, flue gas, soot, etc. which are released into the atmosphere and finally settle down on land and surface water bodies. Nanoparticles present in paints, fabrics and personal care products find their way into the environment through their usage (Biswas and Wu 2005). Some researchers have investigated weathering, mechanical wear of various coatings and the washing of textiles as the causes of the release of nanomaterials into the environment (Shandilya et al. 2015).

2.4 Regulation of Nanomaterials

Engineered nanomaterials, such as nanospheres, nanotubes, nanowires and nanosheets, serve as the promising applicant for a variety of applications. However, the other side of the engineered nanomaterials cannot be overlooked. Due to their extremely small dimensions in the nanoscale level, larger surface area and high reactivity, nanomaterials can penetrate living cells without restraint making them potentially hazardous for environmental safety and a major threat to human health. Keeping this scenario in mind, various research and development (R&D) institutions, universities and industries across the world have now become active, and intense research activity is being undertaken on various projects involving carbon nanotubes, nanowires, nanostructured alloys, ceramic nanoparticles, etc. in evaluating the toxicity and critical exposure levels. In the research laboratories, persons associated with these projects are unintentionally exposed to various nanomaterials. Exposure to nanomaterials can be dangerous if proper handling procedures are not followed and safety measures are not taken while dealing with them. At present, there is insufficient evidence in published scientific and technical literature about the toxicity of nanomaterials, and therefore, their risk remains unidentified. However, research work is being carried on laboratory animals to evaluate the toxic extent of nanomaterials.

Various government agencies have taken up initiatives to plan safety guidelines for scientists and technicians involved in various activities in R&D laboratories to employ the best exercise for safe usage of nanomaterials at their workplaces. It is suggested that the researchers planning to deal with nanomaterials must put into practice a combination of work practices, engineering controls and personal protective equipment to lessen the probable contact to themselves and others and reduce risks associated with them. These precautionary measures will ensure the safe production, handling and use of nanomaterials safely and sustainably to exploit their benefits for the welfare of the society. Over the years, life cycle analysis of chemicals by the industry and other regulatory bodies has become a necessary requisite for identifying, managing and minimizing the possible environmental, health and safety risks from their production to end of the life. This approach also applies to nanomaterials since these are also chemical substances. Looking ahead of the potential risks portrayed by the nanomaterials, there is limited and insufficient information available in the published literature about the actual effects of nanomaterials on animal species, ecosystems or the environment. However, within the limited data available about the toxicology of nanomaterials, the facts are still confusing. There are uncertainties as to how different nanoparticles interact with the environment, how these particles get into the human body and what effects these cause the body. Hence, there is a need for more data to thoroughly investigate these emerging contaminants.

The foremost step in determining the risk and exposure of nanomaterials is the identification of hazardous chemicals or nanomaterials and their associated processes that pose hazards. Assessment of risks connected with nanomaterials involves the incorporation of special care to identify the effects of specific surface chemistry, morphology, shape and size on toxicity caused by them to different organs and organ systems. The fundamental features like surface charge, surface chemistry and particle shape, size and solubility must be taken into consideration while assessing the risks related to nanomaterials.

Because of possession of unique characteristics such as high chemical reactivity; bioactivity; high ability to penetrate organs, tissues and even cells; and higher bioavailability, nanomaterials are considered a better option in biomedical applications, but these sometimes pave way for potential toxicity. Keeping in mind the toxicity potential, several government organizations have implemented legal regulations such as laws and rules to minimize or mitigate the risks associated with nanomaterials. For controlling the potential risks of nanomaterials, only the USA and European Union (EU) have made strong regulatory bodies and legislation to date. However, some protocols have been made by different agencies like the Food and Drug Administration (FDA), the US Environmental Protection Agency (USEPA) and the Institute for Food and Agricultural Standards (IFAS) to deal with and overcome the effects related to nanoparticles and nanomaterials. The FDA has been working on nanomaterials since 2006 for identifying their sources; approximating the impacts on the environment and the risks which they pose to the biological community including humans, plants and animals; and suggesting ways to avoid or mitigate the risk associated with them (Jeevanandam et al. 2018).

3 Environmental Fate and Behaviour of Nanomaterials

To date, there is no direct relevant data in the scientific literature about the fate, activities, behaviour and regulations of nanomaterials in the environment. This is a rapidly developing area of research and a piece of significant knowledge and database will emerge in literature in the upcoming years. Nanoparticles in the air are referred to as ultrafine particles, whereas in water or soil, they are known by the term colloids having different size range (Lead and Wilkinson 2006). Colloidal science forms the basis of fate and entry of nanomaterial into the aquatic environment. Colloids in the aquatic environment show aggregation behaviour (Gustafsson and Gschwemd 1997). The colloidal particles eventually aggregate to form sufficiently larger particles and are transported by the process of sedimentation. Such behaviour of colloids is called colloidal pumping (Honeyman and Santschi 1992; Sigg 1994). Colloids can be used for the removal of metals as metals sorb on the surface of colloids which then form aggregates. The resulting aggregate settles out, thereby transferring metals from water column to sediments. This can be considered as an important process in the self-purification and self-reclamation of water bodies. The same process is applicable for nanomaterials as, because of smaller size and larger surface area, they have more affinity for natural colloids and get sorb onto their surface which fosters their removal from the water column. The phenomenon of aggregation and sedimentation works for the fate of engineered NPs (Sigg 1994). Some nanoparticles are degraded by subjecting them to biotic and abiotic factors resulting in their elimination from the water column. Abiotic degradation may be brought about by hydrolysis and photocatalytic reactions taking place in surface water. Transformation of certain metallic and organic nanomaterials may take place under anaerobic conditions (Nurmi et al. 2005). The behaviour of nanomaterials in a water environment is greatly influenced by the ability of dispersion or solubility of the aqueous medium. In addition to these, the most important factors are the interactions between nanomaterials and the chemicals of natural and anthropogenic origin along with biological and non-biological processes. The rate of settlement of water-based nanoparticles is quite slow as compared to the larger particles made of the same material. Upon entry into the environment, nanoparticles may remain intact or undergo dissolution, speciation, chemical transformation and physical and biological changes such as settling, agglomeration, adsorption, etc. (Naghdi et al. 2017).

Particles of nanomaterials once released in the environment form aggregates with the colloids and other particulate matters present in the environment whether it is soil or water and accumulate in the sediments. In addition to this, other factors like turbulent motion exerted by the benthic organisms and the bioturbation process taking place in the bottom sediments are considered as the chief receptors and sink of nanoparticles in the case of surface waters (Harrison et al. 2003). Nanoparticles and natural colloids interaction will affect the behaviour of nanoparticles. A uniform microlayer consisting of lipids, carbohydrates and protein-rich components and natural colloids containing humic acid may serve as a platform for the sorption of nanomaterials as well as a medium for their transportation over long distances in aquatic environments (Moore 2006). These interactions sometimes will also impede nanoparticle removal efficiency from the water column. In spite of the large number of nanoparticle removal processes known, some insoluble nanoparticles remain in the water column, get dispersed in the aquatic environment and become stabilized. The concentration of nanomaterials in the suspension can be as high as 100 ppm but is more typically in the range of 10–50 ppm. The stability and suspension of particles in the aquatic environment are sensitive to pH, organic matter and ionic strength especially in the case of some metal oxides like TiO_2, ZnO and CeO_2 (Fortner et al. 2005; Keller et al. 2010). The pH of the aquatic environment is considered to be an important parameter affecting the settling rate and sorption of nanomaterials.

As cited by Lin et al. (2010), most engineered nanomaterials occur as aggregates rather than as individual particles in aquatic environments. Therefore, emphasis should be given to transport, transformation, fate and bioavailability of aggregates rather than on individual nanoparticles (Hotze et al. 2010). It is quite difficult to study any material in the nanoscale dimension in the natural system as their spatial and temporal variations, their properties like polydispersity and their complex nature amplify the difficulties in studying them. Hence, to thoroughly investigate nanomaterials present in the environment, it is important to identify and quantify the nanoparticle concentration as well as their speciation to evaluate the behaviour and transport processes and to be aware of their biological interactions.

After gaining insight into the fate and behaviour of nanomaterials in the environment, it is presumed that the fate and entry of nanoparticles largely depend on the characteristic features of both nanomaterials and the receiving environment. The characteristic features include physical, chemical and biological properties.

4 Measurement of Nanomaterials

The advancement in the field of analytical instrumentation allowed for the discovery and detection of many emerging contaminants present in the surface as well as groundwater. Still the identification of the diverse sources of emerging contaminants, their ecotoxicological effects and their impact on humans remains a challenge. Difficulty in their detection is attributed to the low concentration of nanomaterials and the complex nature of the environmental matrices. There is no data in the published literature regarding the accurate concentration of nanomaterials or nanoparticles in the environmental system. It is difficult to quantify exposure levels of nanomaterials once introduced into the environment due to the inadequate understanding of the natural diminution processes.

Progress in analytical methods is still going on to effectively monitor the presence of nanomaterials in the natural media and ecological studies on emerging contaminants (nanomaterials) have been made primarily on modelled exposure setup based on the expected use of nanomaterials.

4.1 Monitoring Science

Environmental monitoring requires rapid and reliable analytical tools that can perform sample analysis with minimal sample handling (Khin et al. 2012). Effectively monitoring nanoparticles in the environment requires meeting several requirements. The foremost important requirements include the detection level, precision and accuracy of the equipment; the analytical methods selected for the analysis must be capable of detecting the relevant concentration, i.e., in the range of nanogram per litre or picogram per litre. These requirements can be met by integrating the existing methods with new and advanced methods which can work at the nanoscale level to ensure effective screening and highly selective detection. Hence, it is important to choose those analytical methods which can afford size measurements. Important parameters like shape, size, external morphology, concentration, particle size, chemical makeup, porosity, the charge carried by the surface, etc. need to be considered while making such measurements.

4.2 Technologies and Approaches for the Characterization, Analysis and Measurement of Concentrations and Fluxes of Nanomaterials in Aquatic Systems

Characterization and analysis of nanomaterials is a very hard task and involves the dependence on various analytical techniques along with some significant analytical methods. The analytical methodology for different emerging contaminants including nanomaterials has grown considerably and requires further improvements in terms of sensitivity and selectivity especially for complex matrices such as wastewater (Bwapwa and Jaiyeola 2019). The analytical techniques have been broadly categorized into different groups depending upon the need of the analysis at the nanoscale, microscale or bulk scale. Figure 3 illustrates the commonly used methods for nanoparticle characterization and analysis. Although microscale resolution techniques characterize nanoparticles at the microscale level, there are still some electron microscopes which have a resolution in the nanoscale region.

Visualization of nanomaterials is commonly done by making use of high-resolution microscopes with resolution in the range of sub-nanometre. These high-resolution microscopes include electron microscopes and scanning probe microscopes. The use of TEM, SEM and AFM not only brings visualization of nanomaterials but also provides information regarding aggregation, dispersion, shape, size and structure (Mavrocordatos et al. 2004; Naghdi et al. 2017). Better analysis of elements requires the coupling of electron microscopes with other analytic tools making a combinational technique known as analytical electron microscopy (AEM). The major limitation associated with the use of electron microscopes is that they require vacuum conditions for their efficient operation which limits their use to solid samples only. The liquid samples need to be dehydrated especially in

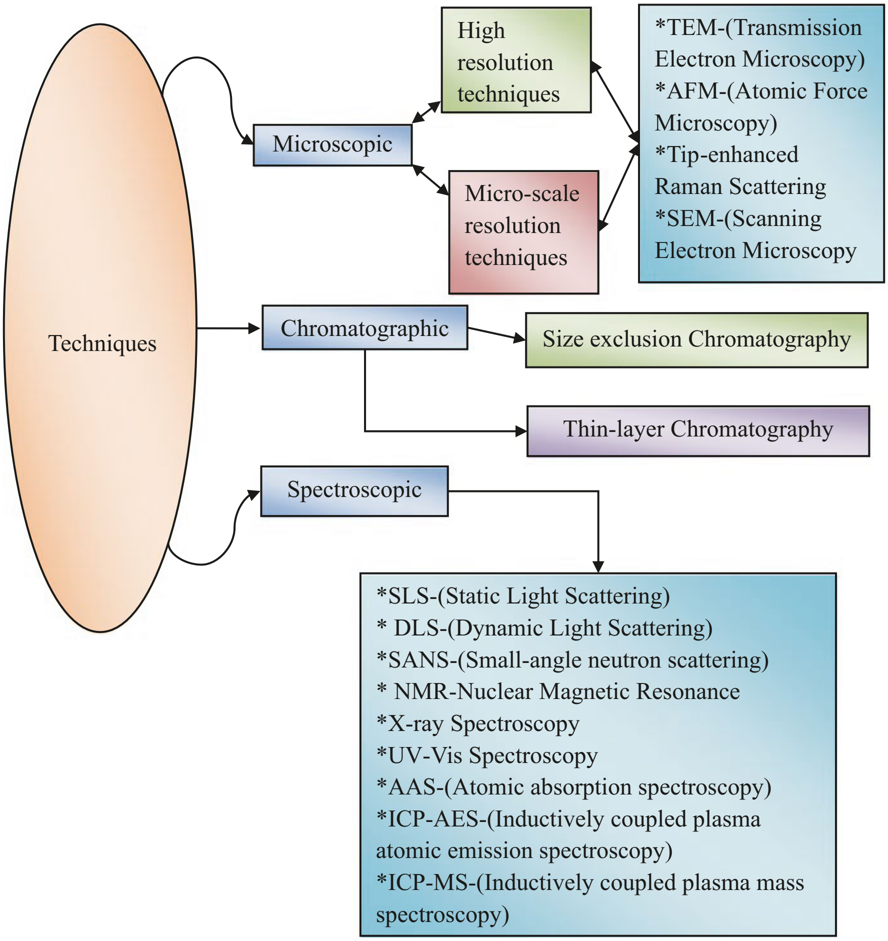

Fig. 3 Nanoparticle characterization techniques. (Naghdi et al. 2017; Mourdikoudis et al. 2018)

the case of SEM and TEM which leads to alteration of surface thereby producing misleading results (Liu 2005).

There is a broad spectrum of spectroscopic techniques that can be used for the analysis and characterization of nanomaterials because of their selectivity and sensitivity (Simonet and Valcarcel 2009). In spectroscopic determination, the use of X-rays, laser light or neutrons as light source facilitates the determination of particle of different composition and diverse size range. X-ray diffraction (XRD), an instrument that comes under X-ray spectroscopy, can differentiate between different phases existing in TiO_2 nanoparticles including anatase, rutile and amorphous phase (Naghdi et al. 2017).

Chromatographic techniques can effectively separate nanoparticles from samples based on the principle of chromatography as these techniques are rapid, sensitive and non-destructive enabling the sample to be used for further analysis. A size fractionation method commonly known by the term size exclusion chromatography (SEC) is widely used for the characterization of nanoparticles particularly TiO_2 particles (Rao et al. 2009). In this technique, particles can be separated based on their hydrodynamic properties which in turn determine their ability to pierce through the porous structure of the column. Thin-layer chromatography (TLC) is another chromatographic technique widely used in nanoparticle characterization. The technique is simple and speedy, enabling the separation process by making use of a thin layer of the adsorbent. Mainly non-volatile mixtures are separated using silica gel as an adsorbent. This technique has been used on silica surfaces to study mobility, deposition and attachment of capped AgNPs on their surface at varying pH and different ionic strength (Thio et al. 2012). In addition to these techniques, certain devices like condensation particle counters (CPCs) are available which can serve as primary tools for the measurement of nanoparticles. Table 2 provides a list of commonly used techniques and the characteristics they depict depending upon the different physical and chemical makeups of nanomaterials. Different techniques are employed in the determination depending upon the phase in which the particle to be examined exists.

Table 2 Characterization of nanomaterials

Characteristics	Techniques/instruments	References
Size	**For samples in solid phase**: SEM, TEM, DLS (dynamic laser light scattering) **For particles in liquid phase**: photon correlation spectroscopy and centrifugation **For gaseous phase**: Scanning Mobility Particle Sizer (SMPS)	Ealias and Saravanakumar (2017), Kato et al. (2010) and Padmavathy and Vijayaraghavan (2008)
Surface area	**Particles in liquid phase**: nuclear magnetic resonance spectroscopy (NMR) **Gaseous phase**: Modified Scanning Mobility Particle Sizer (SMPS) and differential mobility analyser (DMA)	Ealias and Saravanakumar (2017)
Composition	X-ray photoelectron spectroscopy (XPS), chemical digestion followed by wet chemical analysis, UV-Vis spectroscopy	Sharma and Rao (2014), Bzdek et al. (2011) and Daqiao et al. (2016)
Surface morphology	SEM, TEM	Hodoroaba et al. (2014) and Padmavathy and Vijayaraghavan (2008)
Surface charge	**Liquid phase**): zeta potentiometer **Gaseous phase**: differential mobility analyser (DMA)	Ealias and Saravanakumar (2017)
Porosity and pore size	TEM	Prasad et al. (2011)

4.3 Issues in Measurements Related to Wastewater Matrix

It is quite difficult to measure the exact concentration of nanomaterials/nanoparticles in the water because of the complexity of the aquatic matrix. Nanoparticles in the aquatic environment undergo association, aggregation, degradation, settling, etc., making their measurement a complex affair. Moreover, the properties of nanomaterials are also affected by the physical, chemical and biological properties of water. The chemical toxicity and related information cannot be obtained using instrumental analysis. The effect-related quality norms for emerging contaminants are generated by conventional bioassays and emerging bioanalytical systems (Escher et al. 2018). Bioassays and bioanalytical systems are early-warning systems that indicate the presence of unknown compounds by detecting the signals produced by the substances.

5 Environmental Risk Assessment of Nanomaterials

Recent advances in nanotechnology find many applications by using nanoparticles in environmental remediation for the removal of contaminants from water, sewage and air and in environmental instruments such as sensors, green nanotechnology and the reduction of greenhouse gases. The use of nanoparticles offers advantages as well as disadvantages from a sustainability perspective which need to be identified as early as possible. Hence, it becomes necessary to assess the likely environmental impacts of nanomaterials by monitoring their entire life cycle right from their generation to disposal. The life cycle perspective of nanomaterials for risk assessment is depicted in Fig. 4. The environmental impact of nanomaterials can be determined keeping in mind some basic information like how they are used, methods of their separation in water and air medium and their mobility, stability and toxicity. Such basic information about the behaviour and toxicity of nanoparticles along with some data on the expected concentration of nanoparticles is required to assess the risks associated with nanoparticles. Classical approaches used in aquatic ecological assessment may not apply to nanomaterials since exposure assessments classically depend on predicting the soluble portion of the contaminant. The prerequisite for environmental risk assessment of nanoparticles or nanomaterials includes the identification of the sources, the environmental pathways and the applications of nanoparticles as well as the biological species that are sensitive to nanoparticles (Reijnders 2006). The foremost step in ecological risk assessment is the characterization of the exposure scenario followed by the identification of organisms potentially at risk. Quantitative assessment of organism response to nanoparticle exposure facilitates effect assessment. Completion of exposure and effect assessment leads to the accomplishment of risk characterization.

Various studies regarding the life cycle assessment of nanoparticles have been carried out, but only a few actually succeeded as there exists a significant

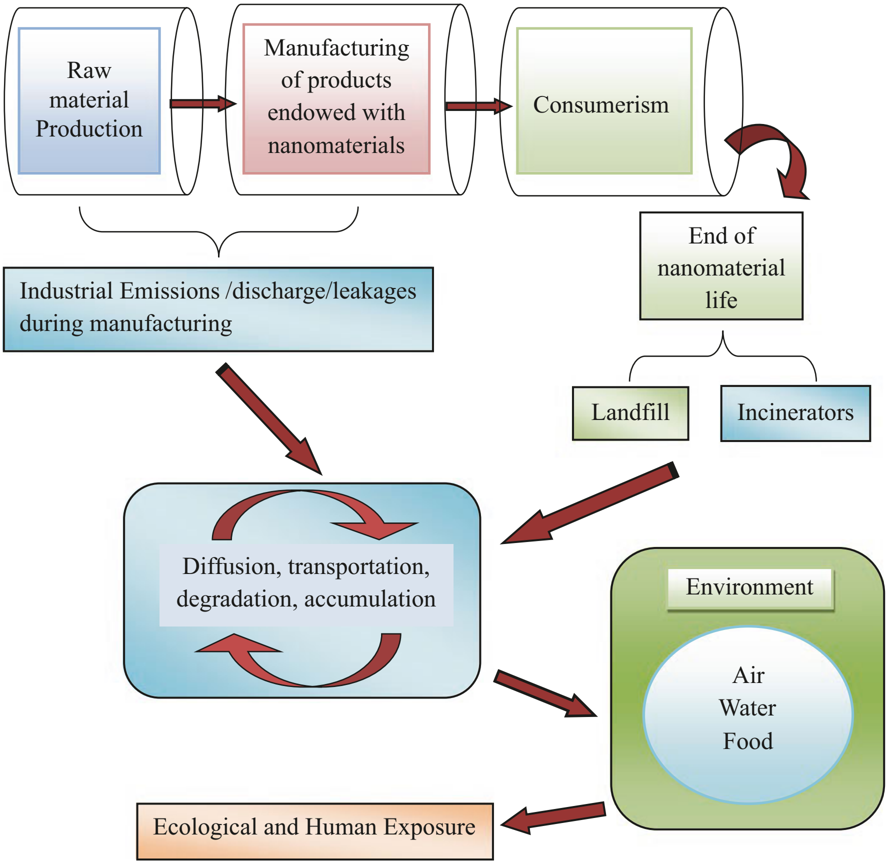

Fig. 4 Life cycle perspective to risk assessment. (Hischier and Walser 2012; Gavankar et al. 2012)

knowledge gap in the field. The usage of nanoparticles in products is poorly documented, emission rates need to be quantified and the impact of nanoparticles on health and the environment is currently unclear (Hischier and Walser 2012; Gavankar et al. 2012).

5.1 Evaluation of Risks on Biological Systems (Both Floral and Faunal) in the Aquatic Environment

As nanoparticles or nanomaterials are used in almost every product used on a daily basis, a large population of humans and of course other living organisms including both terrestrial and marine are exposed to nanomaterial toxicity. The environmental impacts of NPs are expected to increase in the near future. Nanoparticles can enter an organism through inhalation, through ingestion and through dermal route. Upon entry into the body, NPs can translocate to various tissues and organs where they exert potential ill effects. NP toxicity is also accelerated by their ability to organize around the protein concentration.

5.2 Toxicity of Silver Nanoparticles

Nanosilver is widely used in a wide variety of products including consumer and medical products due to the properties of silver at the nanoscale. Of more than 800 consumer products that contain nanomaterials, roughly 30% are claimed to contain silver particles (Wijnhoven et al. 2009). Examples are food packaging materials and food supplements, odour-resistant textiles, electronics and household appliances, cosmetics and medical devices, water disinfectants and room sprays. Some of the applications have resulted in concern for the government and discussions among the public since very little is known about the potential risks of nanosilver. An example is an addition of silver nanoparticles to socks to kill the bacteria associated with foot odour as silver has a remarkable antibacterial property. Silver present in products can easily leak into wastewater during washing, thus potentially disrupting helpful bacteria used in wastewater treatment facilities or endangering aquatic organisms in lakes and streams (Khan et al. 2012). Nanosilver has physical and chemical properties which could pose a serious threat to both human and environmental health. It is hypothesized that the toxic effects of nanosilver are due to a combination of the specific properties of silver nanoparticles and the generation of ions from them. The toxic effects of silver substances are proportional to the rate of release of free silver ions from them.

The wide applications of silver allow for exposure through various routes of entry into the body mainly through inhalation and ingestion. Metallic silver poses minimal health risk, whereas soluble silver compounds are readily absorbed and have the potential to pose an adverse health risk (Drake and Hazelwood 2005). Chronic exposure to silver causes a permanent grey or blue-grey discolouration of the skin particularly in sun-exposed regions and the eye (Drake and Hazelwood 2005). Long-term exposure causes the accumulation of soluble silver compounds in the brain and muscles (Fung and Bowen 1996). Inhalation of nanosilver results in a small increase in blood calcium; no additional effect on haematology and blood chemistry has been reported (Ji et al. 2007). In a case reported by Trop et al. (2006), Acticoat coated with nanosilver used for the treatment of severe burns leads to silver poisoning and elevated levels of liver enzymes (aspartate aminotransferase, alanine aminotransferase and gamma-galactosyltransferase). There are limited studies on the potential toxicities caused by nanosilver (Wijnhoven et al. 2009).

5.3 Toxicity/Toxicology of Carbon Nanotubes

Among the wide range of engineered nanomaterials, CNTs are attracting much attention as they can be potential biomedical applicators because of their promising optical, electronic and mechanical properties. In their original state, CNTs are inert and need to be functionalized to make them reactive. Before going for their real-time applicability in the biological systems, the biocompatibility of the functionalized CNTs and their composite has to be tested. Contradicting reports have been obtained from various scientific tests on cells regarding the toxicity of CNTs. Some reports showed no signs of toxicity, while others indicated them to be highly toxic. Composition and surface functionalization are the two important factors that decide the toxic nature of CNTs (Khalid et al. 2016). Well-functionalized CNTs pose no harm to animal cells, while raw CNTs show severe toxicity even at moderate dosage. Some of the toxic effects of CNTs include an interruption in electron transfer across membranes, disruption of the cell envelope, production of secondary products like dissolved heavy metal ions or reactive oxygen species, oxidation of cell components, induction of genotoxicity and mesothelioma, activation of several cell signalling pathways, etc. (Manke et al. 2013). Raw CNTs cause inflammation and fibrotic reactions in the lungs (Lam et al. 2004; Fujita et al. 2015a, b). Several reports suggest that carbon nanoparticles exert chemical effects within the brain as well as have the ability to affect the integrity of blood-brain barrier (Agarwal and Rathore 2014).

5.4 Toxicology of Metal Oxide Nanoparticles

Metal oxide nanoparticles exhibit unique properties as compared to their larger counterparts which render them very useful for a wide range of applications. The other side of metal oxide nanoparticles has unpredictable effects on the environment and human health. Various in vitro experiments have been carried out to assess the toxic effects of metal oxide nanoparticles. Metal oxides like CoO, Ni_2O_3, Co_3O_4 and CuO have been shown to cause cell death by oxidation stress mechanism, while TiO_2 is used as a negative control. ZnO is significantly toxic to embryonic zebrafish (Wehmas et al. 2015). Metal oxides have been reported to elicit a series of adverse effects such as persistent stress to living organisms including humans and pulmonary damage in humans; could significantly reduce the production of neutrophil counts, mitochondrial damage and DNA damage; and induce cell inflammation, detrimental to cell viability, morphological transformations, cytotoxicity and genotoxicity (Seabra and Durán 2015; Cai et al. 2017; Zhang et al. 2017). The cytotoxicity of SiO_2 nanoparticles towards the human skin has been evaluated, and they have been found to be non-toxic to the human skin. However, amorphous SiO_2 nanoparticles cause inflammation of submucosal cells of the lungs and the release of reactive oxygen species (ROS) leading to apoptosis and decreased cell survival in humans (Seabra and Durán 2015).

5.5 *Toxicology of Nanoagrochemicals*

Nanoagrochemicals, in the form of nanopesticides or nanofertilizers, have become increasingly popular as an applicator in the field of agriculture for plant protection and nutrition. Exposure and toxicity assessment relies on the investigation of the environmental fate of a compound. However, there have been very few studies investigating agrochemicals (Kah et al. 2013: Kah and Hofmann 2014). As given in scientific literature, there have been increasing incentives to develop nanotechnology-based agrochemical products that may be least harmful to the environment relative to conventional agrochemicals (Kah 2015) indicating the positive aspect of nanoagrochemicals. Some studies revealed nano-based agrochemicals to be highly toxic to the aquatic ecosystem, and they are also known to bioconcentrate in fish (Walker et al. 2018). The current level of knowledge seems to be insufficient for a reliable assessment of the risks associated with the use of nanoagrochemicals. Hence, a fair assessment of agrochemicals involves evaluating both the risks and benefits associated with their usage relative to current solutions. Currently, the published literature contains no comprehensive study that evaluates the efficacy and environmental impact of nanoagrochemicals under field conditions (Kah et al. 2018).

6 Nanomaterial Risk Management Programme

Exposure to the engineered nanomaterials can be controlled or minimized in the workplace or research laboratories by adopting a comprehensive risk management programme. The elements of the programme should address elements of hazard surveillance. The risk management programme should include risk analysis, some protective measures like engineering controls and administrative controls and personal protective equipment for controlling and minimizing the exposure to nanomaterials (NIOSH 2012). Figure 5 illustrates the major components of the nanomaterial risk management programme intended to reduce the risks associated with nanomaterials for assuring safety in the workplace and industrial and research facilities.

The risk management programme should ensure the protection of workers dealing with nanomaterials. Implementing effective measures to reduce exposure in the workplace is an early step and primary approach to prevent adverse health effects dealing with nanomaterials (Kuempel et al. 2012).

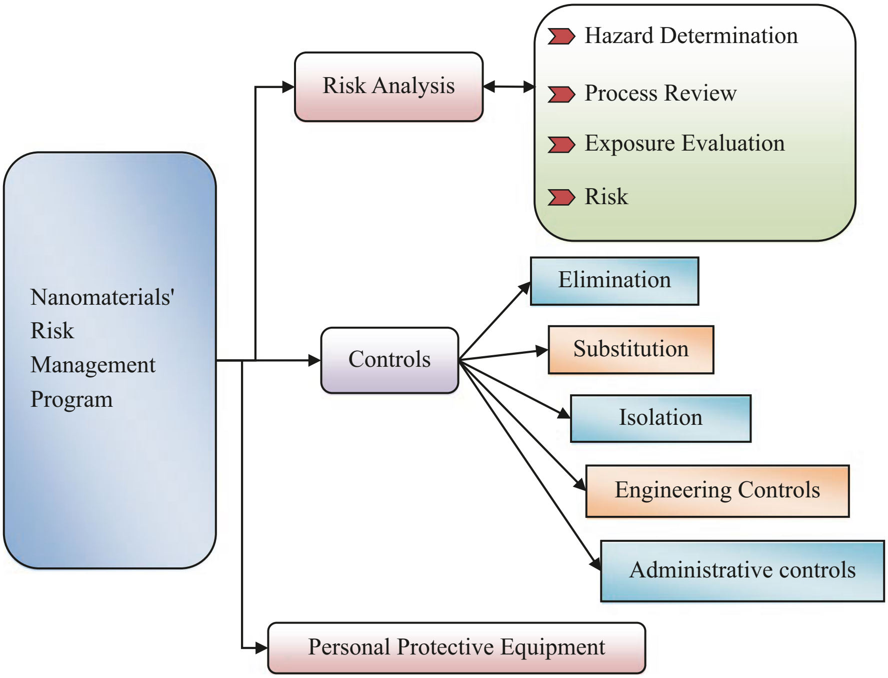

Fig. 5 Components of nanomaterial risk management programme. (NIOSH 2012)

7 Wastewater Treatment Techniques

There are various methods for the treatment of wastewater in terms of emerging contaminants. Basic techniques like filtration, adsorption, reverse osmosis (RO) and advanced oxidation processes (AOPs) can be applied for the removal of emerging contaminants from wastewater. Membrane technologies are rapidly advancing separation processes and are efficiently used nowadays especially in water and wastewater treatment facilities because of their reliability and contaminant removal potential and they also do not produce any harmful by-products. Membranes provide physical barriers to substances because of their pore and molecular size. The advanced version of membrane processes like nanofiltration and use of adsorbents have emerged as a potential and promising technology for the removal of emerging contaminants from wastewater (Khin et al. 2012; Bwapwa and Jaiyeola 2019). Nanofiltration is a filtration process wherein particles less than 0.5 nm–1 nm are rejected by a membrane under the influence of pressure (Gehrke et al. 2015). Nanoadsorbents based on conducting polymers can be used for the removal of heavy metal ions present in wastewater (Zare et al. 2018) and can be efficiently applied in the case of nanomaterials also. A wide spectrum of nanoadsorbents are available which can be used for adsorbing a wide range of nanomaterials because of the presence of active adsorption sites and tailored surface chemistry. Water treatment systems typically involve a series of coupled processes, each designed to remove one or more different substances in the source water, with the particular treatment process being based on the molecular size and properties of the target contaminants. Nanoadsorbents can be used for the remediation of various heavy metal and other metal oxides in nanoscale dimension as they get attached to the specific functional groups present on the surface of nanoadsorbents by the formations of certain bonds, thus facilitating their removal from the wastewater.

7.1 Effectiveness of Treatment Methods

The use of nanofiltration membranes in wastewater treatment has proven to be beneficial as compared to other techniques. It is preferred over reverse osmosis (RO) and can be used as pretreatment before RO to avoid biofouling and scale formation which are limiting factors in the RO process. Nanofiltration can remove almost all the turbidity and microorganisms as well as many divalent ions. It has been found that the nanofiltration process can reduce 37.3% of total dissolved solids, 80% ejection of divalent ions and 90% retention of bivalent cations and 60% retention of monovalent cations (Khin et al. 2012). Because of their outstanding performances in the removal of contaminants in atomic and ionic forms, these can also be applied for the retention of nanoscale materials because of their nanoscale pore size dimensions. It has been found that the nanofibres coated with TiO_2 can retain more than 95% of 60 nm particles at a very high flux rate.

7.2 Costs

As far as the cost of treatment technologies meant for the removal of nanomaterials as emerging contaminants is concerned, the use of these nanoscale technologies can be a costly affair. The production cost of nanomembranes and nanoadsorbents is quite high. Also, there are chances of membrane blocking in the case of nanofiltration membranes because of concentration polarization. Certain nanoparticle coating requires high energy for their activation as in the case of TiO_2 nanoparticles which further adds to the high cost. Also, there is a need for complex multistage process in the production of these technologies. Hence, future research should focus on overcoming these challenges and increase the cost-effectiveness of these treatment technologies.

8 Conclusion

Nanotechnology is a breakthrough technology and has provided us with many benefits over other conventional technologies. No doubt, nanoscale technology has wider applicability and has been used in our day-to-day life process because of its effectiveness and uniqueness and their drawbacks cannot be overlooked. Nanomaterials have emerged as a contaminant of concern in wastewater in recent years which need to be monitored and regulated. Various studies have been carried out in research laboratories regarding the toxicity of nanomaterials and various toxicity tests have been performed on laboratory animals. The results are drastic as the nanoscale materials can easily enter the bloodstream and cell system and bring undesirable alterations. Hence, there is a need to monitor and control these materials in water and other matrices. Various techniques have been developed, and the existing technologies have been modified for the quantification of these nanocontaminants. Among the widely used techniques, spectroscopic techniques have been considered as most appropriate in terms of their selectivity and sensitivity. Still there exist many problems regarding the measurement of concentration and their detection and monitoring in aquatic environment because of their low concentration in the environment and complexity of the environmental matrices as nanomaterials are affected by physical, chemical and biological process in water. Also, there should be implementation of protective plans and programmes to avoid nanomaterial exposure to minimize their toxicity. Further research should focus on overcoming the technical challenges, increase the effectiveness of treatment technologies for the remediation of nanoscale contaminants and enhance the positive side of nanomaterials.

References

Agarwal S, Rathore P (2014) Nanotechnology pros and cons to agriculture: a review. Int J CurrMicrobiol Appl Sci 3(3):43–55

Alagarasi A (2011) Chapter-introduction to nanomaterials. https://maken.wikiwijs.nl/userfiles/2/2ee21d1456a928da66dbaee2507257fcb96bbdcf.pdf

Alivisatos AP, Gu WW, Larabell C (2005) Quantum dots as cellular probes. Ann Rev Biomed Eng 7:55–76

Biswas P, Wu CY (2005) Nanoparticles and the environment. J Air Waste Manage Assoc 55(6):708–746

Bwapwa JK, Jaiyeola AT (2019) Emerging contaminants in drinking water and wastewater, effects on environment and remediation. Int J Appl Eng Res 14(2):539–546

Bzdek BR, Zordan CA, Luther IIIGW, Johnston MV (2011) Nanoparticle chemical composition during new particle formation. Aerosol Sci Technol 45(8):1041–1048

Cai X, Lee A, Ji Z, Huang C, Chang CH, Wang X, Liao YP, Xia T, Li R (2017) Reduction of pulmonary toxicity of metal oxide nanoparticles by phosphonate-based surface passivation. Part Fibre Toxicol 14(1):13. https://doi.org/10.1186/s12989-017-0193-5

Christian P, Von der Kammer F, Baalousha M, Hofmann T (2008) Nanoparticles: structure, properties, preparation and behaviour in environmental media. Ecotoxicology 17(5):326–343

Corma A, Chane-Ching JY, Airiau M, Martínez C (2004) Synthesis and catalytic properties of thermally and hydrothermally stable, high-surface-area SiO2–CeO2 mesostructured composite materials and their application for the removal of sulfur compounds from gasoline. J Catalysis 224(2):441–448

Daqiao H, Jizhi L, Shan J, Yanlei H, Wenjun W, Rongrong W, Bo Y (2016) Synthesis, structure and optical data storage properties of silver nanoparticles modified with azobenzene thiols. Mater Chem Phys 170:108–112

Drake PL, Hazelwood KJ (2005) Exposure-related health effects of silver and silver compounds: a review. Ann OccupHyg 49:575–585

Ealias AM, Saravanakumar MP (2017) November. A review on the classification, characterisation, synthesis of nanoparticles and their application. IOP Conf Ser Mater Sci Eng 263:032019

Escher BI, Aït-Aïssa S, Behnisch PA, Brack W, Brion F, Brouwer A, Buchinger S, Crawford SE, Du Pasquier D, Hamers T, Hettwer K (2018) Effect-based trigger values for in vitro and in vivo bioassays performed on surface water extracts supporting the environmental quality standards (EQS) of the European Water Framework Directive. Sci Total Environ 628:748–765

Fortner JD, Lyon Y, Sayes CM, Boyd AM, Falkner JC, Hotze EM, Alemany LB, Tao YJ, Guo W, Ausman KD, Colvin VL, Hughes JB (2005) C60 in water: nanocrystal formation and microbial response. Environ Sci Technol 39:4307–4316

Fujita K, Fukuda M, Endoh S, Maru J, Kato H, Nakamura A, Shinohara N, Uchino K, Honda K (2015a) Size effects of single-walled carbon nanotubes on in vivo and in vitro pulmonary toxicity. InhalToxicol 27(4):207–223

Fujita K, Fukuda M, Endoh S, Maru J, Kato H, Nakamura A, Shinohara N, Uchino K, Honda K (2015b) Size effects of single-walled carbon nanotubes on *in vivo* and *in vitro* pulmonary toxicity. Inhal Toxicol 27(4):207–223. https://doi.org/10.3109/08958378.2015.1026620

Fung MC, Bowen DL (1996) Silver products for medical indication: risk-benefit assessment. Clin Toxicol 34:119–126

Gavankar S, Suh S, Keller AF (2012) Life cycle assessment at nanoscale: review and recommendations. Int J Life Cycle Assess 17(3):295–303

Gehrke I, Geiser A, Somborn-Schulz A (2015) Innovations in nanotechnology for water treatment. Nanotechnol Sci Appl 8:1–17

Gupta VK, Agarwal S, Saleh TA (2011) Chromium removal by combining the magnetic properties of iron oxide with adsorption properties of carbon nanotubes. Water Res 45(6):2207–2212

Gustafsson O, Gschwemd G (1997) Aquatic colloids: concepts, definitions and current challenges. Limnol Oceanogr 42:517–528

Harrison RM, Harrad SJ, Lead JR (2003) The global disposition of contaminants. In: Hoffman DA, Rattner BA, Burton GA, Cairns J (eds) Handbook of ecotoxicology, 2nd edn. Lewis, Boca Raton, pp 633–651

Hischier R, Walser T (2012) Life cycle assessment of engineered nanomaterials: state of the art and strategies to overcome existing gaps. Sci Total Environ 425:271–282

Hodoroaba VD, Rades S, Unger WE (2014) Inspection of morphology and elemental imaging of single nanoparticles by high- resolution SEM/EDX in transmission mode. Surf Interface Anal 46(10-11):945–948

Honeyman BD, Santschi PH (1992) The role of particles and colloids in the transport of radionuclides and trace metals in the ocean. In Buffle J, van Leeuwen HP, eds, Environmental Particles, Vol 1. Lewis, Boca Raton, FL, USA 379–423

Hotze EM, Phenrat T, Lowry GV (2010) Nanoparticle aggregation: challenges to understanding transport and reactivity in the environment. J Environ Qual 39:1909–1924

Jeevanandam J, Barhou A, Chan YS, Dufresne A, Danquah MK (2018) Review on nanoparticles and nanostructured materials: history, sources, toxicity and regulations. Beilstein J Nanotechnol 9(1):1050–1074

Ji JH, Jung JH, Kim SS, Yoon JU, Park JD, Choi BS, Chung YH, Kwon IH, Jeong J, Han BS, Shin JH, Sung JH, Song KS, Yu IJ (2007) Twenty-eight-day inhalation toxicity study of silver nanoparticles in Sprague-Dawley rats. InhalToxicol 19:857–871

Kah M (2015) Nanopesticides and nanofertilizers: emerging contaminants or opportunities for risk mitigation? Front Chem 3. https://doi.org/10.3389/fchem.2015.00064

Kah M, Hofmann T (2014) Nanopesticides research: current trends and future priorities. Environ Int 63:224–235

Kah M, Beulke S, Tiede K, Hofmann T (2013) Nanopesticides: state of knowledge, environmental fate and exposure modelling. Crit Rev Environ Sci Technol 43:1823–1867

Kah M, Kookana RS, Gogos A, Bucheli TD (2018) A critical evaluation of nanopesticides and nanofertilizers against their conventional analogues. Nat Nanotechnol 13(8):677–684

Kato H, Fujita K, Horie M, Suzuki M, Nakamura A, Endoh S, Yoshida Y, Iwahashi H, Takahashi K, Kinugasa S (2010) Dispersion characteristics of various metal oxide secondary nanoparticles in culture medium for in vitro toxicology assessment. Toxicol in Vitro 24(3):1009–1018

Keller AA, Wang H, Zhou D, Lenihan HS, Cherr G, Cardinale BJ, Miller R, Ji Z (2010) Stability and aggregation of metal oxide nanoparticles in natural aqueous matrices. Environ Sci Technol 44(6):1962–1967

Khalid P, Hussain MA, Suman VB, Arun AB (2016) Toxicology of carbon nanotubes-a review. Int J Appl Eng 11(1):148–157

Khan SS, Mukherjee A, Chandrasekaran (2012) Adsorptive removal of silver nanoparticles (SNPs) from aqueous solution by Aeromonas punctata and its adsorption isotherm and kinetics. Colloids Surf B 92:156–160

Khin MM, Nair AS, Babu VJ, Murugan R, Ramakrishna S (2012) A review on nanomaterials for environmental remediation. Energy Environ Sci 5(8):8075–8109

Klaine SJ, Alvarez PJ, Batley GE, Fernandes TF, Handy RD, Lyon DY, Mahendra S, McLaughlin MJ, Lead JR (2008) Nanomaterials in the environment: behavior, fate, bioavailability, and effects. Environ Toxicol Chem Intl J 27(9):1825–1851

Kuempel ED, Geraci CL, Schulte PA (2012) Risk assessment and risk management of nanomaterials in the workplace: translating research to practice. Ann Occup Hyg 56(5):491–505

Lam CW, James JT, McCluskey R, Hunter RL (2004) Pulmonary toxicity of single-wall carbon nanotubes in mice 7 and 90 days after intratracheal instillation. Toxicol Sci 77(1):126–134

Laurent S, Forge D, Port M, Roch A, Robic C, Vander Elst L, Muller RN (2008) Magnetic iron oxide nanoparticles: synthesis, stabilization, vectorization, physicochemical characterizations, and biological applications. Chem Rev 108(6):2064–2110

Lead JR, Wilkinson KJ (2006) Environmental colloids: current knowledge and future developments. In: Wilkinson KL, Lead JR (eds) Environmental colloids: behaviour, structure and characterization. John Wiley, Chichester, pp 1–15

Lin W, Huang Y, Zhou X, Ma Y (2006) Toxicity of cerium oxide nanoparticles in human lung cancer cells. Int J Toxicol 25:451–457

Lin D, Tian X, Wu F, Xing B (2010) Fate and transport of engineered nanomaterials in the environment. J Environ Qual 39(6):1896–1908

Liu J (2005) Scanning transmission electron microscopy and its application to the study of nanoparticles and nanoparticle systems. J Electron Microsc 54(3):251–278

Manke A, Wang L, Rojanasakul Y (2013) Pulmonary toxicity and fibrogenic response of carbon nanotubes. Toxicol Mech Methods 23(3):196–206

Mavrocordatos D, Pronk W, Boller M (2004) Analysis of environmental particles by atomic force microscopy, scanning and transmission electron microscopy. Water Sci Technol 50(12):9–18

Mehta K, Sata P, Saraswat A, Mehta D (2018) Nanomaterials in water purification. Int J Adv Eng Res Dev. Conference of nanotechnology & applications in civil engineering-2018, vol 5, Special Issue 3(Feb 2018)

Moore MN (2006) Do nanoparticles present ecotoxicological risks for the health of the aquatic environment? Environ Int 32(8):967–976

Mourdikoudis S, Pallares RM, Thanh NT (2018) Characterization techniques for nanoparticles: comparison and complementarity upon studying nanoparticle properties. Nanoscale 10:12871–12934

Naghdi M, Metahni S, Ouarda Y, Brar SK, Das RK, Cledon M (2017) Instrumental approach toward understanding nano-pollutants. Nanotechnol Environ Eng 2(1):3

NIOSH (2012) Publication No. 2012-147, May 2012. https://www.cdc.gov/niosh/docs/2012-147/pdfs/2012-147.pdf

Nurmi JT, Tratnyek PG, Sarathy V, Baer DR, Amonette JE, Pecher K, Wang C, Linehan JC, Matson DW, Penn RL, Driessen MD (2005) Characterization and properties of metallic iron nanoparticles: spectroscopy, electrochemistry, and Kinetics. Environ Sci Technol 39(5):1221–1230

Padmavathy N, Vijayaraghavan R (2008) Enhanced bioactivity of ZnO nanoparticles—an antimicrobial study. Sci Technol Adv Mater 9:035004. https://doi.org/10.1088/1468-6996/9/3/035004

Prasad KPS, Dhawale DS, Sivakumar T, Aldeyab SS, Zaidi JSM, Ariga K, Vinu A (2011) Fabrication and textural characterization of nanoporous carbon electrodes embedded with CuO nanoparticles for supercapacitors. Sci Technol Adv Mater 12(4):044602. https://doi.org/10.1088/1468-6996/12/4/044602

Priyadarsini S, Mukherjee S, Mishra M (2018) Nanoparticles used in dentistry: A review. J Oral Biol Craniofac Res 8(1):58–67

Rao Y, Antalek B, Minter J, Mourey T, Blanton T, Slater G, Slater L, Fornalik J (2009) Organic solvent-dispersed TiO2 nanoparticle characterization. Langmuir 25(21):12713–12720

Reijnders L (2006) Cleaner nanotechnology and hazard reduction of manufactured nanoparticles. Clean Prod 14:124–133

Seabra AB, Durán N (2015) Nanotoxicology of metal oxide nanoparticles. Metals 5(2):934–975

Shandilya N, Bihan OL, Bressot C, Morgeneyer M (2015) Emission of titanium dioxide nanoparticles from building materials to the environment by wear and weather. Environ Sci Technol 49(4):2163–2170

Sharma V, Rao LJM (2014) An overview on chemical composition, bioactivity and processing of leaves of Cinnamomum tamala. Crit Rev Food Sci Nutr 54:433–448

Sigg L (1994) The regulation of trace elements in lakes: The role of sedimentation. In Buffle J, de Vitre RR, eds, The Chemical and Biological Regulation of Aquatic Systems. Lewis, Boca Raton, FL, USA, pp 175–195

Simonet BM, Valcarcel M (2009) Monitoring nanoparticles in the environment. Anal Bioanal Chem 393:17–21

Singh J, Dutta T, Kim KH, Rawat M, Samddar P, Kumar P (2018) 'Green' synthesis of metals and their oxide nanoparticles: applications for environmental remediation. J Nanobiotechnol 16:84. https://doi.org/10.1186/s12951-018-0408-4

Thio BJR, Montes MO, Mahmoud MA, Lee D-W, Zhou D, Keller AA (2012) Mobility of capped silver nanoparticles under environmentally relevant conditions. Environ Sci Technol 46(13):6985–6991

Tran NH, Reinhard M, Gin KYH (2018) Occurrence and fate of emerging contaminants in municipal wastewater treatment plants from different geographical regions-a review. Water Res 133:182–207

Trop M, Novak M, Rodl S, Hellbom B, Kroell W, Goessler W (2006) Silver-coated dressing acticoat caused raised liver enzymes and argyria-like symptoms in burn patient. J Trauma Acute Care Surg 60(3):648–652

Walker GW, Kookana RS, Smith NE, Kah M, Doolette CL, Reeves PT, Lovell W, Anderson DJ, Turney TW, Navarro DA (2018) Ecological risk assessment of nano-enabled pesticides: a perspective on problem formulation. J Agric Food Chem 66(26):6480–6486. https://doi.org/10.1021/acs.jafc.7b02373

Wehmas LC, Anders C, Chess J, Punnoose A, Pereira CB, Greenwood JA, Tanguay RL (2015) Comparative metal oxide nanoparticle toxicity using embryonic zebrafish. Toxicol Rep 2:702–715

Wijnhoven SWP, Peijnenburg WJGM, Herberts CA, Hagens WI, Oomen AG, Heugens EHW, Rosze B, Bisschops J, Gosens I, Meent DVD, Dekkers S, Jong WHD, Zijverden MV, Sips AJAM, Geertsma RE (2009) Nano-silver- a review of available data and knowledge gaps in human and environmental risk assessment. Nanotoxicology 3(2):109–138

Wiesner MR, Lowry GV, Jones KL, Hochella MFJr, Di Giulio RT, Casman E, Bernhardt ES (2009) Decreasing uncertainties in assessing environmental exposure, risk, and ecological implications of nanomaterials. Environ Sci Technol 43:6458–6462

Zare EN, Motahari A, Sillanpää M (2018) Nanoadsorbents based on conducting polymer nanocomposites with main focus on polyaniline and its derivatives for removal of heavy metal ions/ dyes: a review. Environ Res 162:173–195

Zhang L, Xie H, Liu Y, Wang J (2017) Research on nanotoxicity of an iron oxide nanoparticles and potential application. Toxicol: Open Access 3(3). https://doi.org/10.4172/2476-2067.1000130

Pharmaceuticals in Indian Aquatic Environment: Risk and Implications for Management

Bhupandar Kumar, Premanjali Rai, and Paromita Chakraborty

Abstract Pharmaceuticals, a group of emerging contaminants (ECs), have aroused serious concern owing to their detection at levels threatening to the health of the ecosystem. India is one of the top producers and consumers of pharmaceuticals in the world. Recent studies conducted on pharmaceutical residues in the Indian environmental matrices reported unsurpassed levels of antibiotics and nonsteroidal anti-inflammatory drugs (NSAIDs). Reports submit the fact that India carries the largest burden of drug-resistant pathogens with anti-resistant genes (ARGs) in river water of India. Despite posing potential risk to the public health, pharmaceuticals still stand unregulated. Several advanced wastewater treatment technologies such as the photodegradation, adsorption, membrane filtration, catalytic oxidation, etc. have been devised for efficient removal of this special class of chemical compounds. A comprehensive documentation has been provided in the chapter as an attempt to acquire state of knowledge on occurrence, ecological risks, and possible decontamination techniques with respect to pharmaceuticals in the Indian environment.

Keywords Pharmaceutical residue · Emerging contaminant · Indian waters · Antibiotic resistance · Environmental risk · Risk quotient · Remediation techniques

1 Introduction

Although the use of pharmaceuticals is inevitable in our daily lives, the amount of chemicals discharged into the environment is voluminous and is reported to be at par with the amount of pesticides used annually (Daughton and Ternes 1999). As a result of their continuous use and discharge into the environment, pharmaceutical

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compounds accumulate in the environment. PPCPs gained considerable attention as environmental pollutants when the US Geological Survey between 1992 and 2000 reported 82 chemicals, including a variety of PPCPs in 139 waterways (Kolpin et al. 2002). One research revealed 713 pharmaceuticals (142 as transformation products) in the environment (IWW 2014). These organic pollutants are considered a part of emerging contaminants (ECs), which enter the aquatic systems from various point and non-point sources (Archer et al. 2017).

The emerging risks associated with the use of pharmaceuticals were recognized when studies linked their effects with the biological activity in organisms such as feminization of fish, induction of vitellogenin synthesis in male aquatic organisms, and acute renal failure in white-backed vultures (Santos et al. 2010). The pollution of the environment resulting from increased use and discharge of human and veterinary medicines in parent or metabolite form poses a threat to the health of the ecosystem including humans through drinking water supplies and contaminated food products. Their overuse may induce resistance in humans and animals through prolonged exposure.

Although the presence of pharmaceuticals in the environment is an emanating threat to the health of the ecosystem, these groups of chemicals do not face any regulatory guideline on their discharge limits at present. There are no specific legal requirements to monitor the levels of pharmaceuticals even in drinking water on a global scale. Hence, it is important to identify the problems associated with their use and residual effects on the environment so that necessary remedial measures may be adopted.

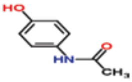
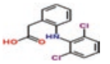
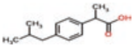
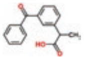
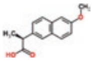
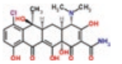
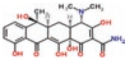
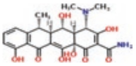
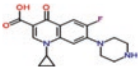
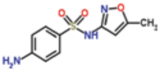
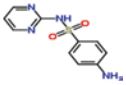
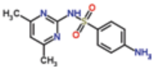
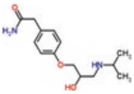
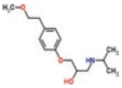
2 Major Classes of Pharmaceuticals

In the year 2008, United States Environmental Protection Agency (US EPA) proposed the universal waste rule and defines pharmaceutical as any chemical product, vaccine or allergen, not containing a radioactive component, that is intended for use in the diagnosis, cure, mitigation, treatment, or prevention of disease or injury in man or other animals (US EPA 2012). Today, pharmaceuticals are not only used for treating human and veterinary medical ailments but are also actively engaged in aquacultural practices and used as herbicides and as growth promoters in animal husbandry. They include a vast group of chemical compounds having different structures, chemical properties, and therapeutic modes of action. Depending on their intended use, pharmaceuticals can be categorized to include the following groups of compounds shown in Table 1. Table 2 shows the physicochemical properties along with the chemical structures of some representative compounds of pharmaceuticals from different groups.

Table 1 Common classes of pharmaceuticals

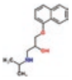
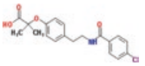
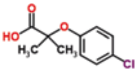
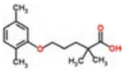
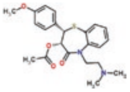
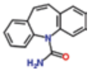
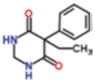
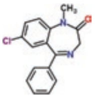
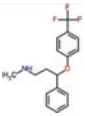
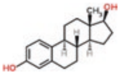
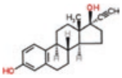
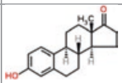
Pharmaceuticals						
Antibiotics	NSAIDs	Antihypertensives	Hormones	Lipid regulators	Anticonvulsants	Antidepressants
Erythromycin	Aspirin	Metoprolol	17β-Estradiol	Bezafibrate	Carbamazepine	Fluoxetine
Amoxicillin	Diclofenac	Propranolol	Estradiol	Clofibric acid	Primidone	Paroxetine
Cefixime	Ibuprofen	Atenolol	Estrone	Gemfibrozil	Dilantin	Diazepam
Levofloxacin	Acetaminophen	Enalapril	Mestranol	Simvastatin	Phenobarbital	Meprobamate
Ciprofloxacin	Indomethacin	Losartan				
Azithromycin	Naproxen	Furosemide				
Doxycycline		Diltiazem				
Norfloxacin						
Ofloxacin						
Spiramycin						
Roxithromycin						
Enrofloxacin						
Cloxacillin						
Ampicillin						
Lincomycin						
Sulfamethoxazole						
Trimethoprim						

Table 2 Chemical properties of pharmaceuticals

Class and compound	CAS	Molecular formula	Molecular weight (g/mol)	Solubility in water	Log K_{ow}	Chemical structure
Nonsteroidal anti-inflammatories						
Acetaminophen	103-90-2	$C_8H_9NO_2$	151.163	100 mg/mL	0.46	
Diclofenac	15307-86-5	$C_{14}H_{11}Cl_2NO_2$	296.149	2.37 mg/L	4.51	
Ibuprofen	15687-27-1	$C_{13}H_{18}O_2$	206.281	<1 mg/mL	3.97	
Ketoprofen	22071-15-4	$C_{16}H_{14}O_3$	254.281	<1 mg/mL	3.12	
Naproxen	22204-53-1	$C_{14}H_{14}O_3$	230.259	>3 mg/mL	3.18	
Antibiotics						
Tetracyclines						
Chlortetracycline	57-62-5	$C_{22}H_{23}ClN_2O_8$	478.880	8.6 mg/mL	−0.62	
Tetracycline	60-54-8	$C_{22}H_{24}N_2O_8$	444.435	50 mg/mL	−1.37	
Doxycycline	564-25-0	$C_{22}H_{26}N_2O_9$	462.450	50 mg/mL	−0.02	
Quinolones						
Ciprofloxacin	85721-33-1	$C_{17}H_{18}FN_3O_3$	331.341	<1 mg/mL	0.28	
Sulfa drugs						
Sulfamethoxazole	723-46-6	$C_{10}H_{11}N_3O_3S$	253.278	<1 mg/mL	0.89	
Sulfadiazine	68-35-9	$C_{10}H_{10}N_4O_2S$	250.277	<1 mg/mL	−0.09	
Sulfamethazine	57-68-1	$C_{12}H_{14}N_4O_2S$	278.330	<1 mg/mL	0.89	
Beta-blockers						
Atenolol	29122-68-7	$C_{14}H_{22}N_2O_3$	266.336	13.3 mg/mL	0.16	
Metoprolol	37350-58-6	$C_{15}H_{25}NO_3$	267.364	16.9 mg/mL	1.88	

(continued)

Table 2 (continued)

Class and compound	CAS	Molecular formula	Molecular weight (g/mol)	Solubility in water	Log K_{ow}	Chemical structure
Propranolol	525-66-6	$C_{16}H_{21}NO_2$	259.343	61.7 mg/L	3.48	
Lipid regulators						
Bezafibrate	41859-67-0	$C_{19}H_{20}ClNO_4$	361.819	>54.3 µg/mL	4.25	
Clofibric acid	882-09-7	$C_{10}H_{11}ClO_3$	214.645	583 mg/L	2.57	
Gemfibrozil	25812-30-0	$C_{15}H_{22}O_3$	250.333	11 mg/mL	4.77	
Antihypertensive						
Diltiazem	42399-41-7	$C_{22}H_{26}N_2O_4S$	414.518	465 mg/L	2.79	
Anticonvulsants						
Carbamazepine	298-46-4	$C_{15}H_{12}N_2O$	236.269	<1 mg/L	2.45	
Primidone	125-33-7	$C_{12}H_{14}N_2O_2$	218.252	500 mg/L	0.91	
Antidepressants						
Diazepam	439-14-5	$C_{16}H_{13}ClN_2O$	284.740	50 mg/L	2.82	
Fluoxetine	54910-89-3	$C_{17}H_{18}F_3NO$	309.326	50 mg/L	na	
Steroids (estrogens)						
17β-Estradiol	50-28-2	C18H24O2	272.321	3.6 mg/L	4.01	
17α-Ethynylestradiol	57-63-6	$C_{20}H_{24}O_2$	296.403	11.3 mg/L	3.67	
Estrone	53-16-7	$C_{18}H_{22}O_2$	270.366	30 mg/L	3.13	

na, not available; information compiled, (1) https://pubchem.ncbi.nlm.nih.gov, (2) https://chemspider.com, (3) www.chemicalland21.com, (4) www.sigmaaldrich.com; Bottoni et al. (2010)

2.1 Nonsteroidal Anti-inflammatory Drugs (NSAIDs)

NSAIDs are mostly carboxylic acid derivatives attached to planar aromatic functionalities, which act by reversible and irreversible inhibition of enzymes involved in stimulus of pain. They are used as mild analgesics, antipyretics, and anti-inflammatories. Out of the diverse pool of pharmaceuticals, such types of over-the-counter (OTC) drugs are extensively consumed due to their quick relief action in pain and easy availability of non-prescription drugs in the market. Approximately 90% of them belong to the commonly administered therapeutic group of nonsteroidal anti-inflammatory drugs (Crouse et al. 2012). Major types of NSAIDs include phenylpyrazolones (e.g., phenylbutazone), oxicams/enol acids (e.g., meloxicam), propionic acid derivatives (e.g., ibuprofen), fenamates (e.g., diclofenac), anilides (e.g., paracetamol), and salicylic acid derivatives (e.g., acetylsalicylic acid).

2.2 Antibiotics

Some major classes of antibiotics include the quinolones, tetracyclines, and sulfonamides. Antibiotics belonging to the class of quinolones are recommended for acute cases of bacterial prostatitis and in sickle cell disease patients where there is a risk of developing osteomyelitis from *Salmonella*. Tetracyclines are broad-spectrum antibiotics primarily used for treatment of various infections and also as growth promoter in animal husbandry. The basic structure of tetracyclines consists of a hydro naphthacene backbone containing four (tetra) fused rings, and the analogs vary primarily by substitutions of the fifth, sixth, or seventh position on the backbone rings. Examples include tetracyclines, chlortetracycline, oxytetracycline, doxycycline, etc. Sulfa drugs are N-substituted derivatives of p-aminobenzene sulfonamide (sulfanilamide) that vary in the amide substitution (R-group) to give analogs (e.g., sulfamethoxazole, sulfamerazine, sulfamethazine, sulfachloropyridazine, etc.). They are used against bacterial, protozoal, parasitic, and even fungal infections in human and animal systems and sometimes as herbicides too. Other subclasses of antibiotics include aminoglycosides, lincosamides, macrolides, and glycopeptides, which are complex molecules exhibiting bulky structure and are bactericidal but slow in action.

2.3 Cardiovascular Drugs

Beta-blockers are particularly used to prevent cardiac arrhythmias and myocardial infarction. They are also widely used to treat hypertension in some cases. The chemical structure of beta-blockers comprises of an aromatic ring structure attached to a side alkyl chain possessing a secondary hydroxyl and amine functional group. Some pharmaceuticals belonging to the class of beta-blockers are propranolol, metoprolol, atenolol, etc.

2.4 Anti-ulcer Drugs

These drugs are used to treat and reduce peptic ulcers and irritation of the gastrointestinal tract. These may include antibiotics to cure helicobacter infections, histamine H2 antagonists to reduce gastric acid secretion, and antacids for symptomatic relief. Examples include omeprazole, famotidine, ranitidine hydrochloride, etc.

2.5 Antihistamines

Antihistamines are used to treat allergies, cold, and flu symptoms by blocking the release of histamine from histamine-1 receptors located in the airways, blood vessels, and gastrointestinal tract. They are taken as inexpensive, generic, and OTC drugs for getting relief from nasal congestion and sneezing, caused due to pollen, dust mites, or animal allergy. Examples of antihistamines are cetirizine, fexofenadine, chlorpheniramine, and diphenhydramine.

2.6 Antidepressant

Antidepressant drugs work by acting on the chemical imbalances of neurotransmitters (serotonin, dopamine, and noradrenaline) in the brain, which are responsible for changes in mood and behavior, thereby reducing symptoms of depressive disorders. They include but are not limited to depression, anxiety, agitation, obsessive-compulsive disorders, major depressive disorder, diabetic peripheral neuropathic pain, neuropathic pain, social anxiety disorder, post-traumatic stress disorder, etc. Examples of antidepressants are amitriptyline, amoxapine, clomipramine, desipramine, doxepin, imipramine, nortriptyline, protriptyline, etc.

2.7 Antiepileptics

Antiepileptics also known as anticonvulsant/antiseizure drugs are used in the treatment of epileptic seizures and bipolar disorders and also used as mood stabilizers. Antiepileptic drugs act in the central nervous system by reducing the overall neuronal activity. This can be achieved either by blocking voltage-dependent sodium channels (e.g., carbamazepine) or by enhancement of the inhibitory effects of the gamma-aminobutyric acid neurotransmitter (e.g., benzodiazepines).

2.8 Hormones

There are two groups of hormones (estrogens and progesterone), which are responsible for development of female secondary sexual characteristics. Small quantities are also produced in males. As drugs, female sex hormones are used to treat menstrual and menopausal disorders and are used as oral contraceptives. Estrogens may be used to treat cancer of the breast or prostate, and progestin (synthetic progesterone) is used to treat endometriosis. Examples include 17β-estradiol, 17α-ethynylestradiol, and estrogen.

All of these compounds have their own chemical structure and properties, which decides their behavior in sorption, elimination, degradation, and other associated fate in the environment. The common classes of pharmaceuticals with their generic names, common uses, possible side effects, and mode of action are presented in Table 3.

3 Pharmaceuticals in Indian Scenario

The Indian pharmaceutical industry boasts an aggressive growth in market size from USD 12.6 billion in 2009 to a projected value of USD 55 billion by 2020 (McKinsey and Company, Inc.). For instance, the potential of Indian pharmaceutical industry can be assessed by the fact that 80% of the antiretroviral drugs used to combat AIDS (acquired immune deficiency syndrome) are supplied globally. More than 50% of the global demand for pharmaceuticals used in vaccination, 40% of generic demand in the USA, and 25% of all the drugs used in the UK are also supplied by the Indian pharmaceutical companies (IBEF 2019). The industry's primary focus has been manufacturing of generic medicines and export of bulk drugs. As per the Department of Pharmaceuticals, Government of India (2018), the growth of the Indian pharmaceutical industry is such that it ranks third by volume on a global basis today, accounting for 10% of global pharmaceutical production (Sharma et al. 2019). With such fast growth and an unprecedented expansion of the pharmaceutical sector, India is bound to be an active hotspot of pharmaceuticals in the environment.

Table 3 Common classes of pharmaceuticals and their common uses, possible side effects, and mode of action

Class/generic name	Common uses	Possible side effects	Mode of action
Aminoglycosides			
Amikacin	Gram-negative bacteria, such as *E. coli*, *Klebsiella*, and *Pseudomonas aeruginosa*	Hearing loss, vertigo, kidney damage	Inhibits synthesis of vital proteins
Gentamicin			
Neomycin			
Tobramycin			
Streptomycin	Tuberculosis		
Carbacephem			
Ertapenem	Bactericidal	GI upset and diarrhea, nausea, allergic	Inhibits cell wall synthesis
Doripenem			
Meropenem			
Cephalosporins			
Cefadroxil	Gram-positive organisms	GI upset and diarrhea, nausea, allergic	Disrupts the synthesis of the peptidoglycan layer of bacterial cell walls
Cefazolin			
Cefalexin			
Cefamandole	Less Gram-positive cover, improved Gram-negative cover		
Cefoxitin			
Cefprozil			
Cefuroxime			
Cefixime	Improved coverage of Gram-negative organisms, except *Pseudomonas*. Reduced Gram-positive cover		
Cefditoren			
Cefoperazone			
Cefotaxime			
Ceftazidime			
Ceftizoxime			
Ceftriaxone			
Glycopeptides			
Teicoplanin	Active against aerobic and anaerobic Gram-positive bacteria including MRSA; vancomycin is used orally for the treatment of *C. difficile* colitis		Disrupts the synthesis of the peptidoglycan layer of bacterial cell walls
Vancomycin			
Telavancin			
Dalbavancin			
Oritavancin			
Lincosamides			
Clindamycin	Staph-, pneumo-, and streptococcal; clindamycin for acne	Pseudomembranous enterocolitis	Inhibits bacterial protein synthesis
Lincomycin			
Macrolides			

(continued)

Table 3 (continued)

Class/generic name	Common uses	Possible side effects	Mode of action
Azithromycin	Respiratory tract infections, streptococcal infections, syphilis	Nausea, vomiting, and diarrhea Hearing loss Jaundice	Inhibits bacterial protein synthesis
Clarithromycin			
Dirithromycin			
Erythromycin			
Roxithromycin			
Penicillins			
Amoxicillin	Wide range of infections; penicillin used for streptococcal infections, syphilis, and Lyme disease	GI upset and diarrhea Allergic reactions Brain and kidney damage (rare)	The same mode of action as other beta-lactam
Ampicillin			
Carbenicillin			
Cloxacillin			
Dicloxacillin			
Flucloxacillin			
Mezlocillin			
Methicillin			
Oxacillin			
Penicillin			
Polypeptides			
Bacitracin	Eye, ear, or bladder infections	Kidney and nerve damage	Inhibits bacterial protein synthesis
Colistin			
Polymyxin			
Quinolones/fluoroquinolone			
Ciprofloxacin	Urinary tract infections, bacterial prostatitis, community-acquired pneumonia, bacterial diarrhea, mycoplasmal infections, gonorrhea	Nausea (rare), irreversible damage to the central nervous system (uncommon)	Inhibits the bacterial DNA replication and transcription
Gatifloxacin			
Gemifloxacin			
Levofloxacin			
Lomefloxacin			
Moxifloxacin			
Nalidixic acid			
Norfloxacin			
Ofloxacin			
Sulfonamides			
Mafenide	Urinary tract infections (except sulfacetamide, used for eye infections, and mafenide and silver sulfadiazine, used topically for burns)	Nausea, vomiting, and diarrhea Allergy Crystals in urine Kidney problems Decrease in WBC count Sunlight sensitivity	Folate synthesis inhibition. Folate is necessary for the cell to synthesize nucleic acids, and in its absence, cells cannot divide
Sulfacetamide			
Sulfadiazine			
Sulfadimethoxine			
Sulfamethoxazole			
Sulfanilamide			
Sulfisoxazole			
Tetracyclines			

(continued)

Table 3 (continued)

Class/generic name	Common uses	Possible side effects	Mode of action
Demeclocycline	Syphilis, chlamydial infections, Lyme disease, mycoplasmal infections, acne rickettsial infections, malaria	GI upset Sensitivity to sunlight Toxicity to pregnant mother Staining of teeth	Inhibits the binding of aminoacyl-tRNA to the mRNA-ribosome complex
Doxycycline			
Minocycline			
Oxytetracycline			
Tetracycline			
Drugs against mycobacteria			
Ethionamide	Antituberculosis		Inhibits peptide synthesis
Rifampicin	Mycobacteria and Gram-positive	Reddish-orange tears and urine	Binds to the RNA polymerase to inhibit transcription
Rifabutin	*Mycobacterium avium* complex	Rash, discolored urine, GI symptoms	
Streptomycin	Antituberculosis	Neurotoxicity	As aminoglycosides
Others			
Chloramphenicol	Meningitis, typhus, cholera. Gram-negative, Gram-positive anaerobes	Rarely: aplastic anemia	Inhibits bacterial protein synthesis
Metronidazole	Anaerobic bacteria; giardiasis, trichomoniasis, and amoebiasis	Discolored urine, headache, metallic taste, nausea	Produces toxic free radicals that disrupt DNA and proteins
Thiamphenicol	Gram-negative, Gram-positive anaerobes. Widely used in veterinary medicine	Rash	A chloramphenicol analog inhibiting bacterial protein synthesis
Tigecycline	Skin/skin structure infections, soft tissue infections. Effective for Gram-positive and Gram-negative	Teeth discoloration	Similar structure with tetracycline, but stronger

(Compiled from-EMA 2019, MSD Manual, O'Rourke et al. 2020)

4 Fate of Pharmaceuticals in Aquatic Ecosystem

After consumption or direct discharge of expired pharmaceuticals, they are eliminated as active metabolites and parent compounds into waste streams to surface waters to contaminate the environment. Drugs discarded in municipal solid wastes and dumped in landfills could undergo degradation or adsorption or leach into water bodies. A study reported drugs in solid waste at levels of 7.4 to 45 mg/kg (Musson and Townsend 2009). Large quantities of veterinary pharmaceutical compounds (VPCs) are used worldwide in the form of feed additives and growth promoters and for prophylactic purposes. After administration of VPCs, they are not completely metabolized inside animal body. As a result, a portion of them is released to the environment in feces and urine. They also enter the environment from spills generated by anaerobic manure storage lagoons, manure fertilization of farm fields, runoff from farm fields, and discharge from aquaculture operations. As these compounds are quite resistant to existing elimination processes, once disposed of in the environment, they are easily transported to different environmental compartments in a pathway similar to human pharmaceuticals. Therefore, VPCs were reported in surface waters, groundwaters, soil, and air, and they carry their own potential for contaminating these environmental sinks.

The hospitals and drug manufacturing units ought to be the most obvious and impressive discharge units of pharmaceuticals. However, the waste streams from such sources rarely undergo any specialized treatment at the conventional WWTPs. The elimination rate of pharmaceuticals in WWTPs has been reported to vary up to 99% depending on the technology applied and the properties of pharmaceutical compounds. This may result in their tendency to (i) mineralize to low molecular weight compounds (CO_2 and H_2O) and (ii) simply resist elimination due to low adsorption coefficients and hydrophobicity, resulting in entrapment by suspended solids and sewage sludge, (iii) or these compounds may also convert into the parent compound in the final effluent from conjugated metabolite resulting from microbial enzymatic cleavage in wastewater and sewage sludge. Thus, WWTPs have been termed as hotspots of pharmaceutical contamination in the overall environment. The effluents loaded with pharmaceuticals are discharged into rivers, lakes, and estuaries. Once pharmaceuticals reach surface water bodies, they may undergo natural attenuation processes such as photolysis or sorption by sediments. The pharmaceuticals retained by sewage sludge may also reach the environment when used as fertilizers on agricultural lands. Hence, a potential source of pharmaceuticals in the environment is agricultural runoff, which leads them into nearby water bodies by runoff during rainfall, or even worse, they may seep into groundwater. The concentration levels of pharmaceuticals most commonly detected in the Indian aquatic environment are discussed in the following section.

5 Pharmaceuticals in the Aquatic Environment

5.1 Surface Water

Several studies have reported pharmaceuticals in surface waters around the world. Mutiyar and Mittal (2012) reported traces of NSAIDs and other pharmaceuticals in the Yamuna river. High level of caffeine has been reported in several surface waters from India, including Yamuna river (0.808 μg/L) (Mutiyar and Mittal 2012), Ganga river (0.743 μg/L) (Sharma et al. 2019), and lakes of Nagpur, Maharashtra (46.97 μg/L) (Archana et al. 2016). Ketoprofen was also found at the highest level of 107 ng/L in the Ganga river (Sharma et al. 2019). The Kaveri and Tamiraparani rivers of South India have also been found to be contaminated by carbamazepine at an average concentration of 28.3 ng/L and triclosan at 944 ng/L (Ramaswamy et al.

2011). In other countries, carbamazepine levels have been reported to be up to 48 ng/L in river waters of France (Bouissou-Schurtz et al. 2014), 11.47 ng/L in China (Zhang et al. 2018), and 0.22 ng/L in the USA (Archer et al. 2017). The Musi river, a tributary of the Krishna river, was detected with a host of fluoroquinolone antibiotics (ciprofloxacin, lomefloxacin, ofloxacin, norfloxacin, enrofloxacin, pefloxacin, and difloxacin) with ciprofloxacin, ofloxacin, and norfloxacin reportedly present at the highest concentrations, up to 5015, 542.4, and 251 μg/L, respectively (Gothwal and Shashidhar 2016). The Kaveri, Vellar, and Tamiraparani rivers were also found to contain NSAIDs (naproxen, diclofenac, ibuprofen, ketoprofen, and acetylsalicylic acid) at maximum concentrations of 28, 103, 200, 100, and 660 ng/L, respectively (Shanmugam et al. 2014). Comparatively, the Sindian river in Taiwan was found to contain NSAIDs including naproxen (270 ng/L), diclofenac (56.5 ng/L), ibuprofen (4350 ng/L), and ketoprofen (45 ng/L) (Lin et al. 2010). The Tiber river in Italy was also contaminated by these NSAIDs at higher level of 264, 120, 210, and 150 ng/L (in the same order) (Patrolecco et al. 2013). In Tehran, the river water contents of NSAIDs were reported to be 0.037 μg/L (ibuprofen), 0.041 μg/L (naproxen), 0.025 μg/L (diclofenac), and 0.041 μg/L (indomethacin) (Eslami et al. 2015). Most of the studies have reported the source of pharmaceutical contamination in the surface water to be wastewater discharge either as effluent from STPs or from drug manufacturing units. However, seasonal variation was also observed in the concentration of sulfamethoxazole during monsoon (0.9 μg/L) and post-monsoon (0.16 μg/L) seasons in the Kaveri river (Iyanee et al. 2013). Mutiyar and Mittal (2014b) reported ampicillin (13.74 μg/L), ciprofloxacin (1.4 μg/L), gatifloxacin (0.48 μg/L), sparfloxacin (2.1 μg/L), and cefuroxime (1.7 μg/L) in effluent from STPs discharging into Yamuna river in Delhi. Fick et al. (2009) reported high level of ciprofloxacin up to 6.5 mg/L in lakes receiving WWTPs in Patancheru, Hyderabad. The Cooum river flowing through the Chennai city was reported to be contaminated with triclocarban (6.18 μg/L), ibuprofen (2.32 μg/L), an antiplatelet metabolite carboxylic acid (1.37 μg/L), atenolol (3.18 μg/L), and amphetamine (0.98 μg/L) (Subedi et al. 2015).

5.2 Groundwater/Drinking Water

Sharma et al. (2019) reported caffeine, ibuprofen, carbamazepine, and ketoprofen levels of 262 ng/L, 49.4 ng/L, 27.2 ng/L, and 23.4 ng/L, respectively, in the groundwater of the Ganga river basin. Jindal et al. (2015) reported diclofenac concentrations at 48 ng/mL and pitavastatin at 0.48 ng/mL in the groundwater sample of Mohali, Punjab. The well waters used for drinking purposes in close proximity to a WWTP of drug manufacturing units in Patancheru, Hyderabad, were detected with antibiotics such as cetirizine (28 μg/L), ciprofloxacin (14 μg/L), enoxacin (1.9 μg/L), and terbinafine (0.055 μg/L) (Fick et al. 2009). NSAIDs such as diclofenac and ibuprofen at 120 and 250 ng/L, respectively, have been reported in groundwater at a depth of 0.5 m below the main trench sewer pipe in London (Ellis et al. 2003). Olaitan et al. (2014) reported average concentrations of diclofenac, chloroquine, paracetamol, and ciprofloxacin at 17.0, 5.0, 3.0, and 1.0 μg/L, respectively, in several wells in a pharmaceutical industrial area of Sango Ota, Ogun State of Nigeria. Benotti et al. (2009), in other countries, detected sulfamethoxazole (0.32 ng/L) and carbamazepine (6800 ng/L) in finished water from drinking water treatment plants in the USA, while energy drinks in China were reported with diclofenac at 8310 ng/L (Zhang et al. 2013).

5.3 Sewage Treatment Plants

Some of the most commonly detected pharmaceuticals reported to occur in the wastewater from Indian sewage treatment plants are carbamazepine (a psychoactive), atenolol (antihypertensive), triclocarban and triclosan (antimicrobials), trimethoprim and sulfamethoxazole (antibacterials), ibuprofen and acetaminophen (analgesics), and caffeine (stimulant). Mutiyar and Mittal (2013) reported amoxicillin in the influent and effluent samples of a STP in Delhi at 172.6 ng/L (influent) and 62.5 ng/L (effluent). In another study by Mutiyar and Mittal (2014b), the influent samples of STP in Okhla, New Delhi, were highly contaminated with antibiotics such as ampicillin, ciprofloxacin, gatifloxacin, sparfloxacin, and cefuroxime at the mean concentration levels of 104.2, 20.1, 2.7, 22.5, and 3.4 μg/L, respectively. The levels of these antibiotics (in the same order) were found to occur at 12.68, 8.0, 1.22, 0.14, and 0.22 μg/L in the effluent samples after the treatment (Subedi et al. 2015). The concentration of sulfamethoxazole in wastewater effluent was 0.23 μg/L (Subedi et al. 2015), 0.63 μg/L (Akiba et al. 2016), and 1.02 μg/L (Prabhasankar et al. 2016). Amoxicillin was also detected in a WWTP of Japan at levels of 100–2000 ng/L (Matsuo et al. 2011). The average concentration of sulfamethoxazole in the WWTPs was similar to the concentrations obtained in a WWTP outlet in Spain (Carballa et al. 2004), while it is lower than the average for Europe (1.7 μg/L, Loos et al. 2013) and Canada (1.8 μg/L, Guerra et al. 2014). Forty-three pharmaceutical compounds along with their 13 metabolites including psychoactives, illicit drugs, and artificial sweeteners were reported in 5 STPs of India (Subedi et al. 2015). The NSAIDs constitute a major portion of the pharmaceuticals consumed, and apart from their extensive usage, NSAIDs are frequently encountered in the environment as these acidic molecules are negatively charged at near neutral pH of wastewater, which escape sorption by sewage sludge and remain at dissolved phase in wastewater (Fent et al. 2006). Ibuprofen, ketoprofen, and diclofenac have been detected at 26.45, 16.21, and 25.68 μg/L levels, respectively, in the wastewater drains of India (Singh et al. 2014). Comparatively, NSAIDs in WWTP effluents of Tehran have been detected at levels of 0.045, 0.054, 0.033, and 0.057 μg/L for ibuprofen, naproxen, diclofenac, and indomethacin, respectively (Eslami et al. 2015).

5.4 Pharmaceutical from Production Facilities and Hospital Wastewater

Wastewater discharges from pharmaceutical production facilities and hospitals are the major potent source of environmental contamination by pharmaceuticals. The levels of ciprofloxacin, cetirizine, metoprolol, enrofloxacin, citalopram, norfloxacin, lomefloxacin, enrofloxacin, and ofloxacin in effluent of bulk drug manufacturers near Hyderabad were up to 31000, 1400, 950, 900, 840, 420, 300, 300, and 160 μg/L, respectively (Larsson et al. 2007). The level of ciprofloxacin in similar wastewater of other countries has been 0.6 μg/L in Canada (Guerra et al. 2014), 1.4 μg/L in Portugal (Santos et al. 2013), 3.7 μg/L in Italy (Verlicchi et al. 2012), and 6.9 μg/L in Australia (Pal et al. 2010). In wastewater from hospital in Ujjain, Madhya Pradesh, were found concentrations of ofloxacin, levofloxacin, ceftriaxone, ciprofloxacin, tinidazole, sulfamethoxazole, metronidazole, and norfloxacin at 73, 81, 60, 237, 88, 81, 3.8, and 23 μg/L, respectively (Diwan et al. 2010). In southern India, two sewage treatment plants (STPs) receiving hospital effluent were also reported to have chloramphenicol (Akiba et al. 2016). They also reported concentrations of trimethoprim (103–285 ng/L), ofloxacin (1715–2469 ng/L), and sulfamethoxazole (207–637 ng/L) in the wastewater from one STP, and from another STP, concentrations were 43–46 ng/L, 500–537 ng/L, and 40–50 ng/L, respectively. Higher concentrations of sulfamethoxazole (307–8714 ng/L) and ofloxacin (3135–24,811 ng/L) have been reported to occur in the hospital effluents of Coimbra, Portugal (Santos et al. 2013). Prabhasankar et al. (2016) reported presence of sulfamethoxazole, trimethoprim, erythromycin, chloramphenicol, naproxen, bezafibrate, and ampicillin in the samples of STP receiving hospital wastewater in Karnataka. Comparatively, higher concentrations of pharmaceuticals from hospital wastewaters in Portugal were reported as 8714 ng/L for sulfamethoxazole, 3963 ng/L for trimethoprim, 7545 ng/L for erythromycin, 6042 ng/L for naproxen, and 1359 ng/L for bezafibrate (Santos et al. 2013).

6 Toxicity of Pharmaceuticals

6.1 Toxicity of Anti-cancer (Antineoplastic) Compounds

Individual and combinations of anti-cancer compounds at varying concentrations are reported to have organism-specific toxicity (Toolaram et al. 2014). For example, EC_{50} of cisplatin and 5-fluorouracil for algae *Pseudokirchneriella subcapitata* is 1.52 mg/L and 0.13 mg/L, respectively, and 0.67 mg/L and 1.20 mg/L, respectively, for cyanobacteria *Synechococcus leopoliensis* (Brezovsek et al. 2014). However, EC_{50} for 5-fluorouracil and cytarabine were reported for *P. putida* is 0.044 mg/L and 17 mg/L, respectively, and 0.1 mg/L and 10 mg/L for *D. magna*, respectively (Zounkova et al. 2010).

6.2 Toxicity of Beta-Blocker Compounds

Beta-blockers act by inhibiting beta-adrenergic receptors, which are a class of receptors critical for normal functioning in the sympathetic branch of the autonomic nervous system in vertebrates. Fishes like other vertebrates possess β-receptors in the heart, liver, and reproductive system, and prolonged exposure to drugs belonging to this therapeutic class may cause deleterious effects in vertebrates. Drugs belonging to this class such as propranolol reduced growth rate of Japanese medaka fish in 2 weeks at 500 μg/L, while exposure to concentration of 0.5–1 μg/L resulted in a decrease of egg production (Huggett et al. 2002). Serotonin is an important neurotransmitter in hormonal and neuronal mechanisms, which is responsible for different regulatory and endocrine functions in vertebrates and invertebrates. Alterations in its levels may cause changes in appetite, immune system, reproduction, and other behavioral functions. In therapeutics, the selective serotonin reuptake inhibitors such as fluoxetine, fluvoxamine, paroxetine, and sertraline are the most widely used synthetic antidepressants (Santos et al. 2010).

6.3 Toxicity of NSAIDs *(Nonsteroidal Anti-inflammatory Drugs)*

NSAIDs act mainly by suppressing the cyclooxygenase (COX) enzyme responsible for synthesis of prostaglandins. Chronic toxicity test on the rainbow trout showed cytological changes in the liver, kidneys, and gills after 28 days of exposure to diclofenac at concentration of 1 μg/L (Triebskorn et al. 2004). They also reported concentration of 5 μg/L of diclofenac resulted in renal lesions and bioaccumulation in the liver, kidneys, gills, and muscles. Among all the NSAIDs, diclofenac is the most studied analgesic compound often detected at trace level in the environmental samples and possesses the highest acute toxicity on aquatic organisms. It was suggested that diclofenac is the most toxic analgesics with commonly reported lowest observed effect concentration (LOEC) of below 100 mg/L (Fent et al. 2006). Diclofenac has also been proven to be acutely toxic to vultures, decimating populations in the Indian subcontinent due to its ubiquitous use in cattle. This drug gained notorious popularity, and the manufacture of diclofenac for veterinary formulations was banned in 2006 after it was known to cause renal lesions in vultures (*Gyps bengalensis*, *Gyps indicus*, and Gyps tenuirostris) which scavenged on treated livestock bodies. Phytoplankton was found to be highly sensitive to diclofenac in acute, high-level exposure with an EC_{50} value of 14.5 mg/L in 96 h (Ferrari et al. 2004).

6.4 Toxicity of Hormones

Hormones, specifically estrogen compounds are some of the earliest pharmaceutical compounds reported to be present in the environment. Their presence has been linked with abnormal reproductive conditions in aquatic organisms, especially fishes. Ethynylestradiol (EE2) is a synthetic estrogen found in oral contraceptive pills with marked estrogenic effects in fish. Very low concentrations <1 ng/L were enough to give rise to an increased female population, and for EE2 concentrations above 3.5 ng/L, fish became completely feminized. The chronic exposure of fathead minnow to concentrations of EE2 at 5–6 ng/L led to feminization of male fish, through production of vitellogenin and disruption in gonadal development, causing intersex, and altered oogenesis in female fishes (Kidd et al. 2007). Such reproductive alterations led to the collapse of the fathead minnow population due to the loss of the young generations, which almost brought this species from the lake near to extinction.

6.5 Toxicity of Antibiotics

Bialk-Bielinska et al. (2011) carried out a systematic analysis of the ecotoxicological potential of many sulfonamide antibiotics on aquatic microorganisms including bacteria and algae. They estimated EC_{50} values of 0.02 mg/L for sulfadimethoxine in the inhibition of duckweed growth to >250 mg/L for 12 sulfonamides in enzyme inhibition assays. Additionally, the presence of elements in environment can potentially increase the toxicity of antibiotic contaminants (Zhang et al. 2012). Antibiotics such as tetracyclines and quinolones in association with copper, zinc, and cadmium, may result in more toxicity. The major concern with regard to the presence of antibiotics in the environment is the prevalence of antibiotic residues, which can result in the development of antibiotic-resistant strains of both environmental and pathogenic bacteria (Martinez 2009; Hong et al. 2013). A positive correlation has been found between antibiotic-resistant microorganisms and concentrations of aquatic antibiotic (Novo et al. 2013). This unwilling or unintentional resistance among commensal organisms is due to mutation in common genes and transfer of antibiotic-resistant genes (ARGs). Some ARGs has been detected in the clinical and non-clinical samples including drinking water (Jiang et al. 2011). With reference to antibiotic resistance, antimicrobial resistance (AMR) is another synonym which can be summed up to be antibiotic, antiviral, antiprotozoal, and antifungal resistance altogether.

Based on the economist from the UK, the impact of AMR is such that currently 700,000 deaths occur globally, and it has been estimated that by 2050, 10 million deaths/year are projected to occur (O'Neill 2016). In India, antibiotic-resistant neonatal infections cause the deaths of nearly 60,000 newborns each year (Laxminarayan et al. 2013). As per the scoping report on antimicrobial resistance in India, more than 70% isolates of Gram-negative bacteria *Escherichia coli*, *Klebsiella pneumoniae,* and *Acinetobacter baumannii* and nearly half of all *Pseudomonas aeruginosa* were resistant to antibiotics of fluoroquinolones set and third-generation cephalosporins. Among the Gram-positive organisms, 42.6% of *Staphylococcus aureus* were methicillin-resistant, and 10.5% of *Enterococcus faecium* were vancomycin-resistant. AMR challenges in India include the uncontrolled use of antibiotics in human as well as veterinary sectors; increased use of antibiotics as growth promoters in animals; inadequate implementation of regulations; limited or no regulations for food and non-food animals, respectively; and, importantly, inadequate interaction among clinicians and lab experts.

The World Health Organization (WHO) (WHO 2017) experts agreed on grouping the pathogens according to the species and the type of resistance and then stratifying the results in three priority tiers, critical, high, and medium, depicted below.

Priority 1: Critical
Acinetobacter baumannii, carbapenem-resistant ***Pseudomonas aeruginosa***, carbapenem-resistant ***Enterobacteriaceae*****,** carbapenem-resistant, cephalosporin-resistant
Priority 2: High
Enterococcus faecium, vancomycin-resistant ***Staphylococcus aureus***, methicillin-resistant, vancomycin-resistant ***Helicobacter pylori***, clarithromycin-resistant ***Campylobacter*****,** fluoroquinolone-resistant ***Salmonella*** spp., fluoroquinolone-resistant ***Neisseria gonorrhoeae***, cephalosporin-resistant, fluoroquinolone-resistant
Priority 3: Medium
Streptococcus pneumoniae, penicillin-non-susceptible ***Haemophilus influenzae***, ampicillin-resistant ***Shigella*** spp., fluoroquinolone-resistant

7 Environmental Risk Assessment (ERA)

The European Commission (Directive 92/18/EEC) specified that the medicinal product for human use must be accompanied by an environmental risk assessment. For this purpose, the European Medicines Agency (EMA) introduced “Note for Guidance” which included the guidelines for assessing the environmental risks of veterinary medicines only to be extended later to pharmaceuticals for human use by Directive 2001/83/EC (Santos et al. 2010). The guidelines recommend a stepwise procedure using acute toxicity tests on model organisms belonging to different phyla such as algae, zooplanktons, fish, and other invertebrates.

An ERA consists of two phases: Phase I, which is a screening phase, and Phase II, a testing phase, which may be conducted based on the results of Phase I. Firstly, Phase I includes calculation of the predicted environmental concentration (PEC) of the compound in surface water ($\mathrm{PEC}_{\text{surface water}}$), an assessment of the mode of action, and results from toxicological tests. A predicted environmental concentration calculation of the compound is restricted to the aquatic compartment ($PEC_{surface\ water}$). In case the $PEC_{surface\ water}$ is less than 0.01 μg/L and no other environmental factors are taken into account, it is assumed that the pharmaceutical is unlikely to pose a risk to the environment. However, if the $PEC_{surface\ water}$ is above 0.01 μg/L, a Phase II assessment is required to be performed. In Phase II, it is required to make all information about the physical, chemical, or toxicological properties of the compound available to the investigator. A tiered approach involving two steps – Step A and Step B – is involved in Phase II. In Step A, an evaluation of the possible fate and effects of the compound is done. If no risk is found during this step, there is no requirement of Step B. If a risk is detected, then the fate and effects of the active substance in the relevant compartment are tested by determination of certain toxicological end points on test organisms using standardized test protocols. Using the results generated from the effect studies performed in Step A, the predicted no-effect concentrations (PNECs) are derived for environmental compartments such as surface water, groundwater, and sewage treatment plants and compared with calculated PEC values. The predicted no-effect concentration was determined by dividing the EC50 by an uncertainty factor which is typically set equal to 1000 (Sanderson et al. 2004). If one or more of the PEC/PNEC ratios or hazard quotient (HQ) exceeds the predefined trigger values (1 for surface water and groundwater compartments and 0.1 for the STP), a Step B assessment should be conducted. Environmental fate studies in Step B may include a bioconcentration study in fish and/or degradation in soil, while effect studies may include testing with terrestrial organisms such as soil microflora, earthworms, springtails, and plants.

In a case study, Sharma et al. (2019) estimated the worst-case scenario of potential health risk of some pharmaceuticals in drinking water (groundwater) along the Ganga river in India. An age-dependent risk quotient (RQ) for each detected compound was calculated by dividing the maximum measured concentration in the groundwater (MC_{GW}) by the corresponding age-dependent drinking water equivalent level (DWEL).

$$RQ = MC_{GW} / DWEL$$

The DWEL values were taken from literature and estimated for seven age categories using different parameters such as the acceptable daily intake or risk-specific dose (RSD) for non-carcinogenic and carcinogenic effects, respectively, age-specific body weights (BW) in kg, daily drinking water intake, etc. The DWELs for all age groups ranged from 4.8 μg/L (for carbamazepine, 1–2 year's age group) to 12.8 mg/L (for acetaminophen, 16–21 year's age group). The RQ >1 indicated the possibility of human health risk, while its value between 0.2 and 1 called for more detailed assessment, whereas RQ ≤ 0.2 was considered of no appreciable concern to human health. For all detected pharmaceuticals, RQs ranged from 1.5×10^{-7} (for acetaminophen, 16–21 year's age group) to 0.0021 (for carbamazepine, 16–21 year's age group). Among different age groups, children (1–11 years) had higher RQs than adolescents (11–21 years) and adults (>21 years).

In the same study, the ecological risk assessment was also performed by calculating RQ (some studies use the term hazard quotient (HQ)) for the detected pharmaceuticals where the RQ was calculated by dividing the maximum river water concentration (MCRW) for each compound by the PNEC for three classes of aquatic organisms, i.e., algae, *Daphnia magna* (a crustacean), and fish. The PNEC values were estimated by dividing the EC_{50} (effective concentration, reducing a biological process by 50%) or LC_{50} (lethal concentration, killing 50% of the organisms) obtained from the literature or by using the US EPA Ecological Structure Activity Relationship (ECOSAR v1.10) model by an assessment factor of 1000. Results of ecological risk assessment showed that the risks were comparatively higher for algae. For example, the RQ of caffeine was as high as 49.5, which was observed for three different aquatic organisms. Similarly, the RQs of triclocarban and triclosan ranged from 0.03 to 0.3 and 0.01 to 3.9, respectively. The RQs for freshwater invertebrates (except for *Daphnia* from triclocarban) and fish were generally lower than 0.1, implying negligible risk of acute/chronic toxicity to these aquatic organisms. An account of the risk quotients for different pharmaceuticals in water matrices has been given in Table 4.

8 Treatment Process for Pharmaceuticals

8.1 Microbial Degradation

In case of long and highly branched pharmaceuticals, the biodegradation is least effective in comparison to molecules with short and unbranched chemical structure (e.g., paracetamol, salicylic acid, diclofenac, and carbamazepine). Saturated aliphatic and aromatic compounds containing sulfur and halogen substituents showed resistance to microbial degradation. Apart from bacteria, white-rot fungus has been reported to be effective in the degradation of pharmaceuticals. In one study, two white-rot fungi *Trametes versicolor* and *Ganoderma lucidum* were used in the removal of a mixture of 13 pharmaceuticals while generating biodiesel from the sludge (Vasiliadou et al. 2016). The removal rates of clofibric acid, atenolol, caffeine, carbamazepine, hydrochlorothiazide, sulfamethoxazole, and sulpiride degradation were below 40%, while diclofenac, gemfibrozil, ibuprofen, progesterone, and ranitidine showed complete removal.

8.2 Phytoremediation

Phytoremediation technique utilizes plants and associated microorganisms in the rhizospheres to transform, remediate, or accumulate toxic environmental contaminants present in ground and surface waters, sediments, and soil. The natural

Table 4 Risk quotient (RQ) of pharmaceuticals in different aquatic matrices

Pharmaceutical	Nation	Matrix	MEC/PEC/ EC50	RQ	Risk level	References
Ofloxacin	USA	Lake Michigan	670 ng/L	41.87	High	Blair et al. (2013)
	China	Surface water	36.73 ng/L	3.67E-04	Low	Zhang et al. (2018)
Ciprofloxacin	India	Hospital wastewater	236.6 μg/L	219.3	High	Mutiyar and Mittal (2014a)
	India	Pharma industrial effluent	31,000 μg/L	36,885.2	High	Mutiyar and Mittal (2014a)
	India	River water	2500 μg/L	4,098.4	High	Mutiyar and Mittal (2014a)
	India	Lake water	6500 μg/L	10,655.7	High	Mutiyar and Mittal (2014a)
	India	Groundwater	1.44 μg/L	23.0	High	Mutiyar and Mittal (2014a)
Tetracycline	China	Surface water	18.86 ng/L	5.55E-06	Low	Zhang et al. (2018)
Sulfamethoxazole	USA	Lake Michigan	810 ng/L	30	High	Blair et al. (2013)
	China	Surface water	42.59 ng/L	0.002	Low	Zhang et al. (2018)
	USA	WWTP	1.34 μg/L	2.27	High	Archer et al. (2017)
	USA	River water	0.89 μg/L	1.51	High	Archer et al. (2017)
Trimethoprim	USA	Lake Michigan	660 ng/L	8.15	High	Blair et al. (2013)
	China	Surface water	20.23 ng/L	0.020	Low	Zhang et al. (2018)
	USA	WWTP	1.45 μg/L	0.07	Low	Archer et al. (2017)
	USA	River water	0.64 μg/L	0.03	Low	Archer et al. (2017)
	France	Drinking water	0.443 μg/L	0.04	Low	Bouissou-Schurtz et al. (2014)
Acetaminophen	USA	Lake Michigan	650 ng/L	1.35	High	Blair et al. (2013)
	China	Surface water	901.73 ng/L	9.80E-02	Low	Zhang et al. (2018)
	USA	WWTP	0.10 μg/L	0.42	Medium	Archer et al. (2017)
	USA	River water	0.04 μg/L	0.17	Medium	Archer et al. (2017)

(continued)

Table 4 (continued)

Pharmaceutical	Nation	Matrix	MEC/PEC/ EC50	RQ	Risk level	References
Naproxen	Iran	WWTP	626 mg/L (EC50)	0.001	Low	Eslami et al. (2015)
	USA	WWTP	2.30 µg/L	0.7	Medium	Archer et al. (2017)
	USA	River water	0.67 µg/L	0.2	Medium	Archer et al. (2017)
	India	River water	28.1 ng/L	0.0028	Low	Shanmugam et al. (2014)
	India	Wastewater drain	1.65 µg/L	>1	High	Singh et al. (2014)
Diclofenac	France	Drinking water	0.016 µg/L	0.00	Low	Bouissou-Schurtz et al. (2014)
	Iran	WWTP	14.5 mg/L	0.015	Low	Eslami et al. (2015)
	USA	WWTP	2.31 µg/L	23.1	High	Archer et al. (2017)
	USA	River water	0.96 µg/L	10.0	High	Archer et al. (2017)
	India	River water	103 ng/L	0.00002	Low	Shanmugam et al. (2014)
	India	Wastewater drain	25.68 µg/L	>1	High	Singh et al. (2014)
Ibuprofen	France	Drinking water	0.019 µg/L	1.9	High	Bouissou-Schurtz et al. (2014)
	Iran	WWTP	5.7 mg/L (EC50)	0.184	Medium	Eslami et al. (2015)
	USA	WWTP	0.66 µg/L	0.13	Medium	Archer et al. (2017)
	USA	River water	0.23 µg/L	0.04	Low	Archer et al. (2017)
	India	River water	200 ng/L	0.02	Low	Shanmugam et al. (2014)
	India	Wastewater drain	26.45 µg/L	>1	High	Singh et al. (2014)
Ketoprofen	France	Drinking water	0.258 µg/L	0	Low	Bouissou-Schurtz et al. (2014)
	USA	WWTP	0.41 µg/L	0.13	Medium	Archer et al. (2017)
	USA	River water	0.39 µg/L	0.13	Medium	Archer et al. (2017)
	India	River water	100 ng/L	0.0064	Low	Shanmugam et al. (2014)
	India	Wastewater drain	16.21 µg/L	>1	High	Singh et al. (2014)

(continued)

Table 4 (continued)

Pharmaceutical	Nation	Matrix	MEC/PEC/EC50	RQ	Risk level	References
Caffeine	USA	Lake Michigan	1400 ng/L	334.47	High	Blair et al. (2013)
	China	Surface water	707.51 ng/L	0.010	Low	Zhang et al. (2018)
	India	Ganga river basin	262 ng/L	49.5	High	Sharma et al. (2019)
Carbamazepine	USA	Lake Michigan	340 ng/L	2.61	High	Blair et al. (2013)
	France	Drinking water	0.018 μg/L	0.00	Low	Bouissou-Schurtz et al. (2014)
	China	Surface water	11.47 ng/L	0.00	Low	Zhang et al. (2018)
	USA	WWTP	0.41 μg/L	0.16	Medium	Archer et al. (2017)
	USA	River water	0.22 μg/L	0.09	Low	Archer et al. (2017)
	India	Wastewater drain	5.42 μg/L	>1	High	Singh et al. (2014)
Atenolol	USA	WWTP	0.49 μg/L	0.005	Low	Archer et al. (2017)
	USA	River water	0.21 μg/L	0.002	Low	Archer et al. (2017)

wetlands act as transitional zones between the land and water system and, in the course, improve the water quality in terms of biological oxygen demand, total suspended solids, metal ions, phosphates, and other organic contaminants such as pesticides and pharmaceuticals. The mechanisms of the plant-based aquatic systems include sorption, sedimentation, volatilization, photodegradation, and microbial degradation. Depending on the mode of loading, depth of bed, soil matrix, presence of vegetation, types and number of plant species, organic and hydraulic loading rates, etc., the pharmaceutical degradation rate varies in a wetland system. In a review study done by Li et al. (2014), 115 pharmaceuticals were studied under 4 types of constructed wetland systems such as the free water surface constructed wetland, vertical subsurface flow constructed wetlands (VSSF CWs), horizontal subsurface flow constructed wetlands, and hybrid constructed wetlands. The VSSF CWs were most efficient in elimination of diclofenac, ibuprofen, naproxen, and salicylic acid, possibly due to higher oxygenations, shorter hydraulic retention time, and low sensitivity toward overloading conditions.

8.3 Membrane Process

Membrane-based removal techniques involve microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) processes, where MF and UF are based on sieving mechanism, while RO and NF are pressure-driven membrane processes. The MF and UF are not considered as suitable pharmaceutical removal process (with the exception of hydrophobic compounds), because of their large pore size. In the case of RO, the pressure difference between filtrate and feed sites of the separation membrane is the driving force during reverse osmosis. High rejection efficiency (>85%) has been reported for diclofenac, ketoprofen, and carbamazepine using NF/RO technologies in a drinking water treatment plant (Radjenović et al. 2007). The main challenges posed by membrane-driven removal processes are clogging of membrane pores by larger molecules and suspended materials, disposal of brine, susceptibility of the membranes toward oxidizing agents, and easy fouling of the membranes. Some of these shortcomings may be improvised with advanced oxidation processes.

8.4 Advanced Oxidation Process

Oxidation reactions involve generation of free radicals, mainly hydroxyl radical, which facilitate conversion of the pharmaceuticals into more biodegradable compounds (Deegan et al. 2011) or simple mineralization into smaller molecules by use of oxidants such as ozone or hydrogen peroxide, catalysts (Fe and TiO_2), and energy source such as ultraviolet-visible radiation, electric current, and ultrasound irradiation. The high reactivity of these free radicals promotes oxidation of organic and inorganic pollutants with high reaction rate constants. Ozonation has been very successful in removal of pharmaceuticals with removal efficiency >90% for some antibiotics (Ternes et al. 2003; Dantes et al. 2008) but <50% for some beta-blockers (Ternes et al. 2003). The electrophilic ozone reacts with electron-rich molecules and hence can directly attack compounds having carbon-carbon double or triple bonds and aromatic groups or at certain oxygen-, nitrogen-, phosphorus-, or sulfur-containing functional group. Fenton reactions involving H_2O_2 in presence of Fe and UV light showed that diclofenac could be completely mineralized by photo-Fenton reactions within 50 min (Ravina et al. 2002). TiO_2 is a promising alternative due to its inert nature, cost-effectiveness, and photostability. The semiconductor oxide such as TiO_2 is excited by photoexcitation of a valence-shell electron generating an electron-hole pair. These holes have high oxidation potential and can generate hydroxyl radicals from water at the particle surface. TiO_2-based photo-oxidations under both simulated light and sunlight conditions led to complete removal of oxytetracycline with 90% mineralization (Zhao et al. 2013).

8.5 Adsorption

Adsorption is the process through which a substance/adsorbate, originally present in one phase is removed from that phase by accumulation at the interface between that phase and a separate solid/adsorbent phase, usually activated carbons. The accumulation may result from physical interactions (e.g., van der Waals forces) or chemical reaction (e.g., sharing of electrons). Ruiz et al. (2010) obtained >90% removal for paracetamol by a commercial activated carbon. The US EPA identifies granular activated carbon as the "best available technology" for treating various organic pollutants (Westerhoff et al. 2005).

8.6 Ionizing Radiation

Wang et al. (2019) reported progress of pharmaceutical degradation by ionizing radiation. Ionizing irradiation of antibiotics is effective for their degradation, resulting in complete removal. They reported that during the process of radiation, with increasing absorbed dose and decreasing initial concentration of pharmaceuticals, the degradation efficiency of pharmaceuticals increases. To improve their removal efficiency, several advanced oxidation processes (AOPs) such as H_2O_2, Fe^{2+}, and Fe^{2+}/H_2O_2, as well as biological treatment processes, are combined with ionizing radiation.

9 Recommendations

One of the most effective ways to reduce the load of pharmaceuticals into the environment is by reducing their consumption. Complementary strategies such as improved sanitation, nutrition, and access to general health care are recommended in order to avoid the use of medicines. Prudent use of veterinary drugs in the agriculture sector is one of the wisest approaches in combating pollution by pharmaceuticals. This consists essentially of implementing various management practices to minimize the use of antibiotics, which are consumed by humans. This reduces the occurrence of cross-resistance toward antibiotics in humans and animals. Product take-back programs by pharmaceutical producers have been particularly active in setting up programs, which allow consumers to return their residual medications to pharmacies at no cost. It is a very effective measure to reduce the disposal of unused pharmaceuticals to municipal sewage systems and private septic tanks. The proposed program includes voluntary or compulsory team for collecting the unused/expired pharmaceuticals to a collection point such as a pharmacy or municipal authority for disposal. However, there is a need for much involvement through research in order to assess the cost-effectiveness of these programs (e.g., types and amounts of medicine being collected, the participation rates, regulatory compliance issues, program costs, funding sources, and final disposal). However, the take-back programs do not come with complete reliance as such programs may increase the risk of accidental poisonings and drug abuse due to the stock piling of unused medications awaiting take-back. In general, the public who are the ultimate users should be aware of the consequences of improper disposal and overuse of pharmaceuticals in their day-to-day life. For this, awareness campaigns and workshops should be conducted for the public. Some of the awareness facts include completing the dosage or the full prescription even if the infection seems to have lessened down. Pharmaceutical companies and other providers should behave in a proactive manner and examine the pathway along with the potential impact of discharging wastewater containing such active pharmaceutical ingredients to the wastewater stream and finally into the downstream waterways.

There is an active research need for tracing the presence of pharmaceutical contaminants in the environment, which includes water, sediments, and biota. A robust detection method is required for determining the presence of pharmaceuticals and their metabolites in the environmental samples. Water monitoring network studies for early detection are essential. More information is needed about the possible negative effects that may occur after long-term environmental exposure to several pharmaceuticals both separately and simultaneously.

References

Akiba M, Sekizuka T, Yamashita A et al (2016) Distribution and relationships of antimicrobial resistance determinants among extended-spectrum-cephalosporin-resistant or carbapenem-resistant escherichia coli isolates from rivers and sewage treatment plants in India. Antimicrob Agents Chemother 60:2972–2980

Archana G, Dhodapkar R, Kumar A (2016) Offline solid-phase extraction for preconcentration of pharmaceuticals and personal care products in environmental water and their simultaneous determination using the reversed phase high-performance liquid chromatography method. Environ Monit Assess 188:1–10

Archer E, Petrie B, Kasprzyk-Hordern B, Wolfaardt GM (2017) The fate of pharmaceuticals and personal care products (PPCPs), endocrine disrupting contaminants (EDCs), metabolites and illicit drugs in a WWTW and environmental waters. Chemosphere 174:437–446

Benotti MJ, Trenholm RA, Vanderford BJ, Holady JC, Stanford BD, Snyder SA (2009) Pharmaceuticals and endocrine disrupting compounds in U.S. drinking water. Environ Sci Technol 43:597–603

Bialk-Bielinska A, Stolte S, Arning J, Uebers U, Boschen A, Stepnowski P, Matzke M (2011) Ecotoxicity evaluation of selected sulfonamides. Chemosphere 85(6):928–933

Blair BD, Crago JP, Hedman CJ, Klaper RD (2013) Pharmaceuticals and personal care products found in the Great Lakes above concentrations of environmental concern. Chemosphere 93:2116–2123

Bottoni P, Caroli S, Caracciolo AB (2010) Pharmaceuticals as priority water contaminants. Toxicol Environ Chem 92(3):549–565

Bouissou-Schurtz C, Houeto P, Guerbet M et al (2014) Ecological risk assessment of the presence of pharmaceutical residues in a French national water survey. Regul Toxicol Pharmacol 69:296–303

Brezovsek P, Elersek T, Filipic M (2014) Toxicities of four anti-neoplastic drugs and their binary mixtures tested on the green alga *Pseudokirchneriella subcapitata* and the cyanobacterium *Synechococcus leopoliensis*. Water Res 52:168–177

Carballa M, Omil F, Lema J, Llompart M, Garcia-Jares C, Rodrıguez I, Gomez M, Ternes T (2004) Behavior of pharmaceuticals, cosmetics and hormones in a sewage treatment plant. Water Res 38:2918–2926

Crouse BA, Ghoshdastidar AJ, Tong AZ (2012) The presence of acidic and neutral drugs in treated sewage effluents and receiving waters in the Cornwallis and Annapolis River watersheds and the Mill Cove Sewage treatment plant in Nova Scotia, Canada. Environ Res 112:92–99

Dantes R, Contreras S, Sans C, Esplugas S (2008) Sulfamethoxazole abatement by means of ozonation. J Hazard Mater 150:790–794

Daughton CG, Ternes TA (1999) Pharmaceuticals and personal care products in the environment: agents of subtle change? Environ Health Perspect 107(suppl. 6):907–938

Deegan AM, Shaik B, Nolan K, Urell K, Oelgemöller M, Tobin J, Morrissey A (2011) Treatment options for wastewater effluents from pharmaceutical companies. Int J Environ Sci Technol 8:649–666

Diwan V, Tamhankar AJ, Khandal RK et al (2010) Antibiotics and antibiotic-resistant bacteria in waters associated with a hospital in Ujjain, India. BMC Public Health 10:1–8

Ellis JB, Revitt DM, Lister P, Willgress C, Buckley A (2003) Experimental studies of sewer exfiltration. Water Sci Technol 47:61–67

EMA (European Medicines Agency) (2019) Categorisation of antibiotics. Accessed 08 Apr 2021 at https://www.ema.europa.eu › documents › report

Eslami A, Amini MM, Yazdanbakhsh AR et al (2015) Occurrence of non-steroidal anti-inflammatory drugs in Tehran source water, municipal and hospital wastewaters, and their ecotoxicological risk assessment. Environ Monit Assess 187:734

Fent K, Weston AA, Caminada D (2006) Review Ecotoxicology of human pharmaceuticals. Aquat Toxicol 76:122–159

Ferrari B, Mons R, Vollat B, Fraysse B, Paxeaus N, Giudice RL (2004) Environmental risk assessment of six human pharmaceuticals: are the current environmental risk assessment procedures sufficient for the protection of the aquatic environment? Environ Toxicol Chem 23(5):1344–1354

Fick J, Söderström H, Lindberg RH, Phan C, Tysklind M, Larsson DG (2009) Contamination of surface, ground, and drinking water from pharmaceutical production. Environ Toxicol Chem 28:2522–2527

Gothwal R, Shashidhar T (2016) Occurrence of high levels of fluoroquinolones in aquatic environment due to effluent discharges from bulk drug manufacturers. J Hazard Toxic Radioact Waste 21(3):05016003

Guerra P, Kim M, Shah A, Alaee M, Smyth SA (2014) Occurrence and fate of antibiotic, analgesic/anti-inflammatory, and antifungal compounds in five wastewater treatment processes. Sci Total Environ 473–474:235–243

Hong P, Al-Jassim N, Ansari MI, Mackie RI (2013) Environmental and public health implications of water reuse: antibiotics, antibiotic resistant bacteria, and antibiotic resistance genes. Antibiotics 2(3):367–399

Huggett DB, Brooks BW, Peterson B, Foran CM, Schlenk D (2002) Toxicity of select beta adrenergic receptor-blocking pharmaceuticals (B-blockers) on aquatic organisms. Arch Environ Cotam Toxicol 43:229–235

IWW (2014) Resulst of a Global Database of Measured Environmental Concentrations (MEC), Geneva conference on Pharmaceuticals in the Environment, 8th–9th April 2014

Iyanee FS, Shimamura K, Prabhasankar VP et al (2013) Occurrence of antibiotics in river water – a case study of the Vrishabhavathi river near Bangalore, India. Symposium on Halogenated Persistent Organic Pollutants, DIOXIN 2013, Daegu, Korea

Jiang L, Hu X, Yin D, Zhang H, Yu Z (2011) Occurrence, distribution and seasonal variation of antibiotics in the Haungpu River, Shanghai, China. Chemosphere 82:822–828

Jindal K, Narayanam M, Singh S (2015) A systematic strategy for the identification and determination of pharmaceuticals in environment using advanced LC–MS tools: Application to ground water samples. J Pharm Biomed Anal 108:86–96

Kidd KA, Blanchfield PJ, Mills KH et al (2007) Collapse of a fish population after exposure to a synthetic estrogen. Proc Natl Acad Sci USA 104:8897–8901

Kolpin DW, Furlong ET, Meyer MT et al (2002) Pharmaceuticals, hormones, and other organic wastewater contaminants in US streams, 1999-2000: a national reconnaissance. Environ Sci Technol 36:1202–1211

Larsson DG, de Pedro C, Paxeus N (2007) Effluent from drug manufactures contains extremely high levels of pharmaceuticals. J Hazard Mater 148:751–755

Laxminarayan R, Duse A, Wattal C et al (2013) Antibiotic resistance-the need for global solutions. Lancet Infect Dis 13:1057–1098

Li Y, Zhu G, Ng WJ, Tan SK (2014) A review on removing pharmaceutical contaminants from wastewater by constructed wetlands: design, performance and mechanism. Sci Total Environ 468–469:908–932

Lin AYC, Panchangam SC, Chen HY (2010) Implications of human pharmaceutical occurrence in the Sindian river of Taiwan: a strategic study of risk assessment. J Environ Monit 12:261–270

Loos R, Carvalho R, António DC et al (2013) EU-wide monitoring survey on emerging polar organic contaminants in wastewater treatment plant effluents. Water Res 47:6475–6487

Martinez JL (2009) Environmental pollution by antibiotics and by antibiotic resistance determinants. Environ Pollut 157(11):2893–2902

Matsuo H, Sakamoto H, Arizono K, Shinohara R (2011) Behavior of pharmaceuticals in waste water treatment plant in Japan. Bull Environ Contam Toxicol 87:31–35

MSD Manual. Accessed 08 Apr 2021 at https://www.msdmanuals.com/en-in/home/infections/antibiotics/overview-of-antibiotics

Musson SE, Townsend TG (2009) Pharmaceutical compound content of municipal solid waste. J Hazard Mater 162:730–735

Mutiyar PK, Mittal AK (2012) Non-Steroidal Anti-Inflammatory Drugs (NSAIDs) in river Yamuna, Delhi: emerging class of urban environmental pollutants. In: Proceeding of: Urban Environmental Pollution (UEP -2012) Conference, At Amsterdam, Netherlands

Mutiyar PK, Mittal AK (2013) Occurrences and fate of an antibiotic amoxicillin in extended aeration-based sewage treatment plant in Delhi, India: a case study of emerging pollutant. Desalination Water Treat 51:6158–6164

Mutiyar PK, Mittal AK (2014a) Risk assessment of antibiotic residues in different water matrices in India: key issues and challenges. Environ Sci Pollut Res Int 21:7723–7736

Mutiyar PK, Mittal AK (2014b) Occurrences and fate of selected human antibiotics in influents an effluents of sewage treatment plant and effluent-receiving river Yamuna in Delhi (India). Environ Monit Assess 186(1):541–557

Novo A, Andre S, Viana P, Nunes OC, Manaia CM (2013) Antibiotic resistance, antimicrobial residues and bacterial community composition in urban wastewater. Water Res 47(5):1875–1887

O'Neill J (2016) Tackling drug-resistant infections globally: final report and recommendations. Review on Antimicrobial Resistance. Accessed 20 Nov 2020 at: https://amrreview.org/sites/default/files/160518_Final%20paper_with%20cover.pdf

O'Rourke A, Beyhan S, Choi Y et al (2020) Mechanism-of-action classification of antibiotics by global transcriptome profiling. Antimicrob Agents Chemother 64:e01207–e01219

Olaitan J, Chimezie A, Bamiro T, Temitope A (2014) Determination of pharmaceutical compounds in surface and underground water by solid phase extraction-liquid chromatography. J Environ Chem Ecotoxicol 6:20–26

Pal A, Gin K, Lin A, Reinhard M (2010) Impacts of emerging organic contaminants on freshwater resources: review of recent occurrences, sources, fate and effects. Sci Total Environ 408:6062–6609

Patrolecco L, Ademollo N, Grenni P, Tolomei A, Barra A, Capri S (2013) Simultaneous determination of human pharmaceuticals in water samples by solid phase extraction and HPLC with UV-fluorescence detection. Microchem J 107:165–171

Prabhasankar VP, Dl J, Balakrishna K et al (2016) Removal rates of antibiotics in four sewage treatment plants in South India. Environ Sci Pollut Res Int 23:8679–8685

Radjenović J, Petrovic M, Barcelo D (2007) Analysis of pharmaceuticals in wastewater and removal using a membrane bioreactor. Anal Bioanal Chem 387:1365–1377

Ramaswamy BR, Shanmugam G, Velu G, Rengarajan B, Larsson DG (2011) GC–MS analysis and ecotoxicological risk assessment of triclosan, carbamazepine and parabens in Indian rivers. J Hazard Mater 186:1586–1593

Ravina M, Campanella L, Kiwi J (2002) Accelerated mineralisation of the drug diclofenac via Fenton reactions in a concentric photo-reactor. Water Res 36:3553–3560

Report on Indian Pharmaceuticals Industry Analysis August (2019). https://www.ibef.org/download/Pharmaceuticals-August-2019.pdf. Accessed 15 Nov 2019

Ruiz B, Cabrita I, Mestre AS, Parra JB, Pires J, Carvalho AP, Ania CO (2010) Surface heterogeneity effects of activated carbons on the kinetics of the paracetamol removal from aqueous solution. Appl Surf Sci 256:5171–5175

Sanderson H, Brain RA, Johnson DJ, Wilson CJ, Solomon KR (2004) Toxicity classification and evaluation of four pharmaceuticals classes: antibiotics, antineoplastics, cardiovascular, and sex hormones. Toxicology 203:27–40

Santos LHMLM, Araújo AN, FachiniA PA, Delerue-Mastos C, Montenegro MCBSM (2010) Ecotoxicological aspects related to the presence of pharmaceuticals in the aquatic environment. J Hazard Mater 175:45–95

Santos LH, Gros M, Rodriguez-Mozaz S et al (2013) Contribution of hospital effluents to the load of pharmaceuticals in urban wastewaters: identification of ecologically relevant pharmaceuticals. Sci Total Environ 461–462:302–316

Shanmugam G, Sampath S, Selvaraj K, Larsson DG, Ramaswamy BR (2014) Non-steroidal anti-inflammatory drugs in Indian rivers. Environ Sci Pollut Res Int 21:921–931

Sharma BM, Bečanová J, Scheringer M et al (2019) Health and ecological risk assessment of emerging contaminants (pharmaceuticals, personal care products, and artificial sweeteners) in surface and groundwater (drinking water) in the Ganges River Basin, India. Sci Total Environ 646:1459–1467

Singh KP, Rai P, Singh AK, Verma P, Gupta S (2014) Occurrence of pharmaceuticals in urban wastewater of north Indian cities and risk assessment. Environ Monit Assess 186:6663–6682

Subedi B, Balakrishna K, Sinha RK, Yamashita N, Balasubramanian VG, Kannan K (2015) Mass loading and removal of pharmaceuticals and personal care products, including psychoactive and illicit drugs and artificial sweeteners, in five sewage treatment plants in India. J Environ Chem Eng Part A 3(4):2882–2891

Ternes TA, Stüber J, Herrmann N, McDowell D, Ried A, Kampmann M, Teise B (2003) Ozonation: a tool for removal of pharmaceuticals, contrast media and musk fragrances from wastewater. Water Res 37:1976–1982

Toolaram AP, Kummerer K, Schneider M (2014) Environmental risk assessment of anti-cancer drugs and their transformation products: a focus on their genotoxicity characterization-state of knowledge and shortcomings. Mutat Res Rev Mutat Res 760:18–35

Triebskorn R, Casper H, Heyd A, Eikemper R, Kohler HR, Schwaiger J (2004) Toxic effects of the non-steroidal anti-inflammatory drug diclofenac. Part II. Cytological effects in liver, kidney, gills and intestine of rainbow trout (Oncorhynchus mykiss). Aquat Toxicol 68:151–166

US EPA (2012) Inaction in Identifying Hazardous Waste Pharmaceuticals May Result in Unsafe Disposal. Report No 12-P-0508. May 25, 2012

Vasiliadou IA, Sánchez-Vázquez R, Molina R et al (2016) Biological removal of pharmaceutical compounds using white-rot fungi with concomitant FAME production of the residual biomass. J Environ Manag 180:228–237

Verlicchi P, Al Aukidy M, Galletti A, Petrovic M, Barceló D (2012) Hospital effluent: investigation of the concentrations and distribution of pharmaceuticals and environmental risk assessment. Sci Total Environ 430:109–118

Wang JL, Zhuan R, Chu L (2019) The occurrence, distribution and degradation of antibiotics by ionizing radiation: An overview. Sci Total Environ 646:1385–1397

Westerhoff P, Yoon Y, Snyder S, Wert E (2005) Fate of endocrine-disruptor, pharmaceutical and personal care product chemicals during simulated drinking water treatment processes. Environ Sci Technol 39:6649–6663

WHO (2017) Global priority list of antibiotic-resistant bacteria to guide research, Discovery, and Development of New antibiotics. Accessed 20 May 2020 at http//:www.who.int

Zhang Y, Cai X, Lang X, Qiao X, Li X, Chen J (2012) Insights into aquatic toxicities of the antibiotics oxytetracycline and ciprofloxacin in the presence of metal: complexation versus mixture. Environ Pollut 166:48–56

Zhang H, Du Z, Ji Y, Mei M (2013) Simultaneous trace determination of acidic non-steroidal anti-inflammatory drugs in purified water, tap water, juice, soda and energy drink by hollow fiber-based liquid-phase micro extraction and ultra-high pressure liquid chromatography coupled to tandem mass spectrometry. Talanta 109:177–184

Zhang P, Zhou H, Li K, Zhao X, Liu Q, Li D, Zhao G (2018) Occurrence of pharmaceuticals and personal care products, and their associated environmental risks in a large shallow lake in north China. Environ Geochem Health 40:1525–1539

Zhao C, Pelaez M, Duan X et al (2013) Role of pH on photolytic and photocatalytic degradation of antibiotic oxytetracycline in aqueous solution under visible/solar light: kinetics and mechanism studies. Appl Catal B 134:83–92

Zounkova R, Kovalova L, Blaha L, Dott W (2010) Ecotoxicity and genotoxicity assessment of cytotoxic antineoplastic drugs and their metabolites. Chemosphere 81(2):253–260

Suspect and Nontarget Screening of Pharmaceuticals in Water and Wastewater Matrices

Sanjeeb Mohapatra, Wojciech Mrozik, Kishor Acharya, and N. Gayathri Menon

Abstract Pharmaceutical compounds are nowadays ubiquitously detected in various environmental compartments around the world. As these compounds are present as complex mixtures and numerous other natural and anthropogenic chemicals, their transformation products (TPs), possible bio-conjugated counterparts, and their detection, quantification, and risk assessment prove extremely difficult. Recent advancements in mass spectrometry coupled with liquid chromatography (LC-MS) have enabled the detection of polar compounds with better reliability, precision, and accuracy. However, detecting trace levels of pharmaceuticals from complex matrices requires highly sensitive and selective techniques and sophisticated sample preparation steps to avoid analyte loss during sample preparation or in transit. Additionally, target analysis involves the use of expensive pharmaceutical standards and the corresponding isotope-labelled internal standards (ISs). Hence, before target analysis, it is much more viable to conduct suspect or nontarget analyses to obtain a more holistic understanding of the nature and composition of such contaminants present in environmental samples. This chapter aims to compare and compile the recent trends in suspect and nontarget screening of pharmaceuticals present in the water and wastewater matrices. Detailed information on the various mass banks, mass analyzers, and workflows for the screening of such contaminants are discussed here in detail.

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1 Introduction

Preserving pristine water quality and reclamation of polluted water resources are two primary focus points in the European Water Policy (EU Water Framework Directive 2013/39/E.U.). Similarly, sustainable development goals (SDG 6.3) aim to improve water quality, which is vital for preserving the health of both ecosystem and human, by removing, minimizing, and significantly reducing various sources of water bodies' pollution. Similar policies and legislations are underway or in force in almost all countries around the globe. However, over the last few decades, thousands of emerging pollutants such as pharmaceuticals and personal care products (PPCPs) have entered into various environmental compartments through wastewater treatment plant (WWTP) effluents (Eregowda and Mohapatra 2020), urban and rural runoffs (Dubey et al. 2021; Mogili and Mohapatra 2021; Mohapatra et al. 2020a, 2021), and untreated waste water from hospitals and pharmaceutical manufacturing industries (Fu et al. 2019; Tran et al. 2018). Besides PPCPs, pesticides, surfactants, and sweeteners comprise another major category of compounds that end up in surface water, primarily due to anthropogenic activities (Liu and Wong 2013). Consequently, a large variety of regulated and unregulated organic contaminants enter receiving water bodies from a wide range of sources, thereby contaminating surface water, groundwater, and even drinking water, as shown in Fig. 1 (Ternes 1998).

Although a plethora of compounds have been reported to enter water bodies, their resultant individual concentration in these water bodies is extremely low (i.e., a few micro- to pictograms). However, at trace environmental concentrations, they still elicit chronic effects in aquatic life and introduce antibiotic resistance in microorganisms (Menon et al. 2020). Hence, they are commonly known as micropollutants or contaminants of emerging concern. Micropollutants are resistant to degradation and persistent in the environment and produce adverse effects, such as endocrine disruption, the spread of antibiotic resistance, and other ecotoxicological effects (Menon et al. 2020; Mohapatra et al. 2020b). Therefore, there is also a growing apprehension about identifying unknown contaminants, including metabolites or transformation products (TPs), which are of ecological concern (Celiz et al. 2009; Michael et al. 2014). Freshwater bodies are particularly of prime concern as several organic micropollutants of high polarity and low or negative pH-adjusted log distribution coefficients (log D) partition into the aqueous phase (Gogoi et al. 2018; Patel et al. 2019). Hydrophobic pharmaceuticals may further sequester in the adipose tissue and biomagnify in the food chain and, even at low concentration, may cause chronic effect (Menon et al. 2020).

Although advancement in environmental analytical chemistry has improved considerably, the reliability, precision, and accuracy with which such micropollutants

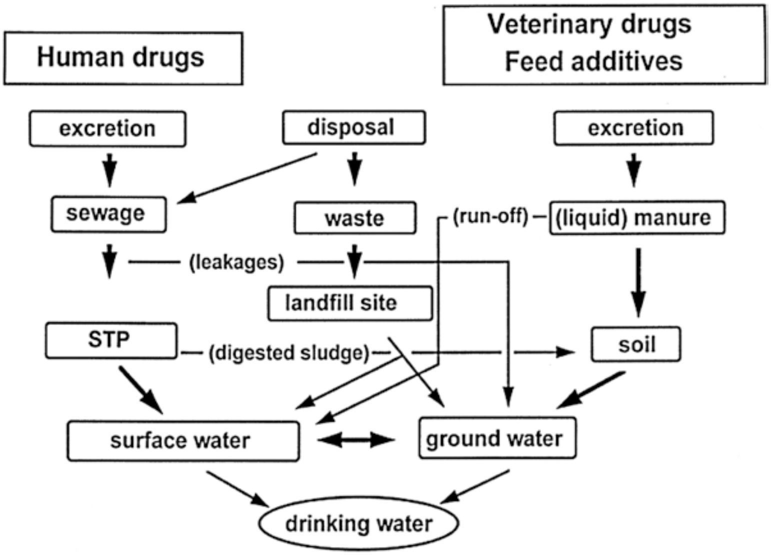

Fig. 1 The pathway of pharmaceuticals from the human body to drinking water. (Adapted from Ternes 1998)

can be quantified, their detections at low concentrations, and effects of complex environmental matrices still pose challenges (Mohapatra et al. 2018; Priyanka and Mohapatra 2020). Environmental analysts have commonly been using liquid or gas chromatography (LC/GC) with various mass spectrometry (MS) analyzers such as single quadrupole or ion trap. Recently, triple quadrupole (QQQ) has gained wide attention due to the detection of a wide range of drug metabolites using MS/MS fragmentation patterns. However, dissolved and particulate organic matter (DOM/POM) interferes with the detection of such compounds by suppressing analyte signals or by enhancing the signals from the matrix elements, eliciting what is referred to as the matrix effect (Keller et al. 2008; Kloepfer et al. 2005). Moreover, analysis of an enormous number of these compounds, including their metabolites and/or TPs of varying physicochemical properties through a common multi-residue method, is complex and practically infeasible. Unavailability of appropriate reference standards and labelled isotopes can lead to an underestimation of quantification during target analysis. During target analysis, the analytes' list rarely exceeds 200–300 compounds, and many contaminants other than the target analytes that might be present in the samples are usually left unanalyzed. Target analysis techniques also require a degree of prior understanding about the type of compounds present in the water body chosen for environmental analysis. This technique is valuable for quantifying a known micropollutant, tracing its transport, and understanding its fate. However, target analysis often falls short when the aim is to identify unknown or nontarget micropollutants.

Nontarget or suspect screening is a powerful technique that can shed light on the different types of compounds present in an environmental sample. In scenarios where prior information is lacking, suspect screening can also assist in better risk assessment. There is an urgent need for developing "universal" screening methods to analyze and detect a wide range of chemicals. It offers more practical and holistic knowledge on several contaminants present in various samples in the absence of reference standards. Moreover, the subsequent searching of any other contaminants, metabolites, or TPs should be attainable even when labelled isotopes are not available in retrospective analyses. This chapter aims to compare and compile the recent trends in suspect and nontarget screening of pharmaceuticals present in the water and wastewater matrices. Detailed information on the various mass banks, mass analyzers, and workflows for the screening of such contaminants are discussed here in detail.

2 Workflow for Suspect Screening and Nontarget Analysis

High-resolution mass spectrometry (HR-MS/MS) and (ultra-)high-performance liquid chromatography (HPLC) together can screen a vast number of polar organic chemicals present in an aqueous medium. Such systems use mass analyzers and detectors of high sensitivity and resolution (>20,000) and at a high mass accuracy of <5 ppm. High resolving power can tentatively identify unknown analytes and record accurate entire mass spectral data with reasonable sensitivity in the absence of reference standards (Brack et al. 2016). These approaches, commonly termed "suspect screening" or "nontarget screening" (NTS), are widely applied in the environmental sector for the identification of unknown compounds. While suspect screening helps identify expected pollutants present in a sample matrix, the NTS approach enables the detection of compounds based on the measured data in the sample without searching for specific masses or substances. The schematic of the target, suspect, and NTS is shown in Fig. 2.

2.1 Suspect Screening

Suspect screening has a massive capability to identify contaminants and several regulated chemicals due to its speedup ability to evaluate unknown peaks. The aspect of no necessity for reference standards has further increased its popularity, specifically in environmental monitoring. It involves identifying compounds based on their MS or MS/MS, retention time (RT), and spectral library matching (Fig. 2). During the suspect screening, HRMS data (HRMS1, i.e., m/z ratio) of the analytes of interest is searched against the spectral libraries by using several features. Some of the features which are used for the suspected analytes are isotopic (and adduct) pattern, MS/MS fragment spectra (HRMS2), and retention time (RT). Such features

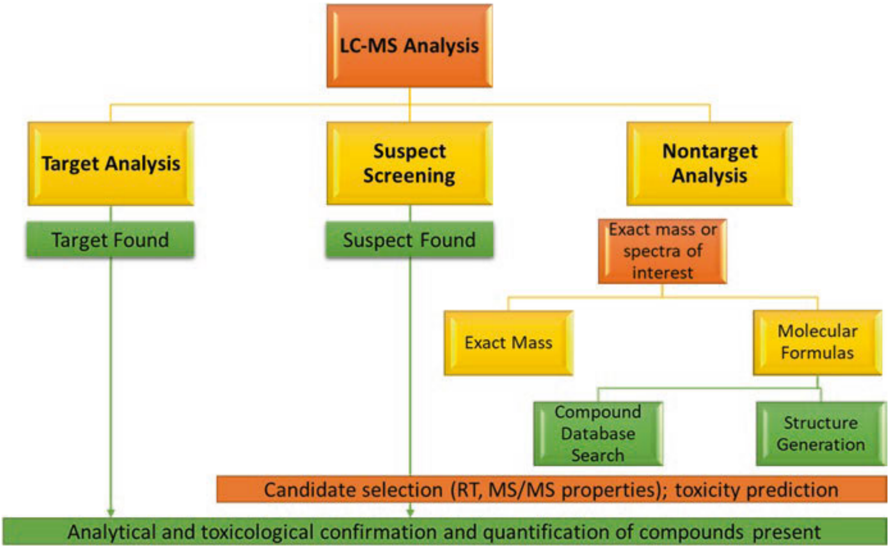

Fig. 2 Schematics of the target, suspect, and NTS. (Reprinted with permission from Brack et al. 2016)

help to identify and confirm the suspects of interest. Many platforms, such as the NORMAN Suspect List Exchange and the US Environmental Protection Agency CompTox Chemicals Dashboard, and several other mass spectral databases, e.g. enviMass and MassBank of North America, are of free access and have been developed to improve screening of unknown analytes.

Pitarch et al. (2016) employed LC-MS- and GC-MS-based technology to screen 1500 micropollutants in surface water and groundwater impacted by the nearest solid waste management facility, with over 3 years of sampling. Elemental composition, RT, main fragment ions, adduct formation, and isotope pattern with Cl^- or Br^- followed by more than 70% database match were included to identify unknowns present in the water samples. Such exercise helped quantify 24 pesticides and their transformation products, 7 pharmaceuticals, 1 drug of abuse (cocaine) and its major metabolite, benzoylecgonine. Singer et al. (2016) proposed a more efficient methodology to avoid false negatives during suspect screening by coupling analytical results and model-based ranking with the help of consumption data, predictable fate information, and a conventional mass balance model developed for activated sludge treatment. The study considered several features, including peak intensity, blank subtraction, peak symmetry, and isotope pattern, as prioritization criteria. Only suspects having peak intensity of $\geq 10^7$ and $\geq 10^8$ for negative and positive mode, respectively, were used for additional processing (Singer et al. 2016). Suspected peaks for which the RT exceeded the 1-min threshold and tailing factor was < 0.5 at 10% peak height were further excluded. In the end, an isotope pattern test was performed on the leftover suspects where isotope abundances (20%) and mass accuracy (< 5 ppm) were the filtering criteria. Such an approach helped identify 26 pharmaceuticals out of 559 suspects that had not previously been reported in Switzerland's surface waters. This approach increased the total number of active pharmaceutical ingredients (APIs) detection by one-third with high selectivity of ≥70%.

In addition to mass accuracy and isotopic fitting, RT and MS/MS spectra evaluation are essential components for identifying unknown pollutants. In this regard, Aalizadeh et al. (2019) suggested a plan to study the RT behavior of around 682 micropollutants based on quantitative structure-retention relationships (QSRR). Support vector machine (SVM) was used to simulate the RT information of all the suspects of interest. Several linear and nonlinear models were also used to identify the suspects based on Equations 1 to 3. Monte Carlo sampling (MCS) was employed to evaluate the acceptable error tolerance of the predicted RT values for both emerging contaminants and biocides obtained from various LC conditions. In this study, both hydrophilic interaction liquid chromatography (HILIC) and reversed-phase liquid chromatography (RPLC) were coupled with QTOF MS to identify several unknowns. A complete data set was developed by incorporating around 1830 and 308 micropollutants analyzed in positive and negative electrospray ionization (ESI), respectively. It was successfully applied in identifying several micropollutants present in wastewater matrices.

$$\begin{aligned}\mathbf{RPLC}-(+)\,\mathbf{ESI}-\mathbf{HRMS}:t_R &= +2.3518(\pm 0.1335)+0.7371(\pm 0.0204)\log D_{(pH\,3.60)}\\ &\quad +1.2389(+0.0696)\,CIC1+0.5584(\pm 0.0396)\,SEigZ\\ &\quad -0.2198(\pm 0.0340)\,RDF020p+0.4155(\pm 0.0306)\,AlogP\end{aligned}$$

$$\begin{aligned}\mathbf{RPLC}-(-)\,\mathbf{ESI}-\mathbf{HRMS}:t_R &= +3.9078(\pm 0.2255)+0.3016(\pm 0.0768)\,XlogP\\ &\quad +0.6128(\pm 0.0543)\log D_{(pH\,6.20)}\\ &\quad +0.1917(\pm 0.0543)\,RDF130m-1.377(\pm 0.3291)\,Mor16p\\ &\quad -0.3062(\pm 0.0695)\,nCconj+0.1103(0.0178)\,MlogP^2\\ &\quad +1.588(0.2461)\,B06[C-C]+0.6183(0.1345)\,F04[Cl-Cl]\end{aligned}$$

$$\begin{aligned}\mathbf{HILIC}-(+)\,\mathbf{ESI}-\mathbf{HRMS}:t_R &= +2.591(\pm 0.1323)-1.233(\pm 0.0227)\log D_{(pH\,3.50)}\\ &\quad -0.1051(\pm 0.0204)\,GGI1+0.2293(\pm 0.0384)\,RDF020p\\ &\quad +0.2410(\pm 0.0322)\,H-050+1.332(\pm 0.1769)\,qnmax\\ &\quad +0.0807(0.0089)\,MlogP^2+0.8120(0.0370)\,AlogP\end{aligned}$$

The expanded terms for the abbreviations can be found in the original article (Aalizadeh et al. 2019).

In recent years, the introduction of ion mobility spectrometry (IMS) has further enhanced the chromatographic TOF MS based identification by separating isomers in complex matrices via geometry/shape of the ionized molecule (Mollerup et al. 2018). In this study, various molecular descriptors, including 827 RTs and 357 collision cross-section (CCS) values from micropollutants, were used to develop quantitative structure-activity relationship (QSAR) by the artificial neural network

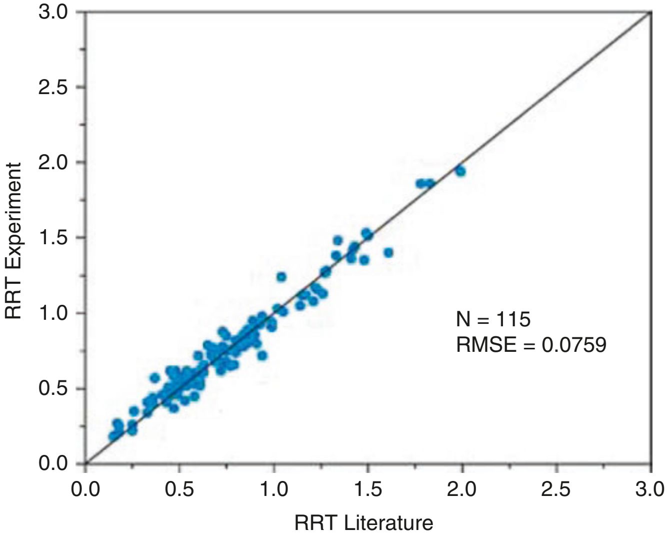

Fig. 3 Comparison of RRT for TPs between experimental results and literature values. (Reprinted with permission from Deeb et al. 2017)
The solid line represents the 1:1 fit; N, number of data points; RMSE, root mean squared error

modeling approach to predict RT or CCS values of various compounds (Mollerup et al. 2018). The 95th prediction error percentiles were within 2-min RT error and 5% relative CCS error in such an approach.

Samanipour et al. (2017) proposed a two-phase algorithm on HPLC-QTOF MS data for suspect screening of around 89 micropollutants present in the wastewater samples obtained from 4 WWTPs. The algorithms were executed to detect several MS features using UNIFI developed by Waters, and XIC peak picking using TASQ developed by Bruker. Similarly, Deeb et al. (2017) screened around 245 suspects (micropollutants) and corresponding ozonated TPs in several full-scale WWTPs. After introducing blank subtraction, filtering mass accuracy (< 5 ppm), peak height (minimum 1000 counts), and isotopic pattern score (≥80%), 189 pollutants were filtered from the parent list of 245 compounds. Additionally, TPs were assigned the most likely structure by using relative retention time (RRT). A cross plot of RRT obtained across reported studies is depicted in Fig. 3.

2.2 *Nontarget Screening*

During NTS, thousands of unique molecular ions are collected comprehensively in HRMS1 full-scan mode. This approach requires a prioritization strategy based on ions/molecules of significance due to massive data sets. Possible structures are normally apportioned by searching their unique features in several databases available in the public domain, including PubChem, maintained by the National Center for

Biotechnology Information (NCBI), and ChemSpider, owned by the Royal Society of Chemistry (RSC). Some of these databases use heavy HRMS2 spectra (MS/MS spectra) and computational tools that majorly handle enormous data for prioritization purposes. Both statistical analysis techniques and physical chemistry theory-based cheminformatics tools are used for high-throughput structure prediction, which further enhances the reliability of NTS-based output. Some of the cheminformatics tools are equipped with in silico fragmentation querying options that are freely accessible to other chemical databases having mass spectral library facilities.

Typical nontarget screening of micropollutants involves preprocessing of HRMS data followed by prioritization and structure elucidation. Various software, including R package, can be used in each step of data preprocessing. Data processing involves a conversion of raw files to centroided mzXML format with ProteoWizard followed by importing into enviMass. A step-by-step approach using cheminformatics tools for structure annotation was outlined by Brack et al. (2016). Isotope-labelled internal standards were applied for recalibration, RT alignment, and intensity normalization. During the processing of chromatograms, several blank subtractions, including subtraction of profiles detected in blanks, procedural blanks, and deionized water samples spiked with isotope-labelled ISs, were done. A polarity-based filter was used to select analytes based on their retention time, i.e., RT < 2 min for higher polarity, 2 to 24 min for medium polarity, and > 24 min for low polarity contaminants. However, compounds eluted at RT <2 min and more than 24 min are advised to be deleted from the data processing due to their high polarity and low polarity nature, respectively. Such compounds eluting either early or late are identified as reduced quality by the active chromatographic method and making it challenging for the assignment of (quasi-)isobaric substances (Albergamo et al. 2019). Additionally, it is recommended to include commonly encountered single-charge ESI adducts, such as [M PLUS_SPI H]$^+$, [M PLUS_SPI Na]$^+$, [M PLUS_SPI NH$_4$]$^+$, and [M PLUS_SPI K]$^+$. However, the inclusion of many positive and negative adducts and also isotopic peaks may further add to the existing quantity of profiled features.

The profiled features and the ideal number of clusters (k) were ranked through hierarchical cluster analysis (HCA) and silhouette analysis, respectively. RMassBank package comes in handy for extracting spectra of high quality for each structure prediction by targeting the highly penetrating topmost 50% ions from each cluster and corresponding HRMS1 and HRMS2 data obtained from the experiments. MetFrag was used to elucidate tentative structure batchwise, while ChemSpider was used to obtain structures of neutral monoisotopic masses of the targeted spectra within 5 ppm mass accuracy. In such a case, the highest amount of candidates per feature and tree depth (MS^n) were set to 5000 and 2, respectively. Their structures recovered by MetFrag were further fragmented in silico in a combinatorial manner and followed by fragment matching obtained from experimental HRMS2 spectra. Additionally, the MetFusion approach was created to compare spectral resemblances with the MoNA spectral library collection built into MetFrag. Finally, a score against tentative candidate structures was defined by seven terms:

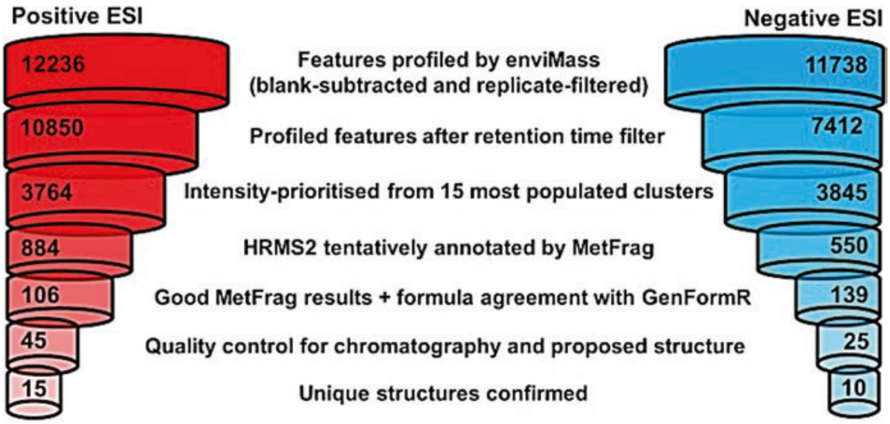

Fig. 4 Data reduction charts for positive ESI (left) and negative ESI (right) data. (Reprinted with permission from Albergamo et al. 2019)

I. FragScore obtained from the in silico fragmentation
II. MetFusion Score obtained by MoNA spectral resemblances by MetFusion approach
III. CSRefs Scores from reference tally on ChemSpider
IV. CSRefs Scores from the number of reference match on PubMed
V. CSRefs Scores from the reference count up on RSC
VI. CSRefs Scores from ChemSpider database
VII. Suspects Scores based on the number of hits

Those scoring terms were further normalized by the highest value found among the potential candidates. The step-by-step approach to identifying several contaminants in the positive and negative ESI mode is shown in Fig. 4.

Peter et al. (2019) explored the potential of HRMS data for quantitative source apportionment in various matrices of the environment. The study hypothesized that unique chemical fingerprints/markers could quantitatively track the contaminant sources in receiving waters via a nontarget analysis approach. Several natural attenuation processes such as retention, attenuation, and dilution of the river water and further dilution of the unique HRMS fingerprints while mixing source waters with the polluted water were considered in evaluating the HRMS data for source appointment. Initially, a series of source dilutions were obtained from a set of samples collected from the field. Nontargeted data analysis was conducted with minimum criteria of peak area > 5000 and peak area fold change > 3x vs. method and solvent blank. Additionally, source dilution curves were tested against the three highest points in the calibration curve.

As mentioned earlier, peak picking, blank subtraction, isotope pattern matching, and peak assignments are the commonly adopted workflow to both nontarget and suspect screening approaches. However, the massive amount of data of the order of thousands generated during the simultaneous scan in HRMS1 and HRMS2 with multiple chromatographic runs requires a suitable post-acquisition tool. Such tools should have the potential for automatic background correction, peak detection, peak resolution, time-shift correction, and, most importantly, feature ranking prior to compound identification. Such chemometric tools with superior capability to deal with huge environmental data are broadly categorized into multiway decomposition and supervised classification methods. Among several multiway decomposition methods, parallel factor analysis (PARAFAC), PARAFAC2, alternating trilinear decomposition (ATLD), and multivariate curve resolution-alternating least squares (MCR-ALS) are some of the most popular techniques to handle such high-resolution chromatographic data. Additionally, MCR-ALS and PARAFAC2 can handle nontrilinearity of the analyte when RT and shapes are changed during several chromatographic runs. Several chemometric classification methods for unsupervised data including principal component analysis (PCA) and hierarchical clustering and supervised classification techniques such as partial least squares-discriminant analysis (PLS-DA) and SVMs have been used to group compounds based on their several features.

Hohrenk et al. (2019) applied multivariate chemometric methods to comprehensively evaluate two full-scan data sets obtained from LC-Q-Orbitrap mass spectrometry for target and NTS of organic micropollutants both in drinking and wastewater samples. This approach has overcome many challenges, including efficient data size reduction, alignment-free tracing of contaminants, tackling spectral interferences and extremely overlapped compounds' elution profiles. It was done via one two-way decomposition step, feature prioritization, and tentative identification of discriminatory contaminants between various classes of water samples. In brief, for every data set, MCR-ALS was applied to resolve chromatographic peaks and the related mass spectra of co-eluting unnecessary and interfering peaks. At that point, halfway, the least squares-discriminant examination was led to explore the conduct of MCR-ALS segments in various water classes and determination of the most significant parts. Acquired univariate measurements were further used to prioritize 24 candidates in wastewater samples. Two-way data recovered from MCR-ALS of LC-MS1 information was likewise used to pick common precursor ions among recovered and measured data. Both MS and MS/MS features were finally utilized to identify prioritized micropollutants (Hohrenk et al. 2019). This step-by-step approach may be applied for the identification of micropollutants in nontargeted mode.

Despite several approaches, the type of instrument, databases used to identify unknowns, and in silico generation of mass fragmentation patterns are essential tools that cannot be ignored. Some of these tools are discussed in the next section.

3 Recent Development in Analytical Instruments (LC/GC-MS/MS) and Mass Banks

Irrespective of whether used in conjunction with GC or LC technique, analysis and collection of the appropriate full mass spectrum, i.e., both MS and MS/MS data, are of significant interest to identify unknowns during soft ionization approach such as electrospray ionization (ESI). While LC-QTOF MS has been used to analyze most of the polar organic compounds, GC-QTOF MS with atmospheric pressure chemical ionization (APCI) technique was used to obtain full spectra of nonpolar analytes or polar analytes after derivatization. The data obtained from GC (APCI)-MS-based approach is characterized by a high abundance of the protonated/molecular ions. Such high-quality data with distinct fragmentation patterns that determine the suspect mass followed by their tentative molecular formula has attracted the GC/MS technique to screen several organic unknown compounds in complex environmental matrices (Portoles et al. 2014). The simultaneous use of the chromatographic techniques coupled and the HRMS instrument accelerates the universal screening of wide-ranging unknowns of varying polarity and volatility as explored elsewhere (Hernandez et al. 2015).

Various chemical databases such as PubChem, ChemSpider, or the Chemical Abstracts Database (Table 1) are developed to screen unknowns and updated periodically. More than 120 million unique compounds are currently listed, of which around 1–2 million compounds are relevant in the field of biology. However, the number of compounds, TPs or metabolites of environmental relevance is still scarce. A few reports have roughly identified around 20% of unique chemicals for untargeted analysis, which is registered in the Metabolomics Workbench (Sud et al. 2016) or the European metabolomics repository - MetaboLights. Additionally, many environmental compounds are registered in some open-source databases such as CompTox Chemicals Dashboard from the US EPA (EPA 2017) and NORMAN Suspect List Exchange. However, prioritization is of utmost priority to accelerate

Table 1 Commonly used compound databases for their identification

Database	Targets	Description	Weblinks
PubChem	Small molecules	Small molecules, metadata	https://pubchem.ncbi.nlm.nih.gov
ChemSpider			http://www.chemspider.com/
ChEBI		Molecules of biological interest	https://www.ebi.ac.uk/chebi/
KEGG	Metabolites	Pathway database, multiple species	https://www.genome.jp/kegg/
MetaCyc			https://metacyc.org/
HMDB		Human metabolites	https://hmdb.ca/
MINE		In silico predicted metabolites	https://minedatabase.mcs.anl.gov/
BRENDA	Enzymes	Enzyme and metabolism data	https://www.brenda-enzymes.org/

Blaženović et al. (2018)

the detection and tentative identification of suspects. Such prioritization was subsequently achieved by referring to predicted toxicity, information on uses and consumption pattern, environmental occurrence frequency, persistence nature, and extent of bioaccumulation (Howard and Muir 2011; Gosetti et al. 2015).

As discussed earlier, searching for unknowns through the databases is the quickest and commonly used approach for the initial screening of compounds present in environmental samples. Spectral databases in the public and commercial domains collectively encompass around one to two million spectral signatures (mass spectra), of which one million unique chemicals are analyzed through GC-MS and LC-MS/MS interface. Wherever reference standards are available, their spectra are included in the databases, while computationally generated in silico spectra were considered for such chemicals for which standards are commercially unavailable. Additionally, these databases, such as the International Chemical Identifier (InChIKey), include metadata, including instrument types, collision energies, ionization mode, and structural information (Heller et al. 2013) and spectral hash code (SPLASH) for uniqueness calculations (Wohlgemuth et al. 2016). Some of the commonly used compound databases adopted from the literature are listed in Table 2 (Blaženović et al. 2018). Among the databases listed, the NIST Library has the highest pools of massive GC-MS spectra (>200,000 compounds) and retention indices (>83,000 compounds) (Vinaixa et al. 2016). If a substance is not listed in the library, identification via the structure generation approach is quite tedious, time-consuming, and especially challenging with low-resolution data (Rasche et al. 2012; Schymanski et al. 2014; Sleno 2012).

While more than 100 million chemicals are listed in the PubChem and ChemSpider databases, only around 1 million chemicals are currently available with mass spectra. Several MS/MS spectra were developed based on principles of quantum chemistry and physical and chemical properties, strategies of in silico fragmentation, and using commercially available reference standards (Table 3). The permutation of suspect screening, spectral libraries, and in silico fragmentation approaches has an enormous capability for rapid and thorough screening of

Table 2 List of commonly used mass spectral databases (Blaženović et al. 2018)

Database	Targets
NIST	EI-MS, CID-MS/MS
Wiley	EI-MS, CID-MS/MS
METLIN	CID-MS/MS
MoNA	EI, MS/MS, MS^n
MassBank	EI, MS/MS, MS^n
mzCloud	MS^n
GNPS	MS/MS
ReSpect	MS/MS, RT

Table 3 Overview of methods for in silico generation of mass spectra (Blaženović et al. 2018)

In silico method	Software	Platform	Description
Quantum chemistry	QCEIMS	EI, MS	Uses chemistry first principles; requires cluster computations
Machine learning	CFM-ID/ CSI:FingerID	EI-MS CID-MS/MS	Requires diverse training sets; fast method
Heuristic approaches	LipidBlast	CID-MS/MS	For specific compound classes (lipids); fast method
Reaction chemistry methods	Mass Frontier	EI-MS CID-MS/MS	Generates only barcode spectra; covers experimental gas-phase reactions

Table 4 Commonly used software tools for in silico fragmentation (Blaženović et al. 2018)

Software	In silico method	Platform
MS-FINDER	Rule-based (hydrogen rearrangement rules)	15 integrated target DBs plus MINE and PubChem
CFM-ID	Hybrid rule-based machine learning	KEGG, HMDB
MetFrag	Hybrid rule-based combinatorial	HMDB, KEGG, PubChem
Mass Frontier	Rule-based (literature reaction mechanisms)	Internal MS database
ChemDistiller	Fingerprint and spectral machine learning	17 different target databases, 130 Mio compounds total
MAGMa, MAGMa PLUS_SPI	Rule-based	PubChem, KEGG, HMDB
CSI:FingerID	Combination of fragmentation trees and machine learning	PubChem and multiple bio databases

micropollutants. Even though in silico methods have been improved significantly over the period, identification of the analyte through commercially available standards is still the required confirmation and quantification criteria. In silico fragmentation approach distinguishes "known unknowns," i.e., compounds present in molecular structure databases yet with no reference standards. In such a case, structures are assigned by ascertaining a score between the experimental spectra and the predicted spectra or predicted fragments. However, a complicated situation arises while identifying "unknown-unknown" compounds are not listed in the databases. A list of in silico methods for the generation of mass spectra is compiled in Table 4. European-wide exchange of information, such as a compilation of suspects' lists, has been recently reported. Looking toward the future, a level of confirmation that would accompany more major development would help nontarget strategies, giving a vital commitment to distinguishing identification purposes. Other incredible identification approaches that have not been applied in the environmental field yet, like LC-NMR, can assume a significant part to confirm the unknowns.

4 Conclusions

Pharmaceuticals are of emerging concern due to their ubiquitous occurrence, persistent nature, and chronic toxicity. However, these compounds are present at a very trace environmental concentration of the order micro- to pictogram levels, which requires highly sensitive and selective detection techniques. Lack of reference standards and the cost involved in buying expensive internal standards hinder the monitoring of such compounds in the environmental matrices. Thus, before conducting target analysis, both suspect and Non Target Screening can not only give an insight to a variety of organic pollutants present in the samples, but also statistical and data mining techniques can help in the identification and structure elucidation of several unknowns. In a single analytical run and without the use of reference and internal standards, such approaches can potentially confirm the presence of each compound in chemical mixtures by referring to several mass banks and workflows. However, additional research on quantitative or semi-quantitative approach for the qualitative data obtained from NTS must be explored.

References

Aalizadeh R, Nika MC, Thomaidis NS (2019) Development and application of retention time prediction models in the suspect and non-target screening of emerging contaminants. J Hazard Mater 363:277–285. https://doi.org/10.1016/j.jhazmat.2018.09.047

Albergamo V, Schollée JE, Schymanski EL, Helmus R, Timmer H, Hollender J, De Voogt P (2019) Nontarget screening reveals time trends of polar micropollutants in a riverbank filtration system. Environ Sci Technol 53:7584–7594. https://doi.org/10.1021/acs.est.9b01750

Blaženović I, Kind T, Ji J, Fiehn O (2018) Software tools and approaches for compound identification of LC-MS/MS data in metabolomics. Metabolites 8. https://doi.org/10.3390/metabo8020031

Brack W, Ait-Aissa S, Burgess RM, Busch W, Creusot N, Di Paolo C, Escher BI, Mark Hewitt L, Hilscherova K, Hollender J, Hollert H, Jonker W, Kool J, Lamoree M, Muschket M, Neumann S, Rostkowski P, Ruttkies C, Schollee J, Schymanski EL, Schulze T, Seiler TB, Tindall AJ, De Aragão Umbuzeiro G, Vrana B, Krauss M (2016) Effect-directed analysis supporting monitoring of aquatic environments - an in-depth overview. Sci Total Environ 544. https://doi.org/10.1016/j.scitotenv.2015.11.102

Celiz MD, Tso J, Aga DS (2009) Pharmaceutical metabolites in the environment: Analytical challenges and ecological risks. Environ Toxicol Chem 28. https://doi.org/10.1897/09-173.1

Deeb AA, Stephan S, Schmitz OJ, Schmidt TC (2017) Suspect screening of micropollutants and their transformation products in advanced wastewater treatment. Sci Total Environ 601–602:1247–1253. https://doi.org/10.1016/j.scitotenv.2017.05.271

Dubey M, Mohapatra S, Tyagi VK, Suthar S, Kazmi AA (2021) Occurrence, fate, and persistence of emerging micropollutants in sewage sludge treatment. Environ Pollut 273:116515. https://doi.org/10.1016/j.envpol.2021.116515

EPA (2017) CompTox Chemistry Dashboard [WWW Document]. United States Environmental Protection Agency

Eregowda T, Mohapatra S (2020) Fate of micropollutants in engineered and natural environment. In: Kumar M, Munoz-Arriola F, Furumai H, Chaminda T (eds) Resilience, response, and risk in water systems. Springer, Singapore, pp 283–301

Fu Q, Malchi T, Carter L, Li H, Gan JJ, Chefetz B (2019) Pharmaceutical and personal care products: from wastewater treatment into agro-food systems. Environ Sci Technol 53:14083–14090. https://doi.org/10.1021/acs.est.9b06206

Gogoi A, Mazumder P, Tyagi VK, Tushara Chaminda GG, An AK, Kumar M (2018) Occurrence and fate of emerging contaminants in water environment: a review. Groundwater Sustain Dev 6. https://doi.org/10.1016/j.gsd.2017.12.009

Gosetti F, Mazzucco E, Gennaro MC, Marengo E (2015) Non-target UHPLC/MS analysis of emerging contaminants in water. In: Pollutants in buildings water and living organisms. https://doi.org/10.1007/978-3-319-19276-5_4

Heller S, McNaught A, Stein S, Tchekhovskoi D, Pletnev I (2013) InChI - The worldwide chemical structure identifier standard. J Cheminform 5. https://doi.org/10.1186/1758-2946-5-7

Hernández F, Ibáñez M, Portolés T, Cervera MI, Sancho JV, López FJ (2015) Advancing towards universal screening for organic pollutants in waters. Journal of Hazardous Materials, 282, 86–95

Hohrenk LL, Vosough M, Schmidt TC (2019) Implementation of Chemometric Tools to Improve Data Mining and Prioritization in LC-HRMS for Nontarget Screening of Organic Micropollutants in Complex Water Matrixes. Anal Chem 91:9213–9220. https://doi.org/10.1021/acs.analchem.9b01984

Howard PH, Muir DCG (2011) Identifying new persistent and bioaccumulative organics among chemicals in commerce II: pharmaceuticals. Environ Sci Technol 45:6938–6946. https://doi.org/10.1021/es201196x

Keller BO, Sui J, Young AB, Whittal RM (2008) Interferences and contaminants encountered in modern mass spectrometry. Anal Chim Acta. https://doi.org/10.1016/j.aca.2008.04.043

Kloepfer A, Quintana JB, Reemtsma T (2005) Operational options to reduce matrix effects in liquid chromatography- electrospray ionisation-mass spectrometry analysis of aqueous environmental samples. J Chromatogr A 1067. https://doi.org/10.1016/j.chroma.2004.11.101

Liu J-L, Wong M-H (2013) Pharmaceuticals and personal care products (PPCPs): a review on environmental contamination in China. Environ Int 59:208–224. https://doi.org/10.1016/j.envint.2013.06.012

Menon NG, Mohapatra S, Padhye LP, Tatiparti SSV, Mukherji S (2020) Review on occurrence and toxicity of pharmaceutical contamination in Southeast Asia.In: Emerging issues in the water environment during anthropocene. https://doi.org/10.1007/978-981-32-9771-5_4

Michael I, Vasquez MI, Hapeshi E, Haddad T, Baginska E, Kümmerer K, Fatta-Kassinos D (2014) Metabolites and transformation products of pharmaceuticals in the aquatic environment as contaminants of emerging concern. In: Transformation products of emerging contaminants in the environment: analysis, processes, occurrence, effects and risks. https://doi.org/10.1002/9781118339558.ch14

Mogili NV, Mohapatra S (2021) Microbial community analysis of wastewater during blackwater treatment, Wastewater Treatment Reactors. BV. https://doi.org/10.1016/B978-0-12-823991-9.00024-1

Mohapatra S, Padhye LP, Mukherji S (2018) Challenges in detection of antibiotics in wastewater matrix. In: Environmental contaminants: measurement, modelling and control. Springer, pp 3–20

Mohapatra S, Menon NG, Mohapatra G, Pisharody L, Pattnaik A, Menon NG, Bhukya PL, Srivastava M, Singh M, Barman MK, Gin KYH, Mukherji S (2020a) The novel SARS-CoV-2 pandemic: possible environmental transmission, detection, persistence and fate during wastewater and water treatment. Sci Total Environ 765

Mohapatra S, Menon NG, Padhye LP, Tatiparti SSV, Mukherji S (2020b) Natural attenuation of pharmaceuticals in the aquatic environment and role of phototransformation. In: Contaminants in drinking and wastewater sources. Springer, Singapore

Mohapatra S, Sharma N, Mohapatra G, Padhye LP, Mukherji S (2021) Seasonal variation in fluorescence characteristics of dissolved organic matter in wastewater and identification of proteins through HRLC-MS/MS. J Hazard Mater 413:125453. https://doi.org/10.1016/j.jhazmat.2021.125453

Mollerup CB, Mardal M, Dalsgaard PW, Linnet K, Barron LP (2018) Prediction of collision cross section and retention time for broad scope screening in gradient reversed-phase liquid chromatography-ion mobility-high resolution accurate mass spectrometry. J Chromatogr A 1542:82–88. https://doi.org/10.1016/j.chroma.2018.02.025

Patel M, Kumar R, Kishor K, Mlsna T, Pittman CU, Mohan D (2019) Pharmaceuticals of emerging concern in aquatic systems: chemistry, occurrence, effects, and removal methods. Chem Rev 119. https://doi.org/10.1021/acs.chemrev.8b00299

Peter KT, Wu C, Tian Z, Kolodziej EP (2019) Application of Nontarget High Resolution Mass Spectrometry Data to Quantitative Source Apportionment. Environ Sci Technol 53:12257–12268. https://doi.org/10.1021/acs.est.9b04481

Pitarch E, Cervera MI, Portolés T, Ibáñez M, Barreda M, Renau-Pruñonosa A, Morell I, López F, Albarrán F, Hernández F (2016) Comprehensive monitoring of organic micro-pollutants in surface and groundwater in the surrounding of a solid-waste treatment plant of Castellón, Spain. Sci Total Environ 548–549:211–220. https://doi.org/10.1016/j.scitotenv.2015.12.166

Priyanka MS, Mohapatra S (2020) Shifts and trends in analysis of contaminants of emerging concern: sulfonamides. In: Kumar M, Munoz-Arriola F, Furumai H, Chaminda T (eds) Resilience, response, and risk in water systems. Springer, Singapore, pp 261–281

Portolés T, Mol JG, Sancho JV, Hernández F (2014) Use of electron ionization and atmospheric pressure chemical ionization in gas chromatography coupled to time-of-flight mass spectrometry for screening and identification of organic pollutants in waters. Journal of Chromatography A, 1339, 145–153

Rasche F, Scheubert K, Hufsky F, Zichner T, Kai M, Svatoš A, Böcker S (2012) Identifying the unknowns by aligning fragmentation trees. Anal Chem 84. https://doi.org/10.1021/ac300304u

Samanipour S, Baz-Lomba JA, Alygizakis NA, Reid MJ, Thomaidis NS, Thomas KV (2017) Two stage algorithm vs commonly used approaches for the suspect screening of complex environmental samples analyzed via liquid chromatography high resolution time of flight mass spectroscopy: a test study. J Chromatogr A 1501:68–78. https://doi.org/10.1016/j.chroma.2017.04.040

Schymanski EL, Jeon J, Gulde R, Fenner K, Ruff M, Singer HP, Hollender J (2014) Identifying small molecules via high resolution mass spectrometry: communicating confidence. Environ Sci Technol:2097–2098. https://doi.org/10.1021/es5002105

Singer HP, Wössner AE, McArdell CS, Fenner K (2016) Rapid screening for exposure to "non-target" pharmaceuticals from wastewater effluents by combining HRMS-based suspect screening and exposure modeling. Environ Sci Technol 50:6698–6707. https://doi.org/10.1021/acs.est.5b03332

Sleno L (2012) The use of mass defect in modern mass spectrometry. J Mass Spectrom 47. https://doi.org/10.1002/jms.2953

Sud M, Fahy E, Cotter D, Azam K, Vadivelu I, Burant C, Edison A, Fiehn O, Higashi R, Nair KS, Sumner S, Subramaniam S (2016) Metabolomics Workbench: An international repository for metabolomics data and metadata, metabolite standards, protocols, tutorials and training, and analysis tools. Nucleic Acids Res 44. https://doi.org/10.1093/nar/gkv1042

Ternes TA (1998) Occurrence of drugs in German sewage treatment plants and rivers. Water Res 32. https://doi.org/10.1016/S0043-1354(98)00099-2

Tran NH, Reinhard M, Gin KYH (2018) Occurrence and fate of emerging contaminants in municipal wastewater treatment plants from different geographical regions-a review. Water Res 133. https://doi.org/10.1016/j.watres.2017.12.029

Vinaixa M, Schymanski EL, Neumann S, Navarro M, Salek RM, Yanes O (2016) Mass spectral databases for LC/MS- and GC/MS-based metabolomics: state of the field and future prospects. TrAC - Trends Anal Chem 78:23–35. https://doi.org/10.1016/j.trac.2015.09.005

Wohlgemuth G, Mehta SS, Mejia RF, Neumann S, Pedrosa D, Pluskal T, Schymanski EL, Willighagen EL, Wilson M, Wishart DS, Arita M, Dorrestein PC, Bandeira N, Wang M, Schulze T, Salek RM, Steinbeck C, Nainala VC, Mistrik R, Nishioka T, Fiehn O (2016) SPLASH, a hashed identifier for mass spectra. Nat Biotechnol 34. https://doi.org/10.1038/nbt.3689

Antifouling Strategies and Environmental Issues in Industrial Cooling Water Systems in Marine Environment

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Abstract The process of biofouling is ubiquitous to surfaces exposed in the marine environment. The problem is common to industries abstracting seawater for condenser cooling purpose like power plants, etc. Biofouling control and environment are two sides of a coin with respect to industrial cooling water system (CWS). Conventionally oxidizing biocides are the choice for biofouling control in CWS. Current regulatory norms for cooling water (CW) discharges in tropical marine environment stipulate a thermal threshold of ΔT of 7 °C from the ambient and a continuous biocidal discharge not exceeding 0.2 mg/L total residual oxidants (TRO) at the outfall. CWS, operating in tropical locations with high fouling pressure, have to tune their biocidal regimes to keep biofouling loads within threshold levels, such that it does not interfere with operations. Large CWS in tropical regions, with high fouling pressure, have to live with certain levels of biofouling, and the biocidal regime has to be tailor-made to treat a CWS depending on the level of cleanliness required, cost, type of organisms and seawater chemistry. Chlorine has been the cost-effective biocide of choice in most of the industrial CWS over the past few decades, due to its cost, availability, ease of handling and well-worked-out chemistry in seawater. However, their interactions with dissolved organics result in the formation of toxic halomethanes, which have been shown to persist and bioaccumulate in marine organisms. Biofouling is an interfacial or surface-associated phenomenon where treating the bulk cooling water with biocides results in requirement of huge biocide inventory and has effects on non-target organisms abstracted in CW. Surface protection in the form of AF coatings will greatly reduce the biocidal inventory and the environmental burden in the vicinity of industrial CW discharges. The two issues need to be handled in an integrated manner increasing industrial productivity as well as minimizing environmental damage.

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1 Introduction

Biofouling may be defined as undesirable accumulation of microorganisms (viz. bacteria, diatoms, fungi, viruses), termed as microfouling/biofilms (soft fouling, slime) and macrofouling (hard fouling) caused by sessile invertebrate organisms and macroalgae, on natural and artificial surfaces exposed to the marine environment. The phenomenon of biofouling is inevitable to surfaces exposed in the marine environment. In the marine environment, macrofouling (fouling by hard-shelled invertebrate organisms) is dominant and overrides microfouling (microbial fouling) within a short period of time, ranging in days (1–15 days), depending on environmental conditions. In general, about 4000 species of organisms have been reported to be involved in the biofouling process (Crisp 1984). Even though a large number of species have been documented, in general, industrial cooling water systems are dominated only by a few handful of species due to various factors like availability of larval forms and density and diversity of organisms at a given geographical location (Venugopalan and Narasimhan 2008).

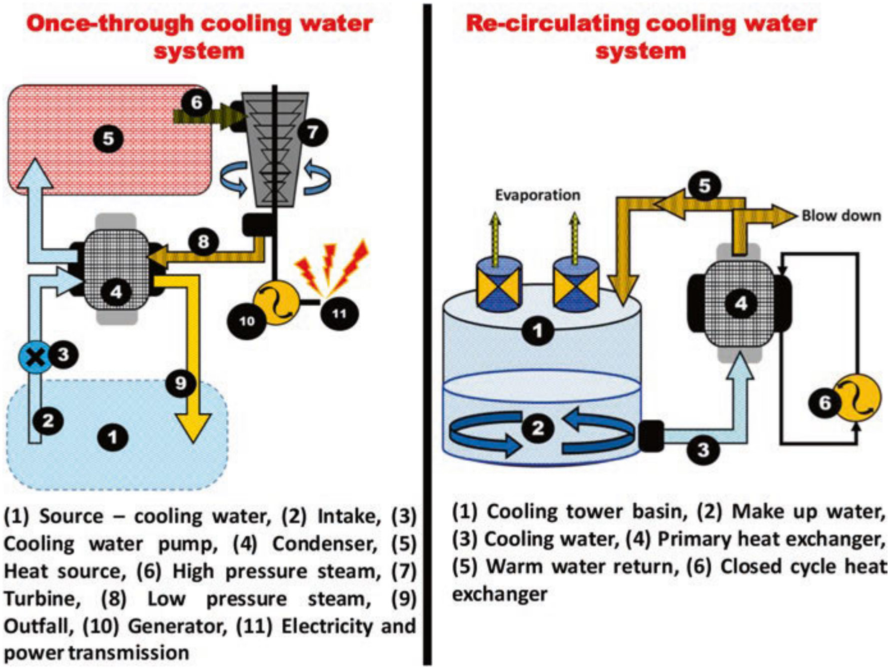
Thermoelectric and nuclear power plants require large amounts of seawater to condense steam from the turbine. Other minor consumers are the paper processing industries, petrochemical industries, and desalination plants, which face similar issues of biofouling. According to a report in 2005, water abstraction for cooling purpose has been estimated to be around 201 gallons per day, most of which was for power generation (NRDC 2014). The amount of cooling water required by any power plant is determined by its thermal efficiency. A nuclear power plant has a typical thermal efficiency of 25–33% compared to 40% efficiency in a modern coal-fired power station. In addition, a 1000 MWe power station generates 2000 MWe of low-grade waste heat which has to be dissipated (Turnpenny et al. 2010, 2012). Many industries are increasingly being located in coastal regions due to requirements of large volumes of seawater for condenser cooling purposes. Cooling water requirements amount to 35 $m^3 sec^{-1}$ for a 500 MWe nuclear power plant (Murthy and Venugopalan 2011). Similarly, for freshwater recirculating cooling system, 400 gallons $MW^{-1} h^{-1}$ of cooling water is required (EPRI and DOE 1997).

2 Types of Industrial Cooling Water System

Thermoelectric power plants work by heating of demineralized water (DM) and converting it into steam. The steam is then used to drive a turbine, which drives a generator to produce electricity. After passage of the steam through the turbine, the steam enters the condensers for condensation (Rankine cycle) of demineralized water (Turchi et al. 2010). The condensed water is returned back to the boiler for regeneration of steam again for production of electricity. The water used by the condensers (heat exchangers) to condense steam is abstracted from nearby water bodies, viz. streams, lakes and oceans. There are basically two predominant types of large industrial cooling water systems, viz. (1) once-through cooling systems and (2) recirculatory cooling systems.

2.1 Once-Through Cooling Water System

Once-through systems abstract large volumes (20–50,000 gallons/MWe h^{-1}, EPRI 2015) of cooling water from natural water bodies like lakes, rivers and oceans. Coastal cooling water systems involve either an offshore intake or a subtidal intake structure located beyond the surf zone to minimize the problem of silt ingress. The intake structure in most cases is designed in such a way that the cooling water is directly conveyed by gravity to an onshore well structure called the forebay which houses the pump house. In a typical power plant (nuclear or fossil-fired plants), the abstracted water from the pump house is then passed through the steam condensers (heat exchangers), and the steam is condensed on the outside of the tubes (Fig. 1). The heat of condensation is absorbed by the water flowing through the tubes, and the water is warmed by 0–10 °C depending on the size and design of the system.


Once-through cooling water system

(1) Source – cooling water, (2) Intake, (3) Cooling water pump, (4) Condenser, (5) Heat source, (6) High pressure steam, (7) Turbine, (8) Low pressure steam, (9) Outfall, (10) Generator, (11) Electricity and power transmission

Re-circulating cooling water system

(1) Cooling tower basin, (2) Make up water, (3) Cooling water, (4) Primary heat exchanger, (5) Warm water return, (6) Closed cycle heat exchanger

Fig. 1 Schematic diagram of once through and recirculating cooling water system (CWS)

This warm water is then returned to the natural source by an outfall structure, either through a surface or submerged discharge. Surface discharges are usually preferred to dissipate the excess heat and to minimize the direct impact of warm water on the natural body. Once-through coastal cooling water systems are prone to heavy biofouling of the intake system structures, concrete and metal pipelines and heat exchangers. Biocides are dosed either on a continuous or intermittent basis to treat the cooling water to deter the organisms from settling on the surfaces in the cooling water system.

2.2 Recirculatory Cooling Water Systems

Recirculatory cooling water systems are similar to once-through system except that these systems are located inland and utilize freshwater bodies as source of cooling water, viz. lakes, streams and rivers (Fig. 1). Recirculating systems comprise of either a closed or open system depending on the size of the plant. Similar to once-through systems, the cold water abstracted from the natural water body flows through the steam condenser, and the steam is condensed outside the tube. However, the heated water leaving the condensers is not returned to the source water body and is pumped to a device such as cooling tower and then to a cooling pond via a cooling canal. The heated water is cooled by the cooling tower and then recirculated. Fresh makeup water is added to the recirculating system to make up for the evaporative losses, and the cycles of concentration in a recirculating system are maintained within a factor value of ~3. Microfouling, aqueous corrosion, scaling and microbial-induced corrosion are problems encountered in recirculatory cooling systems, and strict water quality needs to be maintained in the recirculating water to minimize these problems. In addition to biocides, surfactants, antiscalants and anticoagulants need to be dosed in recirculating systems for effective operations.

3 Operational Problems Due to Biofouling in Industrial CWS

Biofouling of surfaces in industrial cooling water systems and process equipment can have significant negative impact on the operational efficiency of the unit. For an extensive review on the topic, refer to Rajagopal et al. (2012a). In general, biofouling-induced problems in CWS constitute (1) pressure drop across intake lines, (2) head loss at the pump house, (3) blockage of heat exchanger tubes by hard-shelled organisms, (4) reduction in heat transfer and (5) accelerated corrosion (WHOI 1952; Neitzel et al. 1984; Jenner 1998). Heat exchangers (HX) are a vital component of any CWS, and biofilm formation is an important factor affecting their thermal performance. Studies by Ibrahim and Attia (2015) reveal that efficiency of a nuclear power plant is reduced by 0.4478% for an increase in the fouling factor of cooling seawater in the range of 0.00015–0.00035 m^2 K/W, with a power loss of 13319.93 KW. Biofouling leads to reduced heat transfer, flow blockage of condenser tubes, increased fluid frictional resistance and additional maintenance and operational costs (Bott and Tianqing 2004; Murthy et al. 2005). Fouling of heat transfer equipment in industrial cooling systems is a complex process involving two or three different types of foulants. Colonization of surfaces usually commences with biofilms, settlement of biofouling organisms and their growth and then sedimentation (clay, silt); fouling also occurs simultaneously which is difficult to predict. Heat transfer resistance was found to be directly related to the amount of solids accumulated on the HX tubes (Rubio et al. 2014). The degree of fouling in HX tubes was found to increase with the decrease in water velocity (decrease from 2.17 to 1.38 $m^3 s^{-1}$), resulting in an increase in fouling by a factor of 3.5 times (Rubio et al. 2014). Concentration of biocides and dosing pattern have been shown to influence fouling in heat exchangers (HX). Chlorine residuals of 0.4 mg/L for 1 h a day have shown to reduce the fouling factor (R_f) of HX by 50% (Rubio et al. 2015).

4 Sequence of Events Leading to Biofouling of Surfaces

Abiotic surfaces, viz. metals and polymer surfaces, exposed in the marine environment are prone to a sequence of events which leads to biofouling of surfaces (Fig. 2). The first event is the formation of a “conditioning film” (Marshall 1985),

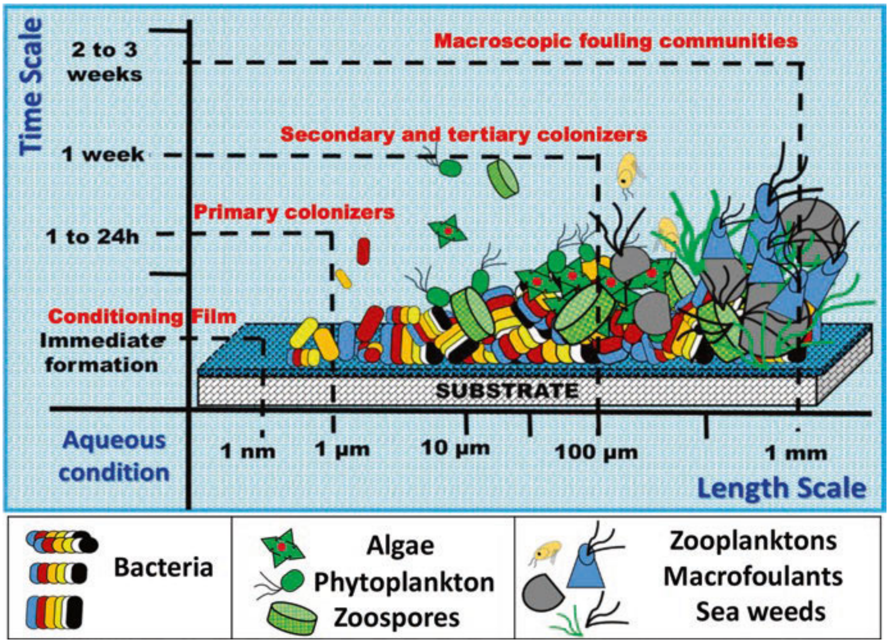


Fig. 2 Pictorial illustration of sequence of biofouling of surfaces in the marine environment

comprising of dissolved organics and humic substances, which occurs within seconds of immersion of surfaces in the aquatic environment. Subsequently, adhesion of bacterial cells occurs resulting in the formation of a biofilm matrix. The phenomenon of adhesion of bacterial cells to the surface was first reported by Zobell (1943); however, it was not until 1978 that Costerton and co-workers proposed the "biofilm theory" (Costerton et al. 1978). It is also now imminent that bacteria switch between planktonic and sessile modes (Chua et al. 2014). The biofilm mode of attachment of microorganisms offers several advantages like (i) increased availability of nutrients and dissolved oxygen, (ii) protection against harsh environments, (iii) resistance to antimicrobials and biocides, (iv) exchange of genetic material and (v) shelter from predation (Wahl 1989; Dang and Lovell 2000; Lewis 2001). It has also been observed that biofilm cells acquire physiological characteristics which are different from their planktonic counterparts (Rollet and Guzzo 2009). It is important to understand the development and members of the biofilm community to develop a suitable antifouling strategy. Modern approaches have aimed at altering the surface charge, surface hydrophobicity, surface free energy, critical surface tension, surface wettability and surface nano-topography to inhibit development of biofilms on surfaces.

The surface colonization by bacteria and the formation of biofilms follow an ordered sequence of events with bacteria comprising the pioneer species to interact with conditioning films (Marshall 1992). The typical structure of formation of biofilms on surfaces involves four different phases which has been initially described by Characklis (1990), and subsequent studies (Little and Wagner 1997; Van Loosdrecht et al. 1997; Stoodley and Stoodley 2004; Stewart and Franklin 2008; Flemming and Wingender 2010) have improved our understanding of the process of biofilm community, colonization, morphology, structure, development, physiology, susceptibility to biocides and detrimental effects to infectious diseases. The steps involve:

1. **Reversible adhesion:** Wherein the bacteria are held to the substratum by weak van der Waals forces of attraction. Desorption of these bacteria may also occur during this phase if the bacterial cells find the environment unsuitable.
2. **Irreversible adhesion:** This step involves the irreversible attachment of bacteria to the surface by the production of exopolymeric substance which is a hydrated polyanionic polysaccharide matrix (Chua 2014; Flemming 2016). This stage precedes the formation of micro-colonies and development of micro-colonies (Donlan and Costerton 2002). In cooling water systems, the EPS or the glycocalyx mediates the adhesion of bacterial cells (Morton et al. 1998).
3. **Biofilm maturation and micro-colony formation:** Wherein the growth and reproduction of the adhered cells and colonization of other complex community members occur comprising of photoautotrophic algae like diatoms and cyanobacteria, yeasts, protists, heterotrophic bacteria, fungi, protozoans, metazoans and viruses along with organic and inorganic debris (Stoodley 2002; de Carvalho 2018). During this phase, the biofilm alters the surface characteristics of the substratum (Busscher and Mei 1995). These modifications may or may not be

involved in influencing subsequent settlement and recruitment of larvae of higher invertebrate organisms (Lappin-Scott and Costerton 1989). Interactions occurring between the primary colonist and the subsequent recruits determine the establishment of certain species on the surfaces and maturation of the biofilm community (Dang and Lovell 2000).

4. **Biofilm detachment and dispersal:** Growth and reproduction of microorganisms colonizing biofilms results in a climax community of multicellular and multispecies biofilms in natural ecosystems. The overall biomass accumulation on a surface is also influenced by the detachment of cells from biofilms to resume a planktonic lifestyle. Involvement of intracellular c-di-GMP has been found to determine the transition from planktonic to biofilm (increased levels) mode and dispersal to planktonic states (decreased levels) from biofilm mode (Chua 2014). The dispersed cells have been shown to demonstrate a unique physiology and a distinct phenotype with enhanced virulence, motility, adhesion and metabolic signatures like altered antimicrobial susceptibilities (Rumbaugh and Sauer 2020). Currently biofilm dispersal strategies are being probed with an aim to eliminate dispersed cells with lower susceptibilities to biocides as a successful antimicrobial strategy. However, it is still unclear how different are dispersed cells with respect to their planktonic counterparts. Rollet and Guzzo (2009) have reported phenotypic differences in the biofilm-forming capacities between planktonic and dispersed cells indicating the existence of a transitional phenotype.

4.1 Invertebrate Larval Settlement and Development of Macrofouling Communities

Macrofouling of industrial cooling water system (CWS) is a universal problem and is more pronounced in countries located in the tropical region due to their high biodiversity. Cooling systems are poorly studied with respect to their biofouling load, species diversity and density, settlement pattern of organisms, peak intensities in settlement, recruitment success, seasonal distribution and climax fouling communities. Knowledge on species involved, their settlement pattern and breeding cycles are important in formulating a successful antifouling strategy for cooling systems (for detailed reviews, see Venkatesan and Murthy 2008). Continuous monitoring using test coupons and surveillance in industrial CWS is a primary requisite as the problem of biofouling is site specific and depends to a great extent on many biotic and abiotic factors (Rodriguez et al. 1993; Roberts and Schmidtz 1991; Gosselin and Qian 1997).

Initially, invertebrate larval settlement behaviour, availability in the water column or abundance determines the population dynamics and community structure on surfaces. Larval availability governs the spatial patterns of settlement observed. Subsequently, competition, predation and disturbances determine the final composition of fouling communities which fluctuate on a temporal basis. The process of larval settlement commences with the behavioural phase of searching for a suitable substratum (Fig. 3) followed by adhesion or permanent attachment to the substratum which triggers metamorphosis to the juvenile stage. Survival of newly settled juveniles up to a certain stage on surfaces is termed as recruitment (Keough and Downes 1982). Substratum cues (both physical and chemical) have been shown to play a major role in inducing settlement of invertebrate larval forms. In the absence of suitable cues from the substratum, the planktonic larval phase has been found to be extended in many larval forms. Sequence of events leading to settlement of larvae is influenced by marine biofilms, which has been found to induce/inhibit or have no effect on settlement of different invertebrate larval forms (Wieczorek and Todd 1998; Hadfield and Paul 2001; Dobretsov et al. 2006; Murthy et al. 2008; Dobretsov and Rittschoff 2020; Rajitha et al. 2020).

In industrial CWS, water flow velocity and shear forces at the surfaces also influence settlement. Settlement is also influenced by colour (Ells et al. 2016) and substrate material (Chase et al. 2016). Larval habitat selection has been shown to influence settlement patterns (Jenkins 2005). Preventing/inhibiting larval settlement is the foremost prerequisite for protection of surface in CWS. Concentration of biocides required to be dosed in CWS for preventing invertebrate larval settlement is far less in magnitude compared to that required for killing of adult organisms. Hence, for a given CWS, the dominant biofouling organisms need to be determined

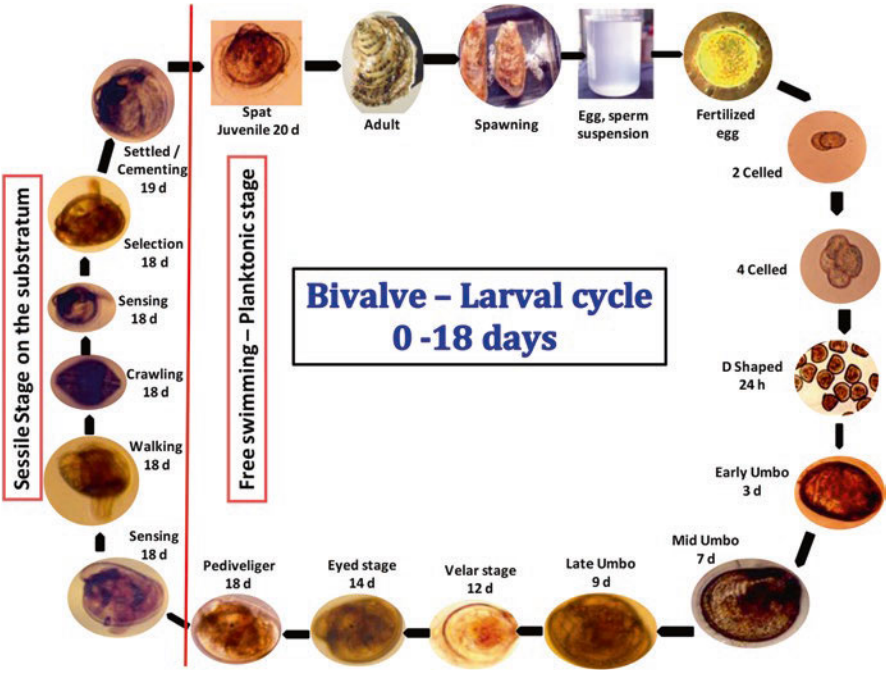


Fig. 3 Life cycle of a bivalve mollusc (*Crassostrea madrasensis,* Preston) depicting different larval stages, sensing of substratum settlement and metamorphosis to juvenile

along with their breeding cycles, peak settlement seasons, biocidal concentration required to inhibit larval settlement and susceptibility of adults to biocides to formulate a suitable biocidal regime. Henceforth, biocidal regimes for industrial CWS have to be tailor-made for a given geographical location.

5 Biofouling in Cooling Water Systems and Fouling Pressure

Macrofouling communities in power plant cooling water systems are unique with respect to their composition, distribution and density which are mainly governed by the geometry, flow patterns in conduits, void zones and zones with small-scale turbulences and biocidal and thermal regimes in a CWS (Bott 1990; Moshchenko and Zvyagintsev 2010; Murthy et al. 2011; Venugopalan 2018). In general, CWS have poor species diversity but high density of certain species compared to nearby natural benthic communities. These communities are resilient to high flow rates and biocidal regimes. They exhibit higher growth rate and high fecundity compared to their benthic counterpart in the nearby shore. Macrofouling communities in CWS of coastal power stations are generally represented by several species of seaweeds, sponges, coelenterates, gorgonians, polychaetes, bryozoans, ascidians, barnacles, bivalve molluscs and associated grazing fauna like amphipods (Rajagopal et al. 1991). In spite of continuous chlorination practised in power stations in countries in the tropical region, biofouling loading on the surfaces of conduits exceeds a threshold limit, which necessitates taking the power station offline for manual cleaning and removal of biofouling debris. Data from one such shutdown evaluation during the year 2009 at a coastal nuclear power station is presented herewith in Fig. 4.

The Madras Atomic Power Station (MAPS) located at Kalpakkam (12’ 33” N, 80’ 11” E) on the east coast of India consists of two units of pressurized heavy-water reactor (PHWR), each with an installed capacity of 235 MWe. The plant

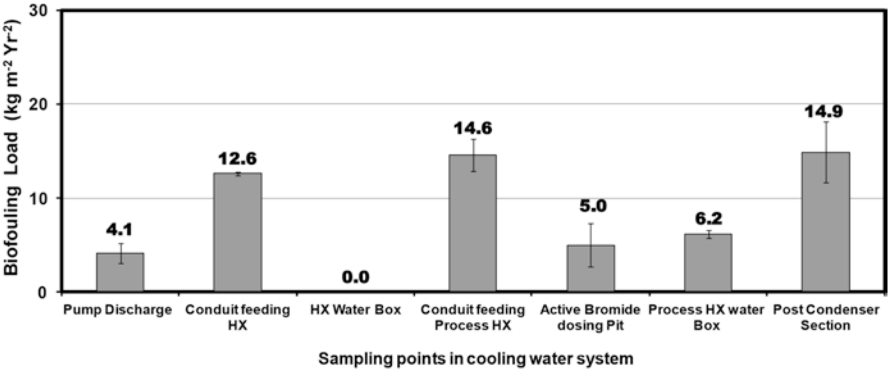


Fig. 4 Typical biofouling loading in cooling water system of a coastal power station using seawater as a coolant and low dose continuous chlorination (0.2 ± 0.1 mg/L)

draws coastal seawater from the Bay of Bengal for condenser cooling purposes at the rate of 35 $m^3 s^{-1}$ at 3 $m s^{-1}$ velocity by an offshore intake located 468 m from the coastline. The cooling water reaches a pump house located on the shore from where it is pumped through the heat exchangers and returned back by a surface discharge. The station practises low-dose continuous chlorination of 0.2 ± 0.1 mg/L with a shock dose chlorination of 0.4 ± 0.1 mg/L twice a week. The auxiliary systems are cooled by the process water heat exchangers which operate at lower temperature and are prone to heavy biofouling. Supplementary biocide in the form of activated bromide is dosed for 1 hour/shift with a residual concentration of 0.1 mg/L. In spite of the strict biocidal regime in vogue, fouling loads of 4–15 kg $m^2 y^{-2}$ were recorded in the conduits of the power station. The major fouling species constitute the barnacles (*Amphibalanus reticulatus*), mussels (*Perna viridis, Perna indica*), oysters (*Crassostrea madrasensis*), brown mussels (*Brachidontes striatulus*), coelenterate hydroids and bryozoans (*Bugula* sp.) and tubeworms (*Hydroides norvegicus*). The loading at different sections of the CWS were near identical during successive shutdown evaluations undertaken from the year 2007 onwards. Such loading on surfaces cast a shadow on the performance of low-dose continuous chlorination at the power station.

To ascertain the efficacy of the present chlorination regime in combating fouling in the conduits, a separate yearlong study was undertaken to record the biofouling loading on different structural materials used in the cooling water system of MAPS. Test coupons were suspended in coastal water and pump house and retrieved after every month up to 12 months for recording biofouling loading and species diversity and density (Fig. 5). Results revealed a loading of 60.4 and

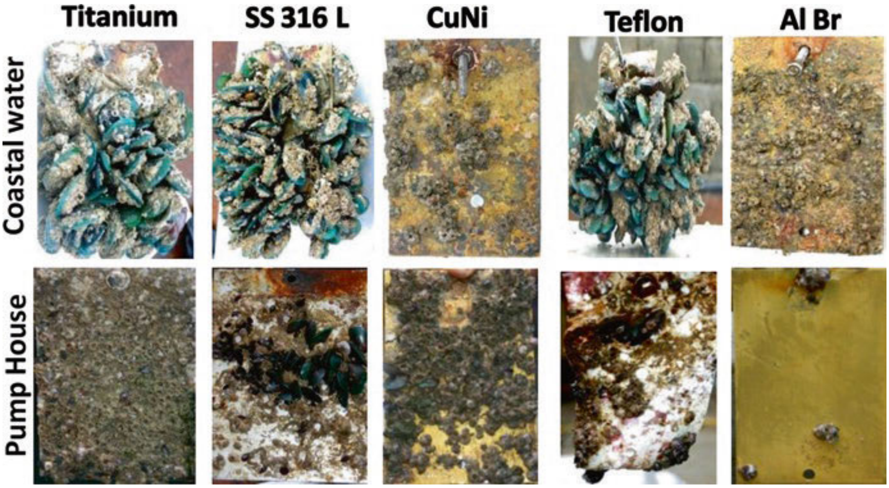


Fig. 5 Photographs of biofouling loading and species colonization on different material surfaces after 365 days exposure in coastal waters and at the pump house of a coastal power station which practices continuous low dose chlorination (0.2 ± 0.1 mg/L)

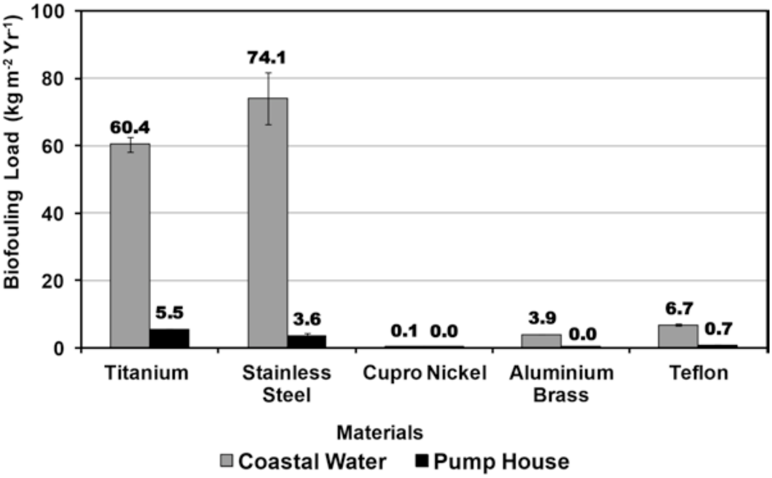


Fig. 6 of biofouling loading on different material surfaces after 365 days of exposure to coastal waters and at the pump house of a coastal power station which practices continuous low dose chlorination (0.2 ± 0.1 mg/L)

74.1 kg m^2 y^{-1} on titanium and steel surfaces with a corresponding decrease of 5.5 and 3.6 kg m^2 y^{-1} at the pump house. Results of the study demonstrated the effectiveness of low-dose continuous chlorination practised at the power station in bringing down the biofouling loading from 74 (coastal waters) to 14 kg m^2 y^{-1} in the conduits (Fig. 6).

6 Biocidal Control of Biofouling in Industrial Cooling Water Systems

Mitigation of biofouling in cooling water systems and heat transfer equipment is vital for their operation. Mitigation techniques broadly fall into two categories: (1) mechanical (use of intake filtration screens) and (2) chemical methods (Cloete et al. 1992; Ludensky et al., 2003; Rajagopal et al. 2003a). Traditionally oxidizing biocides have been used extensively for the control of biofouling in cooling water systems; however, their effects on non-target organisms in the receiving water body also need to be considered. Biocidal regimes for biofilm and macrofouling control vary and should be tailor-made for a cooling system taking into account the density and diversity of both micro- and macro-organisms. The biocidal regime should also be flexible to combat seasonal spikes in settlement of organisms according to their breeding behaviour.

6.1 Choice of Biocides in Cooling Water System and Their By-Products

Biocides for application in CWS can be broadly classified into two groups, viz. oxidizing and non-oxidizing biocides (Table 1). Oxidizing biocides act directly on the cell membranes by altering their permeability and oxidizing them. They also act on proteins and nucleic acids. General disadvantages of oxidizing biocides are their high volatility, oxidant demand in natural water bodies, easy quenching by biofilm components and formation of toxic by-products. Both oxidizing (ClO_2) and non-oxidizing biocides (benzyldimethyldodecylammonium chloride – BDMDAC) have demonstrated the ability to cause detachment of mature biofilms (Liu et al. 2011).

(a) **Chlorine:** Chlorine (gaseous/sodium hypochlorite) has been the biocide of choice in CWS of power plants (Coughlan and Whitehouse 1977) due to its cheap cost, easy handling, known by-products and well-worked-out chemistry in seawater and freshwater bodies (Allonier and Bremond 1999; Jolley et al. 1990). Even though there are some intrinsic issues regarding chlorination of seawater for fouling control, viz. pH dependency of the active biocidal component in seawater (hypochlorous acid – HOCl), reaction with organics and production of by-products, still chlorine is the mainstay biocide in several industrial cooling systems (Table 2). Chlorination of coastal power stations in Europe revealed different classes of chlorination by-products, viz. halogenated phenols, trihalomethanes (THMs), haloacetonitriles and halophenols (Jenner and Khalanski 1997). The production of THMs was linearly correlated to chlorine concentrations in seawater (Abdel-Wahab et al. 2010) with four different speciations, viz. chloroform, bromoform, bromodichloromethane (BDCM) and dibromochloromethane (DBCM). THMs have been suspected of causing cancer, kidney and liver damage, retard foetal growth and birth defects (O'Hagan et al. 2004). Bromoform is the most dominant species present in the effluents of coastal power stations using chlorination, as seawater contains 65% of bromide

Table 1 Common oxidizing and non-oxidizing biocides used in industrial cooling water systems: oxidation potential is given in parenthesis

Oxidizing biocides	Non-oxidizing biocides
Chlorine (1.36)	2,2-Dibromo-3-nitrilopropionamide (DBNPA)
Hypochlorous acid (1.49)	Methylene bis(thiocyanate)
Hypochlorite ion (0.89)	Alkyldimethylbenzylammonium chloride (ADBAC)
Bromine chloride (1.07)	2-(Thiocyanomethylthio)benzothiazole (TCMTB)
Chlorine dioxide (1.50)	Isothiazalones, benzothiazoles
Ozone (2.07)	Didecyldimethylammonium chloride (DDAC)
Hydrogen peroxide (1.77)	Org Sulphur and sulphones, glutaraldehyde
Peracetic acid	Bulab 6002 poly[oxyethylene(dimethyliminio)ethylene dichloride]
Electrochemically activated water	

Table 2 Different chlorination regimes and their application in biofouling control

Chlorination regimes	Application and concentrations
Continuous chlorination	For killing mussels 1–2 ppm (Lewis 1985)
Low-dose continuous chlorination (exomotive)	Mitigate mussels out of the system (James 1967). Not to kill mussels but prevent young ones from settling (Beauchamp 1966). Concentrations of 0.2–0.5 ppm delay settlement for 30% larvae (Khalanski and Bordet 1980)
Intermittent chlorination	Control of slime on HX 0.2 ppm 0.5 h on 1 h off (Murthy et al. 2005)
Shock dose chlorination	For killing soft-bodied animals, algae
Targeted chlorination	For protecting HX pumps, etc. (Mussalli 1985; Chow et al. 1984)
Pulse chlorination (R)	Reduces chlorine inventory by 50% (Polman and Jenner 2002)

which is oxidized to bromine, leading to formation of organo-bromine compounds, which have ecotoxicological effects (Jenner and Khalanski 1997; Rajamohan et al. 2007; Padhi et al. 2012). Bromoform (18–365 μg/L) was the dominant species followed by dibromochloromethane (12–60 μg/L) at a tropical coastal power station (Rajamohan et al. 2007). Subsequent studies by Padhi et al. (2012) revealed seasonal pattern in formation of total THMs with maximum (41 μg/L, month of November) and minimum (12 μg/L, month of February) values recorded at the same power station.

(b) **Chlorine dioxide:** The search for a more efficient environmentally friendly alternate biocide to chlorine favoured chlorine dioxide (Bernarde et al. 1965) as it is not readily quenched by organics or by the biofilm matrix, produces less organo-halogenated by-products and is currently being adopted for treating CWS in power stations (Rajagopal et al. 2012b). Jang et al. (2006) reported that 25 mg/L of chlorine dioxide was able to penetrate 100 μm biofilm indicating its superiority and ability to penetrate much thinner biofilms. Chlorine dioxide is a gas at room temperature, readily soluble in water and reactive to light. Chlorine dioxide works at a broad range of pH (5.0–9.5), does not produce free bromine in seawater and does not react with ammonia and organics to form chloramines. However, ClO_2 produces inorganic by-products such as chlorite ions (ClO_2^-) and chlorate ions (ClO_3^-) (Ambrogi 1997). Chlorine dioxide solutions above a concentration of 30 g/L are explosive, and hence storage and dosing for large CWS is not a recommended practice (Schneider 1997). The use of chlorine dioxide for biofouling control in power stations is gaining importance due to the technological advancements in online chlorine dioxide generators. Chlorine dioxide generated much less trihalomethanes (THMs) than sodium hypochlorite (<1 vs 154 μg/L) (Simmon et al. 2014). Studies measuring in situ production of by-products at an operating nuclear power plant which switched from chlorine to chlorine dioxide (0.28–0.35 mg/L TRO) showed formation of 0.1 μg/L of DBCM and 0.11 μg/L of bromoform (Rajamohan et al. 2016).

(c) **Bromine:** Bromine chloride coupled with sodium hypochlorite is practised as supplementary/targeted biocide for biofouling control in CWS (Burton 1979). The advantages are (1) bromine is a more stable biocide at seawater pH, (2) brominated compounds have more biocidal efficacy than bromine and (3) bromamines formed disappear much faster. In general, bromine is used as a supplementary/targeted biocide for fouling control in heat exchangers (Murthy and Venugopalan 2011).

(d) **Ozone, hydrogen peroxide and peracetic acid:** Ozone is a highly powerful oxidant and decomposes organic substances like humic acids. It is widely used for treatment of drinking water and small cooling towers. It is the least preferred biocide for biofouling control in CWS due to its cost, production of manganese dioxide deposits and short-lived hydroxyl free radicals (Rajagopal et al. 2012b). Ozonation of waters containing bromide or iodide ion results in formation of bromated ions and hypobromous acid and complexing with metal ions to form ozonates (Haag and Holgna 1983). Ozone in seawater produces by-products similar to that of chlorine and hence is not the preferred biocide for seawater cooling systems. Hydrogen peroxide has been found to be effective against microbial fouling and as an algaecide and is used in recirculating CWS. H_2O_2 is considered one of the safest biocides as it disintegrates into oxygen and does not form organo-halogenated compounds. Peracetic acid is an efficient bactericidal agent and used in small recirculating systems and cooling towers (Krammer 1997).

In comparison, non-oxidizing biocides are more selective than oxidizing biocides (Chelossi and Faimali 2006) and do not readily react with organics. Non-oxidizing biocides are wide ranging in action from bactericidal to molluscicides (Rajagopal et al. 2012b). Non-oxidizing biocides cover a wide spectrum of chemical compounds, viz. quaternary ammonium salts, dibromonitrilopropionamide, isothiazolone salts, ortho-phthalaldehyde, organo-sulphur compounds and anionic and non-ionic surface active agents. Non-oxidizing biocides may be more effective against certain type of microorganisms depending on their mode of action which makes them less broad spectrum in their activity when compared to oxidizing biocides. Among these, Clam-Trol, a product with an active substance ADBAC, H-130 M and Bulab 6002 (Table 1) have been used as molluscicides in CWS. Most of these non-oxidizing molluscicides are applied periodically, and their activity is dependent on water temperature and physiological activity of the organisms (Petrille and Werner 1993). Most of these non-oxidizing biocides are widely used for closed recirculating freshwater systems and are not economically viable for application in large once-through seawater systems. Degradation of some of the common biocides like ADBAC and TCMTB ranges from 3 to 29 days in the aquatic environments (Krzeminski et al. 1975; Dobbs et al. 1995).

6.2 Biocidal Regimes for Prevention of Biofilm Formation

The primary focus of biocidal dosings should be to inhibit adhesion of bacteria and diatoms and prevention of biofilm formation. Ideally the biocidal regime should be designed such that disinfection should commence before the onset of biofilms in CWS for a given geographical location. Concentrations required to disinfect established biofilms are high compared to the existing regulatory levels on biocidal discharges (Rajagopal et al. 2003a; Murthy and Venkatesan 2008). Many studies have attributed the biofilm EPS matrix to act as a barrier for the effective penetration of biocides as well as act as quenching agents. However, Morton et al. (1998) proposed that the bacterial cells in biofilms are in contact with the bulk fluid and that the observed resistance of biofilms may be due to the intrinsic mechanisms like phenotypic tolerance and multidrug efflux pumps. Studies by Behnke and Camper (2012) revealed that binary cultures were more tolerant to biocides than single species which may be the reason for the decreased efficacy on natural multispecies biofilms. Most of the studies on efficacy of biocides are carried out with individual bacterial and diatom strains, and the results cannot be directly interpolated to CWS. Natural biofilms are much more complex, biologically and chemically. However, from different laboratory studies, it is revealed that susceptibility towards biocides is dependent on the type of strain, the environmental conditions and the extent of biofilms. Studies using pilot-scale systems showed that a concentration of 1.0 mg/L of NaOCl inactivated more than 99.99% of bacteria in a 30-min interval (Rubio et al. 2015). However, this study pointed out that the legal limit of hourly average concentration in the power plant discharge was 0.5 mg/L TRO. A novel steam vapour system disinfected (99.95%) *E. coli* biofilms on different surfaces with a 3-minute exposure time (Song et al. 2012). To achieve similar levels of disinfection, a concentration of 10 mg/L of sodium hypochlorite was required with a contact time of 10–20 min.

In comparison, photoautotrophic periphyton biofilms are more susceptible to chlorine compared to their bacterial counterparts. Pulse chlorination (once every 6 hours) was effective in reducing the biofouling by these organisms with increase in exposure time (Patil and Jgadeesan 2011). In-use plant levels of chlorine (0.2 mg/L) were found more effective on centric diatoms (*Chaetoceros lorenzianus*) compared to the pennate diatoms (*Navicula* sp.) (Venkatnarayanan et al. 2016b). Booster biocides and metal ions have been shown to inhibit settlement and biofilm development of photoautotrophic biofilms at very low concentrations of 30 nmol l^{-1} (Arrhenius et al. 2014). Concentration as low as 0.02 mg/L was sensitive to the diatom *Achnanthes* sp., and the diatom *Navicula pelliculosa* was sensitive to 0.04 mg/L (Vannoni et al. 2018).

6.3 Biocidal Regimes for Prevention of Barnacle Larval Settlement

Colonization of different sections of CWS by biofoulants commences with the entry of larval forms which settle on surfaces inside the CWS and develop into adults. Among different fouling species, barnacles, tubeworms and oysters cement themselves to the substratum. Even if the encrusting organisms were killed, the hard shell still remains on the surface increasing the wall roughness. The shells have to be manually chiselled resulting in surface damages. Therefore, it is important to prevent settlement of larvae of fouling organisms in CWS. A requisite condition is that a biocidal regime in any CWS should be able to prevent larval settlement. An interesting observation made during another yearlong coupon study at the pump house of MAPS and in coastal waters of Kalpakkam revealed that the existing low-dose continuous chlorination (LDCC) regime of 0.2 ± 0.1 mg/L TRO was effective in preventing green mussel larval settlement, whereas the regime did not prevent settlement of the barnacle (*Amphibalanus reticulatus*) (Fig. 7).

These results led us to look at the biocidal concentrations required to inhibit settlement of larvae of this barnacle. Biocidal exposure time of 20 minutes was chosen as this would be representative of the residence time of seawater in the system from intake to outfall. Three different biocides, viz. chlorine (0.2, 0.5, 1.0 mg/L TRO), chlorine dioxide (0.1, 0.2, 0.5 mg/L TRO) and active bromide (0.2, 0.5, 1.0, 2.0, 5.0 mg/L TRO), were tested to inhibit settlement of barnacle cyprid larvae. Results for in-plant administered levels of chlorine (0.2–0.5 mg/L TRO) did not prevent larval settlement of the barnacles *Amphibalanus reticulatus* (Venkatnarayanan et al. 2016a). Even chlorine dioxide did not inhibit the settlement in this barnacle (Venkatnarayanan et al. 2017). The aluminium brass condenser tubes of the process seawater heat exchangers of the MAPS face tube blockage by this barnacle, and intermittent supplementary biocide in the form of activated bromide is dosed. Results reveal that concentration of up to 5.0 mg/L TRO of active bromide also did not inhibit settlement of larvae (Fig. 8). The increased tolerance of cyprid larvae to different concentrations of oxidizing biocides indicates that certain amount of barnacle fouling is inevitable in CWS.

In comparison to barnacles, very few studies exist on the toxicity of biocides to other larval forms. Studies by Duncan and Waugh (1964) demonstrated sensitivity of nauplii of *Elminius modestus* to chlorine residuals of 2.0 mg/L where all the nauplii were killed. In comparison, veliger larvae of the oyster (*Ostrea edulis*) were comparatively unharmed at concentration of 10.0 mg/L and at 20.0 mg/L showing only growth retardation. Chlorination has been reported to severely reduce shell growth resulting in changes in shell structure and deposition (Thompson and Walker 1997). This study reported mortality of all larval stages at chlorine residuals of 8.0 mg/L and concentrations of 1.0 mg/L produced changes in swimming and crawling behaviour of *Mytilus edulis* larvae. Low-level chlorination of 0.2 mg/L

Fig. 7 Biofouling community on test coupons in kalpakkam coastal waters and at the pump house of MAPS

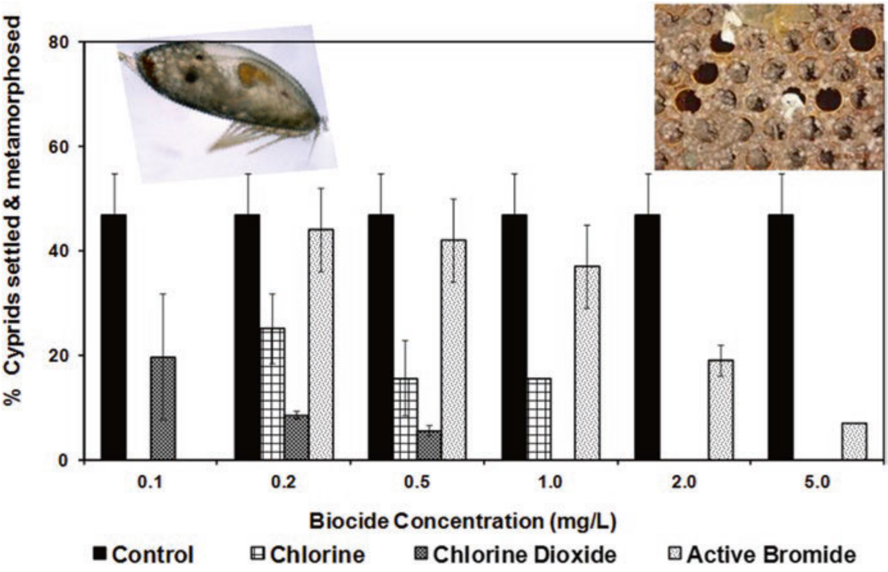


Fig. 8 Comparison of different biocides exposure (20 min) on cyprid settlement. (Data sets presented here are from an independent study and that of values published elsewhere). Insert barnacle cyprid larvae & colonization of process heat exchanger tubes

administered in the CWS of power station has been shown to retard shell growth in the mussel *Mytilus edulis* (Thompson and Walker 2000). Concentrations of 1.0 mg/L elicited about 97% mortality in veliger larvae of the mussel *Mytilus edulis*, whereas concentrations of 0.7 mg/L elicited only 16% of larval mortality (Haque and Kwon 2014). This study showed that 1.0 mg/L chlorine was 4 times more effective than 0.7 mg/L and 15 times more effective than 0.05 mg/L in causing larval mortality. Larval size and increase in concentration of chlorine (from 0.1 to 4.0 mg/L) influenced mortality (Haque and kwon 2015). Settlement of veliger larvae of the zebra mussel, *Dreissena polymorpha*, was reduced by 91% for 2 hours, with daily chlorine dosing of 1.0 mg/L (Bidwell and Lyons 1999). Comparative evaluation of chlorine, H_2O_2 and ozone on veligers of *Dreissena polymorpha* revealed concentrations as low as 0.1 mg/L of chlorine were perceived by the larvae by retracting their velum and foot which impairs sensing and settlement. To achieve complete mortality, concentrations of about 0.5 (18 h)–1.0 (5 h) mg/L were required (Van Benschoten and Neuhauser 1993). The time taken for mortality was shown to be reducing with supplementation of ultrasonic treatment along with chlorination by 1–12% on veliger larvae of *Mytilus edulis* (Haque and Kwon 2016b). Current regulatory norms for continuous discharges for industrial CWS in different countries in the temperate and tropical regions have been set from 0.01 to 0.2 mg/L TRO considering environmental safety. In-plant use concentrations are comparatively far less than the values reported in literature for achieving larval mortality/inhibiting settlement in different organisms. Hence, for an efficient biofouling control in CWS, the biocidal regime has to be tweaked from continuous to intermittent or shock dosing to comply with the discharge norms (Table 3).

6.4 Biocidal Regimes for Killing Adult Fouling Organisms in CWS

Invariably one often encounters a heavily fouled CWS, in spite of a strict biocidal regime in vogue at many industrial sites. This may be due to spikes in settlement during the breeding season which the regime could not handle or breaks in biocide dosing caused due to outage and maintenance of dosing plant. Predominantly bivalves have shown extreme tolerance towards biocidal dosings as they can close their valves and tide over unfavourable environments for long periods of times. Brief opening of valves results in ingress of water with biocides into the mantle cavity which initiates physiological stress leading to mortality. Usually mussels have been shown to grow up to sizes of ~120 mm in CWS. Susceptibilities of adult organisms to biocides are again dependent on size, physiological condition, etc.

Table 3 Concentration and time taken for mortality in adult fouling organisms found in industrial cooling water systems

Fouling organism	Biocidal action and conditions	References
Perna viridis	100% mortality of 12 mm (504 h) and 95 mm (816 h) at 1.0 ppm concentration of Cl_2 100% mortality of 12 mm (30) and 95 mm (48 hours) at 10.0 ppm concentration of Cl_2	Rajagopal et al. (1995)
Brachidontes striatulus	100% mortality of 7 mm (468 h) and 25 mm (570 h) at 1.0 ppm concentration of Cl_2 100% mortality of 7 mm (102 h) and 25 mm (156 h) at 5.0 ppm concentration of Cl_2	Rajagopal et al. (1997)
Dreissena polymorpha	Continuous dosing of 0.5 ppm of Cl_2 required for impairment of shell opening	Rajagopal et al. (2002a)
Mytilopsis leucophaeata	100% mortality of 2 mm (89 days) and 10 mm (109 days) at 0.25 ppm concentration of Cl_2	Rajagopal et al. (2002b)
Dreissena polymorpha	Mortality of attached mussels higher than unattached mussels. At 1.0 mg/L of Cl_2, attached mussels took 451 h for 50% mortality	Rajagopal et al. (2002c)
Cordylophora caspia	Cl_2 concentration of 0.1 mg/L decreased 23% of growth rate and 1.0 mg/L completely inhibited growth	Rajagopal et al. (2002d)
Dreissena polymorpha	100% mortality of 10 mm (1080 h) at 0.25 mg/L of Cl_2	Rajagopal et al. (2002e)
Brachidontes pharaonis	Supplementary biocides NALCO® 77,351 (30% mortality at 1000 mg/L), 73,532 (30% mortality at 1000 mg/L) and 73,503 (50% at 500 mg/L and 90% at 1000 mg/L) tested along with NaOCl	Garaventa et al. (2012)
Perna viridis	100% mortality of 3–4 cm (553 h) and 8–9 cm (588 h) at 0.7 mg/L of Cl_2 100% mortality of 3–4 cm (94 h) and 8–9 cm (114 h) at 9.1 mg/L of Cl_2	Masilamoni et al. (2002)
Perna perna	100% mortality of 9 mm (384 h) at 1.0 ppm and 84 h at 5.0 ppm of Cl_2 100% mortality of 9 mm (228 h) and 34 mm (304 h) at 5.0 ppm of Cl_2	Rajagopal et al. (2003b)
Brachidontes variabilis	100% mortality (288 h) at 1 mg/L of Cl_2	Rajagopal et al. (2003c)
Mytilus edulis	14 and 25 mm of H_2O_2 (1.0, 2.0, 3.0, 4.0 and 5.0 mg/L). 100% mortality was not reached up to 30-day exposure. 14 mm size reached 90%, whereas 25 mm reached 81% at 5.0 mg/L	Haque and Kwon (2016a)
Dreissena polymorpha	18 biocides tested, among which clam-Trol CT-1 showed more sensitivity to mussels	Waller et al. (1993)
Dreissena polymorpha	100% mortality at 5.0 mg/L (157 h) and 2.50 mg/L (264 h)	Martin et al. (1993)
Modiolus philippinarum	100% mortality at 1.0 mg/L of Cl_2 (402 h) and 5.0 mg/L (108 h)	Rajagopal et al. (2006)
Mytilus galloprovincialis	Sublethal concentrations of chlorine and Mexel ® 432 caused damage to gills	Lopez-Galindo et al. (2010)

7 Effect of Industrial CW Discharges on the Marine Environment

Coastal power plants abstract large amounts of surface seawater for condenser cooling purposes by once-through systems discharging the heated effluent back into the environment. In addition, power plant discharges contain residues of biocides dosed for biofouling control. The cooling water contains planktonic organisms (phyto- and zooplanktons), which are abstracted into the system and subjected to mechanical stress (hydraulic stresses at intake screens, strainers, pump impellers and screens and shear stress due to flow, turbulence and abrasion with walls of cooling system), chemical stress (biocides dosed for fouling control) and thermal stress (elevated temperatures on passage through the heat exchangers). The planktonic organisms are momentarily subjected to these stress factors and returned back to the environment. Such entrained planktonic organisms may either survive or succumb to these stress factors (Bamber and Turnpenny 2012; Lewis 2000). Another effect of entrainment is inhibition of photosynthesis by phytoplankton due to chlorination of CWS (Carpenter et al. 1972; Chuang et al. 2009). This may result in reduction of density of certain species in the receiving water bodies. Another effect of power plant intake system is impingement (Bruijs and Taylor 2012). The intake system has different sizes of coarse and fine mesh screens to prevent ingress of fish and other planktonic organisms which eventually are subjected to mechanical stress and damage by impingement on screens.

Apart from these, the significant impact on the receiving water body is caused by the thermal discharges from the power plant (IAEA 1974). Temperature is a vital limiting factor influencing biological organisms, and large thermal discharges affect the spawning and feeding behaviour, reproduction, growth, metabolism and community structure in marine organisms (Langford 1990; Jiang et al. 2009; Mazik et al. 2013). Effects of thermal discharges at spatial scales are classified into near, mid, and far field, whereas the point where the discharge actually meets the receiving water body is termed as the mixing point. Predominantly residues of oxidizing biocides are quenched before they reach the mixing point (Anupkumar et al. 2014). Similarly there have been observations of reduction in temperature when the discharges enter the mixing point. The impact of thermal discharges is directly felt by the intertidal flora and fauna occupying the sandy and rocky shores. The impact is severe on sessile organisms in rocky shores, whereas many of the macrobenthic organisms like the mole crab (*Emerita asiatica*) colonizing the sand beaches have an option to move away from the affected area (Israel et al. 2012). Thermal discharges have been reported to decrease benthic cover (Teixeira et al. 2012). Thermal impacts on planktonic larval forms have also been investigated. Early larval (41–43 h old) stages of the abalone *Haliotis rufescens* succumbed within 1-minute exposure to elevated temperatures of ΔT of 13.3 °C, whereas older larvae (61–63 h old) tolerated for 10 min (Adams and Price 1974). Similarly early larval cleavage stage of the clam *Mercenaria mercenaria* was more sensitive to short-term exposure to temperatures than the late trocophore stages (Kennedy 1974). Another study using barnacle nauplii exposed to 40 °C (ΔT of 12 °C) revealed 40% mortality in stage II nauplii, whereas no mortality was observed with stage VI nauplii (Thiyagarajan et al. 2000). These results point to the increase in thermal tolerance with increase in developmental stages. However, studies by Jiang et al. (2009) reported that the thermal tolerance of copepods increases with rising acclimation temperature.

Thermal tolerance of organisms is a result of long-term natural selection and evolution as a function of environment. Thermal acclimation and upper thermal limits of organisms are important parameters which need to be taken into consideration when stipulating thermal discharge regulations locally. In this context, Vinagre et al. (2019) have developed an indicator baseline of thermal limits for 42 coastal species as vulnerability of each species to warming is dependent on their thermal limits, acclimation response and genetic adaptation potential, which has not been worked out for majority of species (Somero 2010). In India, the CPCB (2010) has formulated a regulation for thermal discharges of coastal power stations stipulating a ΔT of 7 °C for power plants constructed after 1999 and a ΔT of 10 °C for existing power plants. Majority of thermal standards for transitional and coastal (TraC) waters have been adopted based on freshwater limits and have taken requirements of fish ignoring other local flora and fauna (Wither et al. 2012).

8 Conclusions

Thermal and nuclear plants and industries located in the coastal regions operate on a once-through mode, abstracting large volumes of surface seawater for condenser cooling, which is returned back to the water body. Such operations have the potential to cause environmental impacts, viz. (1) on the receiving water body by their discharges, (2) entrainment of organisms in the abstracted water and (3) impingement of organisms. Large seawater cooling systems operating in tropical countries are subjected to immense biofouling pressure. Cooling water discharges are characterized by elevated temperatures and biocidal residues. With increasing environmental awareness, several modifications to discharges have been tested, of which the model wherein the discharged water has been diverted into a culvert and undergoes a transit before it reaches the mixing point is more promising as it reduces the thermal and biocidal load. Environment and cost factors determine the choice of biocide and regime to be adopted. Oxidizing biocides are the most preferred and viable method for fouling control dosed either on a continuous or intermittent mode. The biocidal concentrations in CWS are regulated in many countries, within a range of 0.01–0.2 mg/L TRO, at outfall. Data from literature reveal that biocidal concentrations required to kill adults as well as prevent larval settlement are far higher than the discharge levels prescribed by regulatory bodies. In the current scenario, it is imminent that CWS have to live with certain levels of biofouling. Chlorine dioxide is replacing chlorine in many power stations due to its higher antifouling efficacy and environmentally friendly nature. As biofouling is a surface-associated phenomenon, use of surface protection in the form of antifouling coatings would minimize the biofouling load and thereby reduce biocidal inventory. Surface protection with foul release antifouling coatings and chlorine dioxide dosing seems an effective and environmentally benign option for CWS.

References

Abdel-Wahab A, Khodary A, Bensalah N (2010) Formation of trihalome thanes during seawater chlorination. J Env Protection 1:456–465

Adams JR, Price DG (1974) Thermal shock tolerance of larval Red Abalone (Haliotis rufescens) from Diablo Canyon, California. In: Adams JR, Hurley JF (eds) Environmental investigations at Diablo Canyon 1972–73. Pacific Gas and Electric, Department of Engineering Research, San Ramon, pp 155–175

Allonier AS, Khalanski M, Camel V, Bermond A (1999) Characterization of chlorination by-products in cooling effluents of coastal nuclear power stations. Mar Pollut Bull 38(12):1232–1241

Ambrogi R (1997) Environmental impact of biocidal antifouling alternative treatments on seawater once-through cooling systems. In: Chlorine dioxide and disinfection. Proceedings of First European symposium on chlorine dioxide and disinfection" Rome, Italy, 7–8 Nov 1996, Collana Ambiente vol 17 pp119–132

Anupkumar B, Rao TS, Venugopalan VP, Narasimhan SV (2014) Thermal mapping in the vicinity of an atomic power station. Indian Nuclear Society News 11(162):1–16

Arrhenius A, Backhaus T, Hilvarsson A, Wendt I, Zgrundo A, Blanck H (2014) A novel bioassay for evaluating the efficacy of biocides to inhibit settling and early establishment of marine biofilms. Mar Pollut Bull 87:292–299

Bamber RN, Turnpenny AWH (2012) Entrainment of organisms through power station cooling water systems. In: Rajagopal S, Jenner HA, Venugopalan VP, Khalanski M (eds) Operational and environmental consequences of large industrial cooling water systems. Springer, Boston, MA. https://doi.org/10.1007/978-1-4614-1698-2_10

Beauchamp RSA (1966) Low-level chlorination for the control of marine fouling C.E.G.B. Rep. No. Rd/L/M147

Behnke S, Camper AK (2012) Chlorine dioxide disinfection of single and dual species biofilms, detached biofilm and planktonic cells. Biofouling 28(6):635–647

Bernarde A, Israel BM, Livier VP, Grandstorm ML (1965) Efficiency of chlorine dioxide as a bactericide. Appl Microbiol 13:776–780

Bidwell JR, Cherry DS, Farris JL, Petrille JC, Lyons LA (1999) Effects of intermittent halogenation on settlement, survival and growth of the zebra mussel, Dreissena polymorpha. Hydrobiologia 394:13–62

Bott TR (1990) Fouling Notebook. The Institute of Chemical Engineers, Rugby, England

Bott TR, Tianqing L (2004) Ultrasound enhancement of biocide efficiency. Ultrason Sonochem 11:323–326

Bruijs CMM, Taylor CJL (2012) Fish impingement and prevention seen in the light of population dynamics. In: Rajagopal S, Jenner HA, Venugopalan VP, Khalanski M (eds) Operational and environmental consequences of large industrial cooling water systems. Springer, Boston. https://doi.org/10.1007/978-1-4614-1698-2_10

Burton DT, Margrey SL (1979) Control of fouling organisms in estuarine cooling water system by chlorine and bromine chloride. Environ Sci Technol 13(6):694–686

Busscher HJ, Bos R, van der Mei HC (1995) Initial microbial adhesion is a determinant for the strength of biofilm adhesion. FEMS Microbiol Lett 128:229–234

Carpenter EJ, Peck BB, Anderson SJ (1972) Cooling water chlorination and productivity of entrained phytoplankton. Mar Biol 16:37–40

Characklis WG (1990) Biofilm processes. In: Characklis WG, Marshall KC (eds) Biofilms. New York, John Wiley, pp 195–231

Chase AL, Dijkstra AJ, Harris LG (2016) The influence of substrate material on ascidian larval settlement. Mar Pollut Bull 106:35–42

Chelossi E, Faimali M (2006) Comparative assessment of antimicrobial efficacy of new potential biocides for treatment of cooling and ballast waters. Sci Total Environ 356:1–10

Chow W, Maulbetswch JS, Muddalli YG (1984) Biofouling control through targeted chlorination. Power Engineering October 38–41

Chua SL, Liu Y, Yam JKH, Chen Y, Vejborg RM, Tan BGC, Kjelleberg S, Tolker-Nielsen T, Givskov M, Yang L (2014) Dispersed cells represent a distinct stage in the transition from bacterial biofilm to planktonic lifestyle. Nat Commun 5:4462

Chuang YL, Yang HH, Lin HJ (2009) Effects of a thermal discharge from a nuclear power plant on phytoplankton and periphyton in subtropical coastal waters. J Sea Res 61:197–205

Cloete TE, Brozel VS, Holy A (1992) Practical aspects of biofouling control in industrial water systems. Int Biodeter Biodegr 29:299–341

Costerton JW, Geesey GG, Cheng KJ (1978) How bacteria stick. Sci Am 238:86–95. https://doi.org/10.1038/scientificamerican0178-86

Coughlan J, Whitehouse J (1977) Aspects of chlorine utilization in the United Kingdom. Chesapeake Sci 18(1):102–111

CPCB PCLS/02/2010: Temperature Limit for Discharge of Condenser Cooling Water from Thermal Power Plants (Source: Sixth Edition) pp 50

Crisp DJ (1984) Overview of research on marine invertebrate larvae. 1940–1980. In: Costlow JD, Tipper RC (eds) Marine biodeterioration: an interdisciplinary study. Naval Institute Press, Annapolis, pp 103–126

Dang H, Lovell CR (2000) Bacterial primary colonization and early succession on surfaces in marine waters as determined by amplified rRNA gene restriction analysis and sequence analysis of 16S rRNA genes. Appl Environ Microbiol:467–475

de Carvalho CCR (2018) Microbial biofilms a successful strategy with economic implications. Front Mar Sci 5:126. https://doi.org/10.3389/fmars.2018.00126

Dobbs MG, Cherry DS, Scott JC, Petrille JC (1995) Environmental assessment of an alkyl dimethyl benzyl ammonium chloride based molluscicides using laboratory tests. In: Fifth international zebra mussel and aquatic nuisance organism's conference. Toronto ON 21–24

Dobretsov S, Rittschof D (2020) Love at first taste: induction of larval settlement by marine microbes. Int J Mol Sci 731. https://doi.org/10.3390/ijms21030731

Dobretsov S, Dahms HU, Qian PY (2006) Inhibition of biofouling by marine microorganisms and their metabolites. Biofouling 22:43–54

Donlan RM, Costerton JW (2002) Biofilms: survival mechanisms of clinically relevant microorganisms. Clin Microbiol Rev 15:167–193

Duncan G, Waugh (1964) Observation on the effects of chlorine on the larvae of oysters Ostrea edulis (L) and barnacles Elminius modestus (Darwin). Ann Appl Rid 54:423–440

Electric Power Research Institute (EPRI) and Department of Energy (DOE) (1997) Renewable energy technology characterizations. EPRI, Palo Alto

Ells V, Filip N, Bishop CD, Demont ME, Smith-Palmer T, Wyeth RC (2016) A true test of colour effects on marine invertebrate larval settlement. J Exp Mar Biol Ecol 483:156–161

EPRI (Electric Power Research Institute (2015) Power plant cooling system overview. Guidance for Researchers and Technology Developers, Palo Alto, p 300200194

Flemming HC (2016) EPS – then and now. Micro-organisms 4:41. https://doi.org/10.3390/microorganisms404004

Flemming HC, Wingender J (2010) The biofilm matrix. Nat Rev Microbiol 8:623–633. https://doi.org/10.1038/nrmicro2415

Garaventa F, Corra C, Piazza V, Giacco E, Greco G, Pane L, Faimali M (2012) Settlement of the alien mollusc Brachidontes pharaonis in a Mediterranean industrial plant: bioassays for antifouling treatment optimization and management. Mar Environ Res 76:90–96

Gosselin LA, Qian PY (1997) Juvenile mortality in benthic marine invertebrates. Mar Ecol Prog Ser 146:265–282

Haag WR, Holgna J (1983) Ozonation of bromide-containing waters: kinetics of formation of hypobromous acid and bromate. Environ Sci Technol 17(5):281–287

Hadfield M, Paul V (2001) Natural chemical cues for settlement and metamorphosis of marine invertebrate larvae. In: McClintock J, Baker B (eds) Marine chemical ecology, vol 20015660. CRC Press, Boca Raton, pp 431–461. ISBN 978-0-8493-9064-7

Haque MN, Kwon S (2016a) Physiological effects of biocide on marine bivalve blue mussels in context prevent macrofouling. Journal of Ecology and Environment 40(16). https://doi.org/10.1186/s41610-016-0015-y

Haque NM, Kwon S (2016b) Effects of ultrasonication and its use with sodium hypochlorite as antifouling method against Mytilus edulis larvae and mussel. Environ Geochem Health. https://doi.org/10.1007/s10653-016-9894-1

Haque N, Cho D, Lee JM, Lee DS, Kwon S (2014) Proactive approach for biofouling control: consequences of chlorine on the veliger larvae of Mytilus edulis under laboratory conditions. Environ Eng Res 19(4):375–380

IAEA (1974) Thermal discharges at nuclear power stations: their management and environmental impacts. International Atomic Energy Agency, Vienna. Technical report series no.155

Ibrahim SMA, Attia SI (2015) The influence of condenser cooling seawater fouling on the thermal performance of a nuclear power plant. Ann Nucl Energy 76:421–430

Israel S, Satheesh R, Venugopalan VP, Munuswamy N, Subramoniam T (2012) Impact of power plant discharge on intertidal fauna. In: Rajagopal S, Jenner HA, Venugopalan VP, Khalanski M (eds) Operational and environmental consequences of large industrial cooling water systems. Springer, Boston. https://doi.org/10.1007/978-1-4614-1698-2_10

James WG (1967) Mussel fouling and use of exomotive chlorination. Chem Ind:994–996

Jang A, Scabo J, Hosni AA, Coughlin M, Bishop PL (2006) Measurement of chlorine dioxide penetration in dairy process pipe biofilms during disinfection. Appl Microbiol Biotechnol 72:368–376

Jenkins SR (2005) Larval habitat selection, not larval supply, determines settlement patterns and adult distribution in two chthamalid barnacles. J Anim Ecol 74:893–904

Jenner HA, Taylor CJL, van Donk M, Khalanski M (1997) Chlorination by-products in chlorinated cooling water of some European coastal power stations. Mar Environ Res 43(4):279–293

Jenner HA, Whitehouse JW, Taylor CJL, Khalanski M (1998) Cooling water management in European power stations: biology and control of fouling. Hydroecol Appl 10:1–225

Jiang Z, Zeng J, Chen Q, Huang Y, Liao Y, Xu X, Zheng P (2009) Potential impact of rising seawater temperature on copepods due to coastal power plants in subtropical areas. J Exp Mar Biol Ecol 368:196–201

Jolley RL, Condie LW, Johnson JD, Katz S, Minear RA, Mattice JS, Jacobs VA (1990) Water chlorination: chemistry environmental impact and health effects, vol 6. Lewis Publishers Inc., Michigan. 1023pp

Kennedy VS, Roosenberg WH, Castanga M, Mihursky JA (1974) Mercenaria mercenaria (Mollusca: Bivalvia): temperature-time relationships for survival of embryos and larvae. US Fish Bull 72:1160–1166

Keough MJ, Downes BJ (1982) Recruitment of marine invertebrates: the role of active larval choices and early mortality. Oecologia 54:348–352

Khalanski M, Bordet F (1980) Effects of chlorination on marine mussels. In: Jolly RL, Brungs WA, Cumming RB (eds) Water chlorination chemistry environmental impact and health effects, vol 3. Ann Arbor Science, Ann Arbor, pp 557–567

Krammer JF (1997) Peracetic acid a new biocide for industrial water applications. MP August 42–50

Krzeminski SF, Brackett CK, Fisher JD (1975) Fate of microbiocidal 3-isothiazolone compounds in the environment modes and rates of dissipation. J Agric Food Chem 23:1068–1075

Langford TEL (1990) Ecological effects of thermal discharges. Elsevier Applied Science, London pp 28–103

Lappin-Scott HM, Costerton JM (1989) Bacterial biofilms and surface fouling. Biofouling 1:323–342

Lewis BG (1985) Mussel control and chlorination CERL Report NO TPRD/L/2810/R83

Lewis K (2001) Riddle of biofilm resistance. Antimicrob Agents Chemother 45:999–1007

Lewis RB, Seegert G (2000) Entrainment and impingement studies at two power plants on the Wabash River in Indiana. Environ Sci Policy 3:S303–S312

Little BJ, Wagner PA (1997) In: Nagabhushanam R, Thompson MF (eds) "Succession in microfouling" in fouling organisms in the Indian Ocean: biology and control technology. AA Balkema Publishers 548, Rotterdam

Liu F, Change X, Yang F, Wang Y, Wang F, Dong W, Zhao C (2011) Effect of oxidizing and non-oxidizing biocides on biofilm at different substrate levels in the model recirculating cooling water system. World J Microbiol Biotechnol:2989–2997

Lopez-Galindo C, Chacoff LV, Nebot E, Casanueva JF, Rubio D, Mancera JM, Sole M (2010) Sublethal responses of the common mussel (Mytilus galloprovincialis) exposed to sodium hypochlorite and Mexel® 432 used as antifoulants. Ecotoxicol Environ Saf 73:825–834

Ludensky M (2003) Control and monitoring of biofilms in industrial applications. Int Biodeter Biodegr 51:255–263

Marshall KC (1985) Mechanisms of bacterial adhesion at solid-water interfaces. In: Savage DC, Fletcher M (eds) Bacterial adhesion. Plenum Press, New York, pp 133–161

Marshall KC (1992) Biofilms: an overview of bacterial adhesion, activity, and control of surfaces. ASM News 58:202–207

Martin ID, Mackie GL, Baker MA (1993) Control of the biofouling Mollusc, Dreissena polymorpha (Bivalvia: Dreissenidae), with sodium hypochlorite and with Polyquaternary ammonia and Benzothiazole compounds. Arch Environ Contam Toxicol 24:381–388

Masilamoni G, Jesudoss KS, Nandakumar K, Satpathy KK, Azariah J, Nair KVK (2002) Lethal and sub-lethal effects of chlorination on green mussel Perna viridis in the context of biofouling control in a power plant cooling water system. Mar Environ Res 53:65–76

Mazik K, Hitchman N, Quintino V, Taylor CJL, Butterfield J, Elliott M (2013) Sublethal effects of a chlorinated and heated effluent on the physiology of the mussel, Mytilus edulis L: a reduction in fitness for survival. Marine Pollution Bulletin, pp 123–131

Morton LHG, Greenway DLA, Gaylarde CC Surman SB (1998) Consideration of some implications of the resistance of biofilms to biocides. Int Biodeter Biodegr 41:247–259

Moshchenko AV, Zvyagintsev AY (2010) Macrofouling communities in the cooling system of the Vladivostok heat and power plant. Ocean Sci J 45(1):41–54

Murthy PS, Venkatesan R (2008) Industrial biofilms and their control. In: Flemming H-C, Murthy PS, Venkatesan R, Cooksey K (eds) Marine and industrial biofouling, Springer series on biofilms. Springer Verlag, Berlin, Heidelberg, pp 265–292. https://doi.org/10.1007/7142-2008-14

Murthy PS, Venkatesan R, Nair KVK, Inbakandan D, Syed Jahan S, Magesh Peter D, Ravindran M (2005) Evaluation of sodium hypochlorite for fouling control in plate heat exchangers for seawater application. Int Biodeter Biodegr 55:161–170

Murthy PS, Venugopalan VP, Nair KVK, Subramoniam T (2008) Larval settlement and surfaces: implications in development of antifouling strategies. In: Flemming H-C, Murthy PS, Venkatesan R, Cooksey K (eds) Marine and industrial biofouling, springer series on biofilms. Springer Verlag, Berlin, Heidelberg, pp 265–292. https://doi.org/10.1007/7142-2008-14

Murthy PS, Veeramani P, Mohamed Ershath MI, Venugopalan VP (2011) Biofouling evaluation in the seawater cooling circuit of an operating coastal power plant. Power Plant Chem 13(6):314–319. ISBN 978-1-926773-00-1; TRN:CA1500244102444

Mussalli YG (1985) Condenser-targeted chlorination design. Final report United States

Neitzel DA, Johnson KI, Page TL, Young JS, Daling PM (1984) Correlation of bivalve biological characteristics and service water system design. In: Bivalve fouling of nuclear power plant service water systems. US nuclear regulatory commission. Report No NUREG/CR-4070, Washington DC. 119 pg

NRDC (2014) Power Plant Cooling and Associated Impacts: The need to modernize U.S. Power Plants and protect our Water Resources and Aquatic Ecosystems. IB: 14–04-C www.nrdc.org/policy

O'Hagan J, Birkinshaw K, Masri M, Therkelsen RL (2004) The formation and fate of trihalomethanes in power plant cooling water systems. Palo Alto: Electric Power Research Institute; Consultant report no 500-04-035

Padhi RK, Subramanian S, Mohanty AK, Bramha SN, Prasad MVR, Satpathy KK (2012) Trihalomethanes in the cooling discharge of a power plant on chlorination of intake seawater environmental. Res Eng Des 17(S1):S57–S62. https://doi.org/10.4491/eer.2012.17.s1.s57. pISSN1226-1025 eISSN2005-968X

Patil JS, Jagadeesan V (2011) Effects of chlorination on the development of marine biofilms dominated by diatoms. Biofouling 27(3):241–254

Petrille JC, Werner MW (1993) A combined treatment approaches using a nonoxidizing molluscicide and heat to control zebra mussels. In: Third international zebra mussel conference. Toronto, ON 23–26

Polman HJG, Jenner HA (2002) Pulse-chlorination, the best available technique in macrofouling mitigation using chlorine. Power Plant Chem 4:93–97

Rajagopal S, Venugopalan VP, Nair KVK, Azariah J (1991) Biofouling problems and its control in a tropical coastal power station – a case study. Biofouling 3:325–338

Rajagopal S, Venugopalan VP, Nair KVK, Azariah J (1995) Response of green mussel Perna viridis (L) to chlorine in the context of power plant biofouling control. Mar Freshw Behav Physiol 25:261–274

Rajagopal S, Nair KVK, Van der Velde G, Jenner HA (1997) Seasonal settlement and succession of fouling communities in Kalpakkam east coast of India. Neth J Aquat Ecol 30:309–325

Rajagopal S, der Velde V, der Gaag V, Jenner HA (2002a) Sublethal responses of zebra mussel Dreissena polymorpha to low-level chlorination: an experimental study. Biofouling 19(2):95–104

Rajagopal S, der Gaag V, van der Velde G, Jenner HA (2002b) Control of brackish water fouling mussel, Mytilopsis leucophaeata (Conrad), with sodium hypochlorite. Arch Environ Contam Toxicol 43:296–300

Rajagopal S, Van der Velde G, Jenner HA (2002c) Does status of attachment influence survival time of zebra mussel Dreissena polymorpha exposed to chlorination. Environ Toxicol Chem 21(2):342–346

Rajagopal S, Van der Velde G, der Gaag V, Jenner HA (2002d) Laboratory evaluation of the toxicity of chlorine to the fouling hydroid Cordylophora caspia. Biofouling 18(1):57–64

Rajagopal S, Van der Velde G, Jenner HA (2002e) Effects of low-level chlorination on zebra mussel, Dreissena polymorpha. Water Res 36:3029–3034

Rajagopal S, Van der Welde G, Van der Garg M, Jenner HA (2003a) How effective is intermittent chlorination in control of adult mussel fouling in cooling water systems. Water Res 37:329–338

Rajagopal S, Venugopalan VP, Van der Velde G, Jenner HA (2003b) Tolerance of five species of tropical marine mussels to continuous chlorination. Mar Environ Res 55:277–291

Rajagopal S, Venugopalan VP, van der Velde JHA (2003c) Response of fouling brown mussel, Perna perna (L), to chlorine. Arch Environ Contam Toxicol 44:369–376

Rajagopal S, Venugopalan VP, van der Velde JHA (2006) Control of Modiolid mussels in cooling water systems by continuous chlorination. Arch Environ Contm Toxicol 51:215–222

Rajagopal S, Jenner HA, Venugopalan VP, Khalanski M (2012a) Biofouling control: alternatives to chlorine. In: Operational and environmental consequences of large industrial cooling water systems. Springer, pp 227–271. https://doi.org/10.1007/978-1-4614-1698-2_10

Rajagopal S, Jenner HA, Venugopalan VP, Khalanski M (2012b) Biofouling control: alternatives to chlorine. In: Rajagopal S, Jenner HA, Venugopalan VP, Khalanski M (eds) Operational and environmental consequences of large industrial cooling water systems. Springer, Boston. https://doi.org/10.1007/978-1-4614-1698-2_10

Rajamohan R, Vinnitha E, Venugopalan VP, Narasimhan SV (2007) Chlorination by-products in the cooling water system of a coastal electric plant. Curr Sci 93:1608–1612

Rajamohan R, Venugopalan VP, Natesan U (2016) Chlorine dioxide as antifouling biocide results in reduced trihalomethanes in condenser effluents at a coastal power station. Indian J of Geo Marine Science 45(12):1638–1644

Rajitha K, Nancharaiah YV, Venugopalan VP (2020) Insight into bacterial biofilm-barnacle larvae interactions for environmentally benign antifouling strategies. Int Biodeter Biodegr 149:104937

Roberts D, Rittschof D, Holm E, Schmidt AR (1991) Factors influencing initial larval settlement: temporal spatial and surface molecular components. J Exp Mar Biol Ecol 150:203–211

Rodriguez SR, Ojeda FP, Inestrosa NC (1993) Settlement of benthic marine invertebrates. Mar Ecol Prog Ser 97:193–207

Rollet C, Gal L, Guzzo J (2009) Biofilm-detached cells, a transition from a sessile to a planktonic phenotype: a comparative study of adhesion and physiological characteristics in Pseudomonas aeruginosa. FEMS Microbial Letters 290:135–142

Rubio D, Lopez-Galindo C, Casanueva JF, Nebot E (2014) Monitoring and assessment of an industrial antifouling treatment seasonal effects and influence of water velocity in open once-through seawater cooling system. Appl Therm Eng 67:378–387

Rubio D, Casanueva JF, Nebot E (2015) Assessment of the antifouling effect of five different treatment strategies on a seawater cooling system. Appl Therm Eng 85:124–134

Rumbaugh KP, Sauer K (2020) Biofilm dispersion. Nat Rev Microbiol. https://doi.org/10.1038/s41579-020-0385-0

Schneider R (1997) Generation of chlorine dioxide. In: Proceedings of "First European symposium on chlorine dioxide and disinfection" Rome, Italy 7–8 Nov 1996. Collana Ambiente 17:27–37

Simon XE, Berdalet E, Gracia FEF, Llorens J (2014) Seawater disinfection by chlorine dioxide and sodium hypochlorite. A comparison of biofilm formation. Water Air Soil Pollut 225:1921

Somero GN (2010) The physiology of climate change: how potentials for acclimation and genetic adaptation will determine winners and losers. J Exp Biol 213:912–920

Song L, Wu J, Xi C (2012) Biofilms on environmental surfaces: evaluation of the disinfection efficacy of a novel steam vapour system. American J of Infection control:1–5

Stewart PS, Franklin MJ (2008) Physiological heterogeneity in biofilms. Nat Rev Microbiol 6:199

Stoodley P, Sauer K, Davies DG, Costerton JW (2002) Biofilms as complex differentiated communities. Annu Rev Microbiol 56:187–209

Stoodley HL, Costerton JW, Stoodley P (2004) Bacterial biofilms: from the natural environment to infectious diseases. Nat Rev Microbiol 2:95–108. https://doi.org/10.1038/nrmicro821

Teixeira TP, Neves LM, Araiijo FG (2012) Thermal impact of a nuclear power plant in a coastal area in South-Eastern Brazil: effects of heating and physical structure on benthic cover and fish communities. Hydrobiologia 684:161–175

Thiyagarajan V, Nancharaiah YV, Venugopalan VP, Nair KVK, Subramoniam T (2000) Relative tolerance of cirripede larval stages to acute thermal shock: a laboratory study. J Thermal Biology 25:451–457

Thompson JS, Seed R, Richardson CA, Huf L, Walker G (1997) Effects of low level chlorination on the recruitment behaviour and shell growth of Mytilus edulis Linnaeus in power station cooling water. Sci Mar 61(2):77–85

Thompson JS, Richardson CA, Seed R, Walker G (2000) Quantification of mussel (Mytilus edulis) growth from power station cooling waters in response to chlorination procedures. Biofouling 16(1):1–15

Turchi C, Wagner M, Kutscher C (2010) Water use in parabolic trough power plants: summary results from WorleyParsons' analyses. National Renewable Energy Laboratory, Golden

Turnpenny AWH, Coughlan J, Ng B, Crews P, Bamber RN, Rowles P (2010) Cooling water options for the new generation of nuclear power stations in the UK SC070015/SR3 Environment Agency, Rio House, Waterside Drive Bristol BS324UD ISBN: 978-1-84911-192-8

Turnpenny AWH, Bruijs CMM, Wolter C, Edwards N (2012) Regulatory aspects of choice and operation of large scale cooling systems in Europe. In: Rajagopal S, Jenner HA, Venugopalan VP, Khalanski M (eds) Operational and environmental consequences of large industrial cooling water systems. Springer, Boston. https://doi.org/10.1007/978-1-4614-1698-2_10

Van Benschoten JE, Jensen JN, Brady TJ, Lewis DP, Sferrazza J, Neuhauser EF (1993) Response of zebra mussel veligers to chemical oxidants. Water Res 27(4):575–582

Van Loosdrecht MCM, Picioreanu C, Heijnen JJ (1997) A more unifying hypothesis for the structure of microbial biofilms. FEMS Microb Ecol 24:181–183

Vannomi M, Creach V, Barry J, Sheahan (2018) Chlorine toxicity to Navicula pelliculosa and Achnanthes spp. in a flow-through system: the use of immobilised microalgae and variable chlorophyll fluorescence. Aquat Toxicol 202 pg 80–89

Venkatesan R, Murthy PS (2008) Macrofouling control in power plants, In: Marine and Industrial Biofouling (eds) Flemming, H.C., Murthy P.S., Venkatesan, R., Cooksey K., Springer Series on Biofilms 4:265–291

Venkatnarayanan S, Murthy PS, Kirubagaran R, Venugopalan VP (2016a) Effect of chlorination on barnacle larval stages: implications for biofouling control and environmental impact. Int Biodeter Biodegr 109:141–149

Venkatnarayanan S, Murthy PS, Nancharaiah YV, Kirubagaran R, Venugopalan VP (2016b) Chlorination induced damage and recovery in marine diatoms: assay by SYTOX(R) green staining. Mar Pollut Bull. https://doi.org/10.1016/j.marpolbul.2016.12.059

Venkatnarayanan S, Murthy PS, Kirubagaran R, Venugopalan VP (2017) Chlorine dioxide as an alternative antifouling biocide for cooling water systems: toxicity to larval barnacle Amphibalanus reticulatus (Utinomi). Mar Pollut Bull. https://doi.org/10.1016/j.marpolbul.2017.01.023

Venugopalan VP (2018) Industrial seawater cooling systems under threat from the invasive green mussel Perna viridis. ASEAN J Sci & Technol Develop 35(1–2):65–69

Venugopalan VP, Narasimhan SV (2008) Operational and environmental issues in cooling water treatment: two sides of same coin? Water Digest 11:12–21

Vinagrea C, Diasa M, Cerejaa R, Abreu-Afonsoa F, Floresc AAV, Mendoncaa V (2019) Upper thermal limits and warming safety margins of coastal marine species-indicator baseline for future reference. Ecol Indic 102:644–649

Wahl M (1989) Marine epibiosis. I. Fouling and antifouling: some basic aspects. Mar Ecol Prog Ser 58:175–189. https://doi.org/10.3354/meps058175

Waller DL, Jeffrey J, Rach W, Cope G, Marking LL (1993) Toxicity of candidate molluscicides to zebra mussels (Dreissena polymorpha) and selected nontarget organisms. J Great Lakes Res 19(4):695–702

WHOI (1952) Marine fouling and its prevention. United states Naval Institute, Annapolis, p 388

Wieczorek SK,Todd CD (1998) Inhibition and facilitation of settlement of epifaunal marine invertebrate larvae by microbial biofilm cues, Biofouling: The Journal of Bioadhesion and Biofilm Research, 12:1–3, 81–118. https://doi.org/10.1080/08927019809378348

Wither A, Bamber R, Colclough S, Dyer K, Elliott M, Holmes P, Jenner H, Taylor C, Turnplenny A (2012) Setting new thermal standards for transitional and coastal (TraC) waters. Mar Pollut Bull 64:1564–1579

Zobell CE (1943) The effect of solid surfaces upon bacterial activity. J Bacteriol 46:39–56

Part II

Monitoring of Organic Micropolluntants and Their Associated Risks

Fate, Transport, and Effects of Pharmaceuticals and Personal Care Products in Urban Environment

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Abstract In the race of technological advancement for better health and better lifestyle, research has founded a strong base to bring out new antibiotics, vaccines, generic medications, and personal care products (PCPs) for the people. On the other hand, the risk and effects concerning residues of pharmaceuticals and personal care products (PPCPs) in the urban environment are a vital challenge to combat. The biotic components of the environment are most vulnerable to the impacts induced by PPCPs. Though the PPCPs are detected in the range of nanograms per liter to micrograms per liter in water, air, and soil, they are potential endocrine disruptors and carcinogens, environmentally persistent, and hostile. Correlations between urban lifestyles, healthcare infrastructures, and PPCPs clearly pose threatening images on the fate, transport, and effects of PPCPs. Hence, this chapter individually focuses on the origin of PPCPs in the environment, the fate and transport of PPCPs

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in urban environment, and eco-toxicological impacts on aquatic and human genera by providing strong evidence and finally presents the prospective on PPCPs and plausible future trends in urban environments.

Keywords PPCPs · Wastewater · Antibiotics · Urban environments · Fate and transport

1 Introduction

Water is the most vital element needed for the existence of life and to maintain the equilibrium of the ecosystem. Today, the world is witnessing exponential increase of industries, population, and cultivation which have created stress on the water. On the other hand, the world is faced with the challenge of managing wastewater. Now, we see the paradigm shift in the concern for conventional water quality parameters like organic load, turbidity, total solids, and heavy metals and physical parameters like odor, color, and pH to micropollutants, pharmaceuticals, and personal care products (PPCPs) (Jurado et al. 2012). The receiving water bodies have become intolerant owing to the large quantities of untreated or partially treated wastewater released back in them that comprise higher levels of complex and unknown chemicals that are pseudo-persistent in such environments. Hence, it is imperative to address the complex mixtures of toxins and contaminants for a sustainable future. The above stated "complex and unknown chemicals" are mostly different compounds derived from products used in our day-to-day lives. These contaminants are collectively called CECs; these are being detected frequently and have serious eco-toxic effects (Xu et al. 2019). There are a number of studies conducted on CECs worldwide, yet the majority of studies are the cases of developed countries. These primary studies aimed at quantification and few of in vitro studies to showcase ill effects on humans and aquatic species. Therefore, there is a lack of information related to the behavior of each CECs in different environment matrices. Also, no established fate is known for which the extent of effects induced are unexposed. The aftermaths of CECs are under scrutiny, and the statistics on CECs analyzed from 2002 to 2011 conclude that >50% of the chemicals produced come under the environmentally unsafe category, and > 70% among these chemicals have direct environmental impacts (Gavrilescu et al. 2015). Moreover, the pace of research focusing the identification and establishing their environmental fate and removal is sorely slower than their usage and discharge.

Hence, this chapter attempts to discuss the significant information on fate, transport, and effects of PPCPs in urban environments. Specifically, literature-based findings and inferences quoted in this chapter are substantiated by providing examples. It is anticipated that the information on PPCPs will motivate the readers to take up studies that would focus on life cycle assessment of particular PPCPs where its origin to removal strategies would be illustrated.

1.1 PPCPs as one of the CECs

As time progresses, several new medications and personal care products are introduced to markets for protection and better lifestyle of people, respectively (Harikaranahalli Puttaiah et al. 2020). The pharma-patient transactions today is like selling a lifestyle rather than protection against diseases. Parallel to this, people relentlessly use products like perfumes, sunscreens, and cosmetics in their daily routine (Eregowda and Mohapatra 2020). The term PPCPs is coined to collectively tag pharmaceuticals (compounds/ingredients) and personal care products (compounds/ingredients). PPCPs are a varied cluster of chemicals that comprise prescription and non-prescription drugs, veterinary medicines, dietary supplements, diagnostic mediators, and a large range of consumer products such as fragrances, musks, sunscreens, stimulants, and cosmetics (Priyanka and Mohapatra 2020; Dubey et al. 2021). Due to their ubiquitous usage and consumption, PPCPs are released into natural water components by anthropogenic deeds such as wastewater transmission and treatment, domestication of animals, application of fertilizers, landfill leachate, etc. (Menon et al. 2020). Further, they readily enter the surface and groundwater with an average concentration of ng/L to mg/L. It is noteworthy that continuous exposure to PPCPs could cause ill effects on non-target organisms and induce detrimental effects on humans and ecosystems (Sui et al. 2015). The probable reasons behind considering PPCPs as a principal CECs are regularly occurring sources of chemicals from commonly used personal products and medicines, ever growing demand of personal and medical goods, continuous use of such supplies leading to continuous release and accumulation of parent and its moieties in the environment, and anticipated ecological hindrance targeting aquatic and human species due to its presence in surface and sub-surface water bodies (Jelić et al. 2012). Further, it is necessary to distinguish between pharmaceuticals and personal care products to apprehend their unique characteristics which label them as paramount CECs.

1.1.1 Pharmaceutical Contaminants

Person's instinct for a cure is very obvious, which is mostly brought from pharmaceutical compounds. Pharmaceuticals are defined as prescription, non-prescription, and veterinary drugs used against infectious and non-infectious diseases on humans and animals (Boxall et al. 2012). Today, the consumption of a wide variety of drugs and its subsequent discharge into wastewater streams has given enough platform for these pharmaceuticals to manifest so as to cause a negative impact on health and ecosystem. Below are some vital categories of pharma compounds that are known to cause serious imbalances in humans and non-target organisms (Leng et al. 2020).

- Antibiotics.

Complex biomolecules that stimulate growth and targets inactivation of pathogens (Mohapatra et al. 2018). Some of the antibiotics, which are commonly detected in the environment, are amoxicillin, erythromycin, ciprofloxacin, penicillin, etc.

- Estrogens and Other Hormones.

Compounds that mediate growth and physical development in all the living species. They are also labelled as endocrine-disrupting compounds (EDCs) accounting its adverse effects that alter endocrine functioning in organisms. Commonly detected hormones are estrogen, estriol, and estrone, labelled as natural hormones, while 17α-ethinylestradiol and associated moieties are synthetic ones (Menon et al. 2020).

- Nonsteroidal Anti-inflammatory Drugs (NSAIDs).

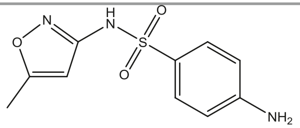
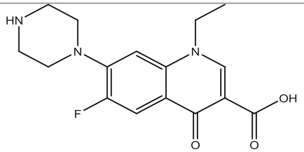
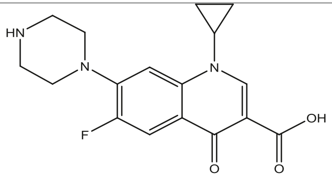
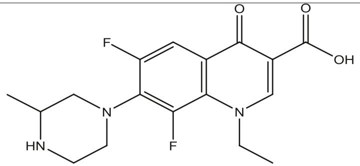
NSAIDs have a subset of prescription and non-prescription medicines belonging to analgesics, antipyretics, or anti-inflammatory types (Menon et al. 2020). For example, aspirin, ketoprofen, ibuprofen, naproxen, paracetamol, diclofenac, mefenamic acid, etc. are the frequently detected NSAIDs.

Apart from these three categories, there are numerous other classifications of drugs like beta-blockers, lipid regulators, contraceptives, antidepressants, biomarkers, etc. (Priyanka and Mohapatra 2020).

1.1.2 Personal Care Products

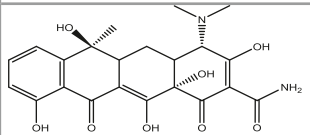
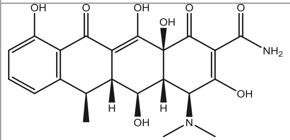
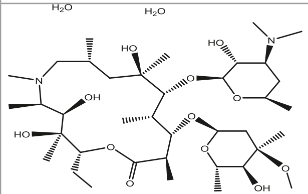
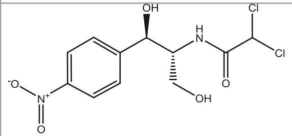
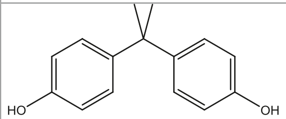
Personal care products largely comprise all synthetic agents or chemicals that we use in our daily routine ranging from soaps and detergents, perfumes and fragrances, antimicrobials and disinfectants, sunscreens and lotions, food and dietary supplements, and other maintenance products (Dubey et al. 2021). The usage of these compounds has tremendously increased for quick and promising actions. In addition, these products aim at cleanliness or hygiene that results in improved life expectancy. In contrast, some of these chemicals induce subtle changes in population when present in different media, for which they are considered as a pollutant. Typical examples of personal care products causing environmental impacts are nitro musks and polycyclic musks (fragrances) which are present in perfumes, soaps and shampoos, lotions and creams (cosmetics), insect repellents, sunscreens, detergents, and cleaning agents, etc. Other personal care products are saccharin and sucralose used as artificial sweeteners, triclosan used as bactericide in wide variety of healthcare products, Benzophenone-3 and Benzophenone-2, which are most common UV-filter used in sunscreens and other cosmetics, etc. The list of personal care products that belong to CECs is exhaustive. One such definitive list that covers most of PPCPs is the NORMAN list (NORMAN NETWORK, 2016). Table 1 presents a broad view of different PPCPs along with their characteristics.

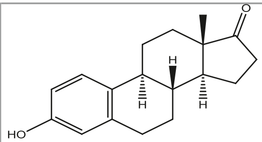
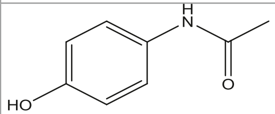
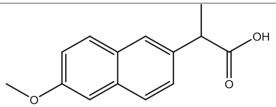
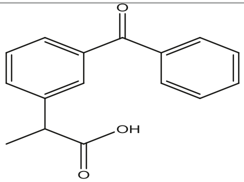
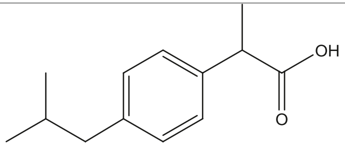
Table 1 General characteristics of important PPCPs

Compound	Structure	Accessed from: PubChem®, National Library of Medicine, USA				Mean concentration (ng/L) Xu et al. (2019)
		pKa	LogK$_{ow}$	m/z (top peak)	Solubility (in water)	
Sulfamethoxazole		5.7	0.89	156	610 mg/L at 37 °C	2.92
Norfloxacin		6.32	0.46	276	0.28 mg/mL at 25 °C	4.07
Ciprofloxacin		6.09	0.28	288	30,000 mg/L at 20 °C	107.19
Lomefloxacin		5.64	−0.23	308.1	6 mg/mL at 25 °C	212

(continued)

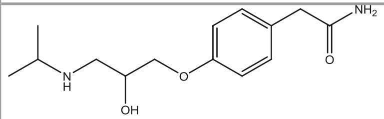
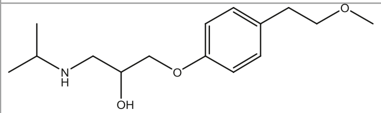
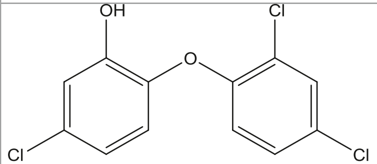
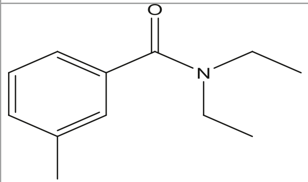
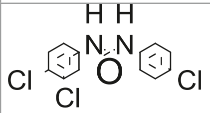
Table 1 (continued)

		Accessed from: PubChem®, National Library of Medicine, USA				
Compound	Structure	pKa	LogK$_{ow}$	m/z (top peak)	Solubility (in water)	Mean concentration (ng/L) Xu et al. (2019)
Tetracycline		3.3	−1.37	426	231 mg/l at 25 °C.	2.61
Doxycycline		3.09	−0.02	428	50 mg/ml	6.24
Azithromycin		8.5	4.02	592.4	2.37 mg/L at 25 °C	12.01
Chloramphenicol		7.49	1.14	159	2.5 mg/mL at 25 °C	0.58
Bisphenol A		9.6	3.32	201.07	300 mg/L at 25 °C	332.75

Estrone		10.33	3.13	271	0.003 g/100 mL at 25 °C	2.76
Paracetamol		−4.4	0.46	110	14,000 mg/L at 25 °C	18.73
Naproxen		4.15	3.8	231	15.9 mg/L at 25 °C	15.88
Ketoprofen		4.45	3.12	209	51 mg/L at 22 °C	9.05
Ibuprofen		5.3	3.97	161	21 mL/l at 25 °C	11.38

(continued)

Table 1 (continued)

Compound	Structure	Accessed from: PubChem®, National Library of Medicine, USA				Mean concentration (ng/L) Xu et al. (2019)
		pKa	LogK_{ow}	m/z (top peak)	Solubility (in water)	
Atenolol		9.6	0.16	225	26.5 mg/mL at 37 °C	0.35
Metoprolol		9.7	1.88	191.1	1000 mg/mL at 25 °C	3.08
Triclosan		7.9	4.76	141.98	10 mg/L at 20 °C	3.72
Diethyltoluamide		−0.95	2.02	119	912 mg/L at 25 °C	19.72
Triclocarban		12.7	4.342	127	0.11 mg/L at 20 °C	7.83

1.2 A Global PPCP Lookout

Understanding the global status of PPCP contamination is very important to develop a sustainable management framework today. The environmental contamination by various CECs especially PPCPs is considered as a chief indicator of pollution (Kümmerer 2003). For decades, every national and international environmental agency has defined water quality based on microbes, nutrient (nitrogen (N), phosphorus (P), and potassium (K)) load, and heavy metal occurrences. These traditional quality parameters are expressed in terms of biochemical oxygen demand (BOD), chemical oxygen demand (COD), dissolved and suspended solids, and physical aspects like odor, color, etc. Also, the discharge standards and limits are prescribed. However, no proper worldwide regulations are set for micropollutants like CECs. In the late 1990s, The European Union (EU) and United States Environmental Protection Agency (US EPA) identified and developed a watch list of priority pollutants (Ellis 2006). A total of 129 priority contaminants were recognized based on technical input such as their occurrence, environmental stability, structure, toxicity, and accessible chemical standards. The EU announced a list of 33 priority pollutants categorized based on similar inputs in its water policy in the year 2000 (WFD 1984). After them, many developing countries have collaborated to develop regulations and analytical techniques prevailing the conventional and priority pollutants, collectively labelled as “persistent organic pollutants” or “bioaccumulative chemicals of concern” (Ellis 2006). This section briefly discusses the worldwide PPCP occurrence with suitable examples from developed and developing countries.

- Asia.

Initial studies undertaken by Chinese scientists in 2005 have reported that pharmaceuticals like ketoprofen, diclofenac, carbamazepine, naproxen, ibuprofen, and clofibric acid were detected in groundwater and river water and some traces in tap water. They have reported concentrations of each PPCPs in the range of several ng/L to few μg/L (Lin et al. 2005). Interestingly, the medications administered to the pets were recovered from contaminated soil, manure, sub-surface water, and vegetables. They concluded that the transmission of drugs occurs via agricultural water in Tianjin, China. Analytes, namely, pefloxacin, ofloxacin, chlortetracycline, sulfadoxine, lincomycin, tetracycline, sulfamethoxazole, chloramphenicol, and sulfachloropyridazine, were found in vegetables in the order of 0.1 to 532 μg/kg (Hu et al. 2010). Similarly, there are numerous reports on occurrences of PPCPs including synthetic estrogens, antibiotics, anti-inflammatory, beta-blockers, UV filters, etc. in Chinese rivers, sludge, sediments, and wastewater treatment plants recently. A study conducted by a Thailand-based team evaluated ecological impact of 14 pharmaceutically active compounds isolated from water canals, wastewater treatment streams, and rivers. Important analytes were caffeine and few painkillers that exited at elevated levels (~μg/L). Hazard quotients estimated for compounds like mefenamic acid, ciprofloxacin, acetylsalicylic acid, and diclofenac suggested potential ecological and health risks (Tewari et al. 2013). India is also facing ecological risks from PPCP contamination. A classic example of PPCPs could be the study in Hyderabad, India, where effluent of a drug manufacturing firm contained extreme level of ciprofloxacin up to 31 mg/L. From the same area, drinking, surface, and groundwater had 1.2 mg/L of cetirizine and 6.5 mg/L of ciprofloxacin that was revealed by Fick and team (Fick et al. 2009). This proves that wastewater from drug manufacturing units are major contributors of many CECs. Another study on isolation of different classes of medications like antibacterial and antiepileptics and preservatives was carried out by Ramaswamy et al. (2011). Sediment samples were collected from three Indian rivers which showed triclosan being present in all samples at higher quantities of 32.1, 46.9, and 85.3 ng/g, respectively (Ramaswamy et al. 2011). Apart from China, Thailand, and India, smaller countries like Vietnam, Korea, and Japan also have the problem of PPCP contamination.

- Europe.

Richardson and Bowron have reported occurrence of 25 pharmaceuticals in the River Lea, UK, with an average concentration of 1 μg/L three decades ago (Richardson and Bowron 1985). Another report from 2008 conducted on River Taff and River Ely in the UK reported the presence of illicit drugs, mediations, and endocrine-disrupting compounds that were traced from release of effluent into rivers. In addition, this study discovered the multiplicity of compounds as antiepileptic (carbamazepine and gabapentin), antibacterial (amoxicillin and erythromycin), and anti-inflammatory (ibuprofen and naproxen) (Kasprzyk-Hordern et al. 2008). Similarly, Germany, Switzerland, and other developing countries of Europe have reported the detection of different PPCPs in environmental components. Few reports also correlate the seasonal variation of PPCP load in surface and sub-surface waters.

- USA and Canada.

PPCP residues are repeatedly being detected in the waters of the USA. A comprehensive survey was undertaken in 2002 which revealed presence of few emerging contaminants like antibiotics, tranquilizers, analgesics, anti-inflammatories, phthalates, steroids, synthetic hormones, and fire retardants. Surprisingly, the quantities of analgesic, plasticizers, and steroids were found in elevated levels as high as 10–150 g/L, whereas other PPCPs were in the range of 19 to 6000 mg/L (Kolpin et al. 2002). Apart from prescribed medications, other non-prescribed drugs for treating infections are reaching the rivers and streams in the USA. Another important study carried by Blair et al. (2013) showed that Lake Michigan was constantly contaminated with PPCPs like triclosan, caffeine, sulfamethoxazole, and metformin. These chemicals were detected in samples collected from the periphery of the lake up to 3.2 km away. Also, the ecological risk from these PPCPs was of medium or high degree, indicating a significant threat (Blair et al. 2013). Canadian researchers have testified the presence of different classes of PPCPs in different environmental matrices like soil, sediments, and water bodies. A study by Metcalfe et al. (2003) that sampled the effluent of different sewage treatment plants in Canada found presence of acidic and neutral micro-contaminants. In this study, carbamazepine and other lipid regulators were present in higher levels up to 2.3 μg/L. The study inferred that origin of these PPCPs was mostly from sewage treatment plants and surface waters in the vicinity (Metcalfe et al. 2003). Another piece of work concluded that apart from treatment plants that are major contributors of PPCPs, septic systems in the proximity of agricultural fields also release these pharmaceutical products (Wu et al. 2009). Finally, it is readily acceptable that all developed and developing countries are facing the issue of PPCP contamination since the last two to three decades, out of which some of them have implemented preliminary regulations to mitigate its effects based on the pathways, transport, and effects of toxic PPCPs.

2 Pathways and Transport of PPCPs in the Environment

The diverse classes of PPCPs occur in environmental components due to its extensive usage that chiefly include drinking water, domestic wastewater, sludge, surface water (lakes, ponds, rivers, marine), and groundwater (Ashfaq et al. 2019). The sources of PPCPs can be divided as "point" and "nonpoint" depending on how they are released into the environment. Although anthropogenic activities are the principal source of PPCPs that enter the ecosystem, municipal wastewater including raw and treated water are carriers of PPCPs (Brown et al. 2006). Complementing PPCPs from human and animal use, effluents from all healthcare facilities are contributors of PPCPs. Yet another origin of PPCPs is from direct disposal of unused, expired, and unwanted medications, cosmetics, household chemicals, etc. through sinks or toilets and solid wastes. Interestingly, the landfills and the leachate are another pathways of PPCP transport (Yi et al. 2017). Some of the miscellaneous pathways of PPCPs could be from seepage from effluent conduits, leaky septic tanks, infiltrations from wastewater treatment units, and atmospheric depositions. Apart from aforementioned sources and pathways of PPCPs, most of the veterinary drugs may reach the environment through terrestrial runoff from animal sheds and wind-borne migration of chemicals applied to crops (Howard and Muir 2011). In a nutshell, PPCPs once used or refused or released enter carriers like wastewater, soil, or air, depending on its mobility, reach, or accumulate in any of the natural components. Finally, they undergo structural and physical modifications by the influence of various intrinsic and environmental factors that produce numerous metabolites with toxic nature or unknown properties that throw adverse health and ecological imbalances.

The transport behavior of PPCPs is very complex which is governed by physicochemical properties of PPCPs and the receiving environmental matrix. Mostly, PPCPs possess low volatility, maximum polarity, and high hydrophilicity, for which they migrate primarily through the aqueous medium and also via food-chain dispersion (Caliman and Gavrilescu 2009). As a preface to understanding the fate of PPCPs in the environment, the transport phenomenon of PPCPs is to be realized. Their transport behavior depends on the sorption of particular PPCPs during treatment of wastewater soil, sludge, and sediments. For instance, there are reports of PPCPs recovered from treatment plant sludge and its secondary use in the agricultural fields. This would certainly make the way for PPCPs to enter the environment (Dong et al. 2016). Consequently, the crops uptake some quantity of PPCPs that directly risks consumer health (Wu et al. 2015). Likewise, the transport of PPCPs may result in accumulation in the sediments. This condition has maximum probability of release of PPCPs into the overlaying water by which the benthic species are continuously exposed to them and undergo adverse effects (Gilroy et al. 2012). Therefore, understanding the eco-toxicological impacts of PPCPs in the environment seems imperative.

3 Fate of PPCPs in the Environment

As discussed in the previous sections, PPCPs enter water components of our environment mostly through anthropogenic discharges, agricultural runoffs, and industrial and urban effluents (Mohapatra et al. 2021). After entering the water media (surface and subsurface), they undergo modifications like transportation, structural disintegration, sorption, transformation, degradation, etc. by the influence of various factors like treatment techniques, geochemical settings, physicochemical properties of their own, and solution chemistry. It is very significant to know the fate of PPCPs that provide insights of adverse effects on ecosystem, human, animal, and aquatic biota. Here, the fate of PPCPs in groundwater and during wastewater treatment is discussed.

3.1 Fate of PPCPs in Groundwater Environments

It is very important to know the fate of PPCPs in subsurface matrices as they are equally prone to pose ecological and health risks as surface water bodies. Till date, PPCPs are detected in soils, sediments, and water environments. Three principal modes of changes to PCPPs in groundwater may be either due to degradation, adsorption, or migration/transportation within the matrix or across the matrix. Though some amount of PPCPs are eliminated by natural actions, they enter groundwater through soil (Laws et al. 2011). The fate of PPCPs in groundwater is influenced by critical factors such as physicochemical characteristics of individual PPCP and the geochemical processes at the soil-aquifer interfaces (filtration, adsorption, mixing, degradation, etc.) (Jurado et al. 2019). First, *Groundwater Ubiquity Score* (GUS) that determines the mobility in groundwater judges the influence of physicochemical properties of PPCPs that are indicating the fate. To arrive at the GUS score of any PPCPs, half-life and partition coefficient of PPCPs in soil are vital. Depending on the GUS, specific micropollutants are identified as “leachers” and “non-leachers” (Stuart et al. 2011). Second, geochemical actions like sorption, degradation, transformation, dilution, and migration of PPCPs influence their fate in groundwater. PPCPs tend to attach to organic matter in soil or clay particles, which in-turn depend on molecular structure, solubility, and hydrophobicity. For example, an anticonvulsant, carbamazepine, and a fibrate, gemfibrozil, were found to possess poor adsorption to soil, while the antibacterial/fungal agent, triclosan, displayed high adsorption and readily persisted in soil (Yu et al. 2013). Interestingly, the type of soil also controls the extent of mobility and sorption of PPCPs. Teijon et al. (2013) inferred that naproxen, an anti-inflammatory drug, has lower affinity to adsorb on to sandy material that suggests its high mobility in groundwater matrix (Teijón et al. 2013). Apart from the abovementioned co-factors, environmental parameters like pH and ionic concentration affect the transport and adsorption of PPCPs in groundwater. For instance, Zhang et al. (2014) established that low pH values promoted the sorption of sulfonamides as they occurred as cations at lower pH (Zhang et al. 2014). Concomitantly, the hydraulic circumstances also impact the adsorption and transportation of PPCPs in subsurface. The combination of maximum hydraulic conductivity and velocity in the saturated or unsaturated zone makes the area vulnerable to PPCP contamination (Rønde et al. 2017). In addition, the transmissivity of the soil type influences the magnitude of PPCP contamination. It was revealed that groundwater below alluvial residues could be readily contaminated from wastewater runoff through aquifers due to elevated transmissivity of the alluvium (Bruchet et al. 2005). These findings also indicate that soil texture is one among the important factors that control PPCP migration with groundwater. Further, degradation of PPCPs is another factor that apprise on the fate of PPCPs. Usually, unlike simple organic pollutants that undergo complete mineralization with the action of microbial consortium under aerobic or anaerobic conditions, PPCPs are believed to decompose partially owning to its complex and stable molecular structures. As such, when PPCPs undergo imperfect degradation, it produces hazardous metabolites or even remains as parent molecules for long periods (Burke et al. 2014). The miscellaneous physicochemical properties of each PPCPs result in different degrees of biodegradation. For example, caffeine and paracetamol that are frequently used undergo maximum degradation in the course of wastewater treatment and subsurface transport, whereas carbamazepine and sulfamethoxazole resist biodegradation (Kanakaraju et al. 2018). In summary, the fate of PPCPs in groundwater depends on one numerous factor, and, hence, it is very important to reveal the degree of contribution of each factor to elucidate the meticulous fate of PPCPs in groundwater (Fig. 1).

3.2 Fate of PPCPs in Wastewater Treatment Plants

The detailed understanding of the conventional treatment processes stands as a prerequisite to comprehend the fate of PPCPs. Usually, the primary treatment setup will have physicomechanical units like filters, grit chambers, and sedimentation tanks that remove settleable solids. Next, the secondary treatment aims to eliminate a major portion of organic content by means of biological activities (aerobic or anaerobic) using activated sludge process, membrane bioreactors, fixed bed bioreactors, etc. Finally, some treatment plants have tertiary treatment to recover

FIGURES AND TABLES

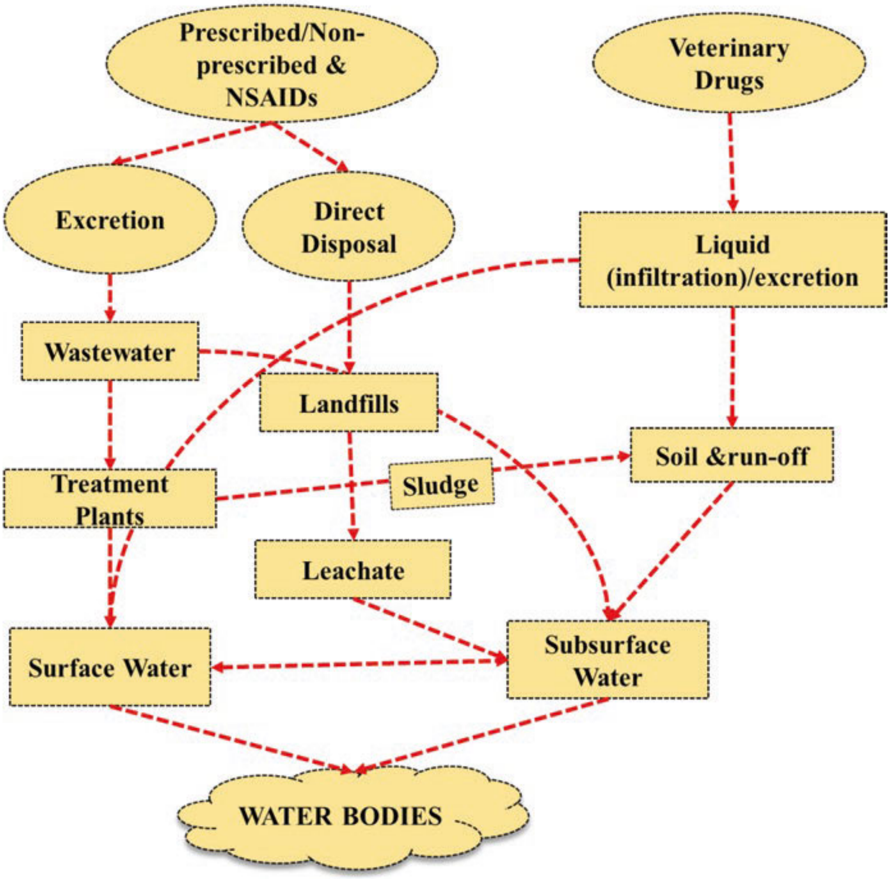


Fig. 1 Schematic of plausible sources and pathways of PCPPs in the environment

phosphorus or a disinfection unit to kill pathogens. However, these processes do not target complete removal of PPCPs, for instance, diclofenac and carbamazepine are resistant to microbial degradation. Most of the conventional treatment processes including chemical, biological, and photocatalytic degradation of PPCPs transform them into unknown or toxic metabolites. In support of this, Schlüter-Vorberg et al. (2015) showed that the acyclovir drug is being transformed into N-(4-carbamoyl-2-imino-5-oxoimidazolidin)-for-mamido-N-methoxyacetic acid and carboxyacyclovir that are more dangerous than the parent compound (Schlüter-Vorberg et al. 2015). Similarly, the beta-blocker agent, atenolol, was converted into atenolol acid through amide hydrolysis and hydroxylation of hypoglycemic component glibenclamide in the sludge. Besides, the formation of transformation products or generation of disinfection by-products (DBP) by the action of organic matters with disinfecting agents like ozone, chlorine, etc. is a serious threat to the consumers (Richardson 2011). DBPs are mostly carcinogenic or genotoxic in nature that are persistent in all types of aqueous matrices (Li and Mitch 2018). Next, considering the type of biological action, the typical degradation occurs in the aerobic and anoxic stages. The aerobic type of degradation has a maximum biological activity that could significantly transform PPCPs. Hence, the fate of PPCPs during wastewater treatment depends on the removal technique in use. In most of the cases, PPCPs are converted into toxic by-products that are detrimental to aquatic lives and terrestrial beings.

4 Effects of PPCPs on the Environment

It is important to discuss the ill effects caused by PPCPs and their associated metabolites on the ecosystem which comprise aquatic organisms, terrestrial species, livestock, and humans. It is known that the principal sources of PPCPs are industries, institutions, agrifield runoffs, and domestic households. Below are some general characteristic features of these PPCPs through which adverse effects are transmitted.

- Persistence.

The conventional water/wastewater treatment plants fail to eliminate PPCPs because of their unique physicochemical properties and chemical stability. Thus, PPCPs prevail in the water matrices. Also, all pharmaceuticals are not persistent, but they are constantly released into the environment which are labelled as "pseudo-persistent." The long-term presence or non-degradable nature of PPCPs poses serious risk to every living organism.

- Bioaccumulation.

Bioaccumulation of PPCPs is commonly observed in aquatic lives. Though the detection of PPCPs is less in freshwater, non-degraded or persistent PPCPs tend to enter the food chain especially affecting fishes. For example, in the species *Gambusia holbrooki*, also known as mosquito fish, the uptake of caffeine, diphenhydramine, diltiazem, carbamazepine, and ibuprofen was found with bioaccumulation factors of 2.0, 16, 16, 1.4, and 28, respectively (Wang and Gardinali 2013). In addition to the reports of bioaccumulation in fishes, algae are equally vulnerable for similar effect.

- Toxicity.

The major concern of PPCPs in the aquatic environment is that they lead to toxicity which makes bizarre conditions to human health interfering with the endocrine to produce undesirable effects (Menon et al. 2020). Persistent pharmaceutical agents like polychlorinated biphenyls, perfluoroalkyl substances, and polybrominated diphenyl ethers show biologically high impact at low doses for a specific target site. These unintentional toxins released into the environment act as an eco-toxicant

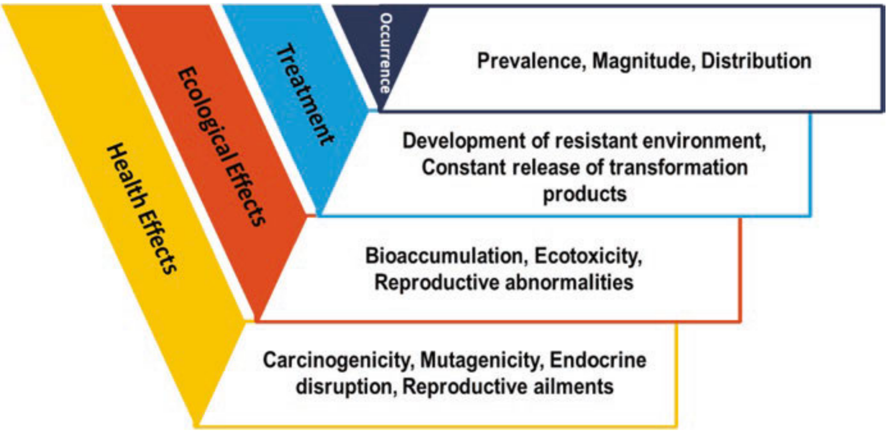


Fig. 2 Infographic describing important aspects of fate and effects of PPCPs in the environment

which influences the aquatic biota (Fabbri and Franzellitti 2016). Fabbri et al. (2016) revealed that antiepileptic drugs in combination (carbamazepine and lipid-lowering agent clofibric acid) exhibit more adverse effects on *Daphnia magna* than single compounds at equivalent concentration. This explained that combination of low concentrated drugs may lead to adverse toxicology than when in a single compound state (Fabbri and Franzellitti 2016). Also there are antibiotic resistant strains in the market within the natural bacteria which are extensively used in animal husbandry and medicine which cause emergence of more evolved strains of antibiotic-resistant bacteria leading to threat in treatment of various infectious diseases caused by pathogenic bacteria. Further, the discussion concentrates on the impacts of PPCPs on specific categories of ecosystems with convincing examples (Fig. 2).

4.1 Ecotoxicology Effects

Every year, thousands of tons of PPCPs are manufactured that are anticipated to induce some physiological changes. But there is less or no information on the impacts of PPCPs on the environment specifically on marine and terrestrial species. It is established that the parent compounds along with its secondary metabolites are very harmful when present in the ecological matrices. The PPCPs tend to persist in such matrix due to their unique physicochemical properties and make their way via conventional water/wastewater treatment plants. Although the PPCPs are detected in the range of micrograms to nanograms, their precise impact on the non-target organism is not fully determined. It is established that the prolonged exposure and synergistic effect of clustered PPCPs in trace concentrations pose serious threat to the ecosystem (Organization 2015). Most of the PPCPs are bioactive molecules that

Table 2 Toxicity of selected PPCPs with respect to *Daphnia magna* [a] *(48 h), Cyclotella meneghiniana,* [b] *and Selenastrum capricornutum* [c]

Compound	Class	L/EC$_{50}$ (mg/L)	PEC (µg/L)	PNEC (µg/L)	PEC/PNEC
Acetaminophen	Analgesic	30.1[a]	16.5	9.2	1.8
Carbamazepine	Anticonvulsant	31.6[b]	0.14	31.6	0.0044
Diclofenac	Anti-inflammatory	123.3[a]	0.14	10	0.014
Sulfamethoxazole	Antibiotics	0.146[c]	0.95	0.146	6.3
Trimethoprim	Antibiotic	167.4[a]	0.21	120.7	0.0017

L/EC$_{50}$ Acute median effective concentration, *PEC* predicted environmental concentration, *PNEC* predicted no effect concentration

affect aquatic organisms. For example, Goldfish exposed to gemfibrozil at higher concentrations for 2 weeks recorded a bio-concentration factor of 113 (Mimeault et al. 2005). Similarly, Vernouillet et al. (2010) reported the bio-accumulation of the drug carbamazepine in algae (Vernouillet et al. 2010). The ecotoxicity data on the aquatic species are usually reported by conducting acute toxicity tests, but there is no authentic results on the chronic effects imparted. It is assumed that the fishes are the most vulnerable species to PPCPs as the mobility of PPCPs will be maximum in aqueous matrix (Li 2014). Chronic exposure may lead to impairments related to reproduction in fishes. Mehinto et al. (2010) have anticipated diclofenac residues have direct ill effects on fishes (Mehinto et al. 2010). Also, pharma residues have direct effect on algal family, and their nutrient cycles and energy metabolisms are disrupted in presence of carbamazepine and diclofenac (Vannini et al. 2011). Interestingly, long-term and continuous exposure to sulfamethoxazole induces chronic toxicity in algae resulting in hindering the photosynthesis (Liu et al. 2011). Generally, synthetic hormones that enter the marine environment through PPCPs hinder the endocrine systems of aquatic organisms that results in imbalance of homeostasis and reduced secretions of natural hormones and impaired reproduction. Apart from aforementioned examples of ill effects of PPCPs on ecosystems, the presence of antibiotics in soil and water leads to the development of antibiotic-resistant bacteria. There is positive correlation between the increase of resistant strains and presence of very low concentrations of antibiotics. However, there is insufficient reports on the chronic effects of antibiotics on aquatic organisms. Table 2 shows toxicity of few well-known PPCPs.

Besides the influence of PPCPs on aquatic species, terrestrial livestock are also vulnerable to the side effects of PPCPs. A classic example of lethality due to PPCPs was noticed in the 1990s when enormous number of vultures died in India and Pakistan, which was rooted as infections, but later, it was revealed that they suffered from kidney failure after consuming discarded domestic animals which were administered with the anti-inflammatory drug diclofenac. Specifically, when particular conserved species are exposed to PPCPs, there are physiological manifestations related to hormones, puberty, lactation and reproduction.

4.2 Effect on Human Life

Human beings are relentlessly exposed to PPCPs in their daily life by the use of chemical compounds, cosmetics, medications, and other environmental components through air, water, and soil. Some of the significant factors that vary the impacts on humans are the type and concentration of PPCPs, distribution of PPCPs in the environment, the pharmacokinetics of individual components, potential bioaccumulation of specific PPCPs, etc. (Daughton 2008). However, extensive research is essential to determine the detailed impacts on humans for long-term exposure to trace levels of PPCPs, and unfortunately, there are no reports on influences due to mixtures of PPCPs at their lower concentrations on human health. International agencies like the US EPA and US FDA do not consider the effects caused by PPCPs until clear evidence is showcased. This indicates that we are lacking testing or screening for each PPCPs in our environment. Also, the health risk assessments have not been initiated to draw authentic evidence to link PPCP contamination with human health impacts.

5 Challenges and Future Perspective

The present chapter attempted to provide wide spectrum of information on the PPCPs emphasizing its fate, transport, and effects. It is realized that PPCPs are one among the CECs due their frequent detection and ongoing assessment of associated effects on living organisms. PPCPs are finding its ubiquitous usage due to improving lifestyle of people. Though the discussions focused on the sources, pathways, fate, and effects of PPCPs, there are only limited information on collective valuation of one or more PPCPs. In addition, all the quoted examples to discuss the effects of PPCPs on aquatic and human beings were in vitro studies or mathematical estimations. No established results exist on the complete life cycle assessment of individual PPCPs. There are very few attempts where environmental scientists have collaborated with healthcare workers and risk managers to comprehend the fate, transport, and effects of PPCPs, which needs to be encouraged now. Apart from such collaborations, it is important to involve all the stakeholder and beneficiaries to discuss and move forward to frame guidelines and standards like other traditional pollutants. Global database of PPCPs contamination and mitigation strategies are the need of the hour. Till date, scientists have confirmed the sources of PPCPs, its pathways in the environment, and viable detection protocols and evaluated their fate in water matrices. However, the multidimensional approach comprising analytics, toxicology, and remediation of a PPCPs must be on minds of researchers now. There is very little research on the efficient degradation of PPCPs and fate of PPCPs that consider the transformation products. In addition, no specific reports are available on chronic effects from the exposure to very low concentrations of PPCPs. Human health risks are merely anticipated, but no specific evidence are recognized. All in all, the fate and effects of PPCPs are very intricate but deemed to be serious for a sustainable living.

References

Ashfaq M, Li Y, Rehman MSU et al (2019) Occurrence, spatial variation and risk assessment of pharmaceuticals and personal care products in urban wastewater, canal surface water, and their sediments: a case study of Lahore, Pakistan. Sci Total Environ 688:653–663. https://doi.org/10.1016/j.scitotenv.2019.06.285

Blair BD, Crago JP, Hedman CJ, Klaper RD (2013) Pharmaceuticals and personal care products found in the Great Lakes above concentrations of environmental concern. Chemosphere 93:2116–2123. https://doi.org/10.1016/j.chemosphere.2013.07.057

Boxall ABA, Rudd MA, Brooks BW et al (2012) Pharmaceuticals and personal care products in the environment: what are the big questions? Environ Health Perspect 120:1221–1229. https://doi.org/10.1289/ehp.1104477

Brown KD, Kulis J, Thomson B et al (2006) Occurrence of antibiotics in hospital, residential, and dairy effluent, municipal wastewater, and the Rio Grande in New Mexico. Sci Total Environ 366:772–783. https://doi.org/10.1016/j.scitotenv.2005.10.007

Bruchet A, Hochereau C, Picard C et al (2005) Analysis of drugs and personal care products in French source and drinking waters: the analytical challenge and examples of application. Water Sci Technol 52:53–61. https://doi.org/10.2166/wst.2005.0224

Burke V, Richter D, Hass U et al (2014) Redox-dependent removal of 27 organic trace pollutants: compilation of results from tank aeration experiments. Environ Earth Sci 71:3685–3695. https://doi.org/10.1007/s12665-013-2762-8

Caliman FA, Gavrilescu M (2009) Pharmaceuticals, personal care products and endocrine disrupting agents in the environment – a review. Clean (Weinh) 37:277–303

Daughton CG (2008) Pharmaceuticals as environmental pollutants: the ramifications for human exposure. In: International Encyclopedia of public health. Elsevier Inc., pp 66–102

Dong R, Yu G, Guan Y et al (2016) Occurrence and discharge of pharmaceuticals and personal care products in dewatered sludge from WWTPs in Beijing and Shenzhen. Emerg Contam 2:1–6. https://doi.org/10.1016/j.emcon.2015.10.003

Dubey M, Mohapatra S, Tyagi VK et al (2021) Occurrence, fate, and persistence of emerging micropollutants in sewage sludge treatment. Environ Pollut 273:116515. https://doi.org/10.1016/j.envpol.2021.116515

Ellis JB (2006) Pharmaceutical and personal care products (PPCPs) in urban receiving waters. Environ Pollut 144:184–189. https://doi.org/10.1016/j.envpol.2005.12.018

Emerging substances | NORMAN. https://www.norman-network.net/?q=node/19. Accessed 15 Jul 2020

Eregowda T, Mohapatra S (2020) Fate of Micropollutants in Engineered and Natural Environment. pp 283–301

Fabbri E, Franzellitti S (2016) Human pharmaceuticals in the marine environment: focus on exposure and biological effects in animal species. Environ Toxicol Chem 35:799–812. https://doi.org/10.1002/etc.3131

Fick J, Söderström H, Lindberg RH et al (2009) Contamination of surface, ground, and drinking water from pharmaceutical production. Environ Toxicol Chem 28:2522–2527. https://doi.org/10.1897/09-073.1

Gavrilescu M, Demnerová K, Aamand J et al (2015) Emerging pollutants in the environment: present and future challenges in biomonitoring, ecological risks and bioremediation. N Biotechnol 32:147–156. https://doi.org/10.1016/j.nbt.2014.01.001

Gilroy ÈAM, Balakrishnan VK, Solomon KR et al (2012) Behaviour of pharmaceuticals in spiked lake sediments – effects and interactions with benthic invertebrates. Chemosphere 86:578–584. https://doi.org/10.1016/j.chemosphere.2011.10.022

Harikaranahalli Puttaiah S, Menon S, Shivamurthy Ravindra Y et al (2020) Preparation of supporting photocatalysts for water treatment using natural sunlight as an alternative driving energy. Mater Today Proc. https://doi.org/10.1016/j.matpr.2020.08.020

Howard PH, Muir DCG (2011) Identifying new persistent and bioaccumulative organics among chemicals in commerce II: pharmaceuticals. Environ Sci Technol 45:6938–6946. https://doi.org/10.1021/es201196x

Hu X, Zhou Q, Luo Y (2010) Occurrence and source analysis of typical veterinary antibiotics in manure, soil, vegetables and groundwater from organic vegetable bases, northern China. Environ Pollut 158:2992–2998. https://doi.org/10.1016/j.envpol.2010.05.023

Jelić A, Petrović M, Barceló D (2012) Pharmaceuticals in drinking water. In: Handbook of environmental chemistry. Springer Verlag, pp 47–70

Jurado A, Vàzquez-Suñé E, Carrera J et al (2012) Emerging organic contaminants in groundwater in Spain: a review of sources, recent occurrence and fate in a European context. Sci Total Environ 440:82–94. https://doi.org/10.1016/j.scitotenv.2012.08.029

Jurado A, Walther M, Díaz-Cruz MS (2019) Occurrence, fate and environmental risk assessment of the organic microcontaminants included in the watch lists set by EU decisions 2015/495 and 2018/840 in the groundwater of Spain. Sci Total Environ 663:285–296. https://doi.org/10.1016/j.scitotenv.2019.01.270

Kanakaraju D, Glass BD, Oelgemöller M (2018) Advanced oxidation process-mediated removal of pharmaceuticals from water: a review. J Environ Manage 219:189–207

Kasprzyk-Hordern B, Dinsdale RM, Guwy AJ (2008) The occurrence of pharmaceuticals, personal care products, endocrine disruptors and illicit drugs in surface water in South Wales, UK. Water Res 42:3498–3518. https://doi.org/10.1016/j.watres.2008.04.026

Kolpin DW, Furlong ET, Meyer MT et al (2002) Pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999−2000: a National Reconnaissance. Environ Sci Technol 36:1202–1211. https://doi.org/10.1021/es011055j

Kümmerer K (2003) Promoting resistance by the emission of antibiotics from hospitals and households into effluent. Clin Microbiol Infect 9:1203–1214. https://doi.org/10.1111/j.1469-0691.2003.00739.x

Laws BV, Dickenson ERV, Johnson TA et al (2011) Attenuation of contaminants of emerging concern during surface-spreading aquifer recharge. Sci Total Environ 409:1087–1094. https://doi.org/10.1016/j.scitotenv.2010.11.021

Leng Y, Bao J, Xiao H et al (2020) Transformation mechanisms of tetracycline by horseradish peroxidase with/without redox mediator ABTS for variable water chemistry. Chemosphere 258:127306. https://doi.org/10.1016/j.chemosphere.2020.127306

Li WC (2014) Occurrence, sources, and fate of pharmaceuticals in aquatic environment and soil. Environ Pollut 187:193–201

Li XF, Mitch WA (2018) Drinking water disinfection Byproducts (DBPs) and human health effects: multidisciplinary challenges and opportunities. Environ Sci Technol 52:1681–1689. https://doi.org/10.1021/acs.est.7b05440

Lin W-C, Chen H-C, Ding W-H (2005) Determination of pharmaceutical residues in waters by solid-phase extraction and large-volume on-line derivatization with gas chromatography–mass spectrometry. J Chromatogr A 1065:279–285. https://doi.org/10.1016/j.chroma.2004.12.081

Liu B, Nie X, Liu W et al (2011) Toxic effects of erythromycin, ciprofloxacin and sulfamethoxazole on photosynthetic apparatus in Selenastrum capricornutum. Ecotoxicol Environ Saf 74:1027–1035. https://doi.org/10.1016/j.ecoenv.2011.01.022

Mehinto AC, Hill EM, Tyler CR (2010) Uptake and biological effects of environmentally relevant concentrations of the nonsteroidal anti-inflammatory pharmaceutical diclofenac in rainbow trout (Oncorhynchus mykiss). Environ Sci Technol 44:2176–2182. https://doi.org/10.1021/es903702m

Menon NG, Mohapatra S, Padhye LP et al (2020) Review on occurrence and toxicity of pharmaceutical contamination in Southeast Asia. pp 63–91

Metcalfe CD, Koenig BG, Bennie DT et al (2003) Occurrence of neutral and acidic drugs in the effluents of Canadian sewage treatment plants. Environ Toxicol Chem 22:2872–2880. https://doi.org/10.1897/02-469

Mimeault C, Woodhouse AJ, Miao X-S et al (2005) The human lipid regulator, gemfibrozil bioconcentrates and reduces testosterone in the goldfish, Carassius auratus. Aquat Toxicol 73:44–54. https://doi.org/10.1016/j.aquatox.2005.01.009

Mohapatra S, Padhye LP, Mukherji S (2018) Challenges in detection of antibiotics in wastewater. Matrix:3–20

Mohapatra S, Menon NG, Padhye LP et al (2021) Natural attenuation of Pharmaceuticals in the Aquatic Environment and Role of Phototransformation, pp 65–94

Organization WH (2015) WHO multi-country survey reveals widespread public misunderstanding about antibiotic resistance

Priyanka MS, Mohapatra S (2020) Shifts and trends in analysis of contaminants of emerging concern: sulfonamides. pp 261–281

Ramaswamy BR, Shanmugam G, Velu G et al (2011) GC-MS analysis and ecotoxicological risk assessment of triclosan, carbamazepine and parabens in Indian rivers. J Hazard Mater 186:1586–1593. https://doi.org/10.1016/j.jhazmat.2010.12.037

Richardson SD (2011) Disinfection by-products: formation and occurrence in drinking water. In: Encyclopedia of environmental health. Elsevier Inc., pp 110–136

Richardson ML, Bowron JM (1985) The fate of pharmaceutical chemicals in the aquatic environment. J Pharm Pharmacol 37:1–12

Rønde V, McKnight US, Sonne AT et al (2017) Contaminant mass discharge to streams: comparing direct groundwater velocity measurements and multi-level groundwater sampling with an in-stream approach. J Contam Hydrol 206:43–54. https://doi.org/10.1016/j.jconhyd.2017.09.010

Schlüter-Vorberg L, Prasse C, Ternes TA et al (2015) Toxification by transformation in conventional and advanced wastewater treatment: the antiviral drug acyclovir. Environ Sci Technol Lett 2:342–346. https://doi.org/10.1021/acs.estlett.5b00291

Stuart ME, Manamsa K, Talbot JC, Crane EJ (2011) Emerging contaminants in groundwater

Sui Q, Cao X, Lu S et al (2015) Occurrence, sources and fate of pharmaceuticals and personal care products in the groundwater: a review. Emerg Contam 1:14–24. https://doi.org/10.1016/j.emcon.2015.07.001

Teijón G, Candela L, Sagristá E, Hidalgo M (2013) Naproxen adsorption-desorption in a Sandy aquifer matrix: characterisation of hysteretic behavior at two different temperature values. Soil Sediment Contam 22:641–653. https://doi.org/10.1080/15320383.2013.756446

Tewari S, Jindal R, Kho YL et al (2013) Major pharmaceutical residues in wastewater treatment plants and receiving waters in Bangkok, Thailand, and associated ecological risks. Chemosphere 91:697–704. https://doi.org/10.1016/j.chemosphere.2012.12.042

Vannini C, Domingo G, Marsoni M et al (2011) Effects of a complex mixture of therapeutic drugs on unicellular algae Pseudokirchneriella subcapitata. Aquat Toxicol 101:459–465. https://doi.org/10.1016/j.aquatox.2010.10.011

Vernouillet G, Eullaffroy P, Lajeunesse A et al (2010) Toxic effects and bioaccumulation of carbamazepine evaluated by biomarkers measured in organisms of different trophic levels. Chemosphere 80:1062–1068. https://doi.org/10.1016/j.chemosphere.2010.05.010

Wang J, Gardinali PR (2013) Uptake and depuration of pharmaceuticals in reclaimed water by mosquito fish (Gambusia holbrooki): a worst-case, multiple-exposure scenario. Environ Toxicol Chem 32:1752–1758. https://doi.org/10.1002/etc.2238

WFD (1984) Official journal of the European Communities. Anal Proc 21:196. https://doi.org/10.1039/ap9842100196

Wu C, Witter JD, Spongberg AL, Czajkowski KP (2009) Occurrence of selected pharmaceuticals in an agricultural landscape, western Lake Erie basin. Water Res 43:3407–3416. https://doi.org/10.1016/j.watres.2009.05.014

Wu X, Dodgen LK, Conkle JL, Gan J (2015) Plant uptake of pharmaceutical and personal care products from recycled water and biosolids: a review. Sci Total Environ 536:655–666

Xu M, Huang H, Li N et al (2019) Occurrence and ecological risk of pharmaceuticals and personal care products (PPCPs) and pesticides in typical surface watersheds, China. Ecotoxicol Environ Saf 175:289–298. https://doi.org/10.1016/j.ecoenv.2019.01.131

Yi X, Tran NH, Yin T et al (2017) Removal of selected PPCPs, EDCs, and antibiotic resistance genes in landfill leachate by a full-scale constructed wetlands system. Water Res 121:46–60. https://doi.org/10.1016/j.watres.2017.05.008

Yu Y, Liu Y, Wu L (2013) Sorption and degradation of pharmaceuticals and personal care products (PPCPs) in soils. Environ Sci Pollut Res 20:4261–4267. https://doi.org/10.1007/s11356-012-1442-7

Zhang YL, Lin SS, Dai CM et al (2014) Sorption-desorption and transport of trimethoprim and sulfonamide antibiotics in agricultural soil: effect of soil type, dissolved organic matter, and pH. Environ Sci Pollut Res 21:5827–5835. https://doi.org/10.1007/s11356-014-2493-8

Carbamazepine Residues in Wastewater and River Water: Occurrence and Estimation of Use and Disposal of this Drug in a Small Community in Western Kentucky

Peng Shangwu and Bommanna G. Loganathan

Abstract Carbamazepine (5H-dibenz[b,f]azepine-5-carboxamide, CBZ) is one of the most commonly used pharmaceutical drugs to treat pain symptoms, epilepsy, trigeminal neuralgia, and diabetes insipidus. CBZ is considered as one of the highly persistent pharmaceutical drugs and emerging pollutants in the environment. The objective of this study was to determine the disposal/contamination levels of CBZ in water samples collected from wastewater treatment plant effluent, Bee Creek, Clarks River, and Red Duck Creek, Kentucky. Enzyme-linked immunosorbent assay (ELISA) method was used to quantify CBZ in the samples. The results revealed that water samples from various sampling locations contained detectable concentrations of CBZ. The concentration of CBZ followed the order of WWTP Samples > Clarks River ≥ Downstream Bee Creek > Red Duck Creek > Upstream Bee Creek. In effluent samples from Murray Wastewater Treatment Plant (MWWTP), the mean concentration of CBZ was 32.8 ng/L. Estimated discharge of CBZ was 655 mg/day (range 588–704 mg/day). Estimated total loading (based on dissolved phase only) from the community was 728 mg/day. Estimated per capita use of this drug in this small community is 36.4 µg/capita/day. This preliminary study provides evidence that CBZ is a potential environmental contaminant in these waters.

Keywords Pharmaceuticals · Carbamazepine · Wastewater · Effluent · Disposal · River water · Clarks River · Bee Creek · ELISA · Western Kentucky

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1 Introduction

Indiscriminate disposal of unused and expired pharmaceuticals leads to environmental contamination. Pharmaceuticals are one of the emerging environmental pollutants that have been detected in surface water, groundwater, municipal wastewater, biosolids, and fish (Kolpin et al. 2002; Subedi and Loganathan 2016; Björlenius et al. 2018). The United States Environmental Protection Agency (US EPA) and the health organization of the European Commission (EC) have documented that some environmentally persistent pharmaceuticals are of great concern due to their adverse effects on the environment and wildlife including humans (Daughton and Ternes 1999; Jones-Lepp and Stevens 2007; Ramirez et al. 2009; European Commission 2012). Recently, there have been studies suggesting the pharmaceutical drug, carbamazepine (CBZ) to be a persistent marker of sewage and not efficiently removed by wastewater treatment processes resulting in contamination of receiving waters (Matamoros et al. 2007; Nakada et al. 2008; Skees et al. 2018). This study was conducted to determine CBZ levels in water samples collected from Murray Wastewater Treatment Plant (MWWTP) effluent, Bee Creek, Clarks River, and Red Duck Creek, Kentucky.

CBZ is mainly used as an anticonvulsant and analgesic all over the world. CBZ has been prescribed to treat physical and mental illness, including epilepsy, trigeminal neuralgia, pain syndromes, diabetes insipidus, etc. (Okuma and Kishimoto 1998; Novartis 2018). CBZ also acts as a mood stabilizer to help in the treatment of bipolar disorder, reducing mood swings and mania (Okuma and Kishimoto 1998; CAMH 2009). CBZ was first synthesized by Schindler in 1960 (Benes et al. 1999) and is one of the most frequently prescribed drugs in adults and children (Fig. 1). It became a widely used commercial drug for more than 40 years with several brand names such as Tegretol, Carbatrol, Tegretol XR, and Epitol in different countries (Carbamazepine 2011 www.drugs.com). CBZ is the most preferred anticonvulsant for pediatric seizure disorders (Miao and Metcalfe 2003).

CBZ is a white or nearly white powdered crystal and sparingly soluble in water (17.7 mg/L at 25 °C), but it dissolves in methanol, tetrahydrofuran, ethanol, and

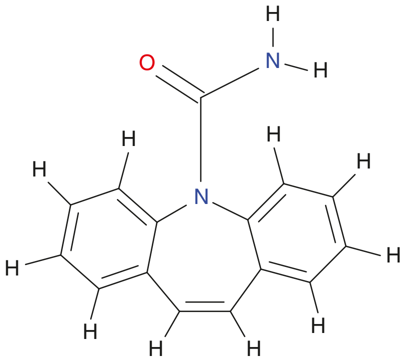

Fig. 1 Carbamazepine (5H-dibenz[b,f]azepine-5-carboxamide), $C_{15}H_{12}N_2O$, Molar mass: 236.27

acetone at room temperature (Oetken et al. 2005; Liu et al. 2008). The mechanism of CBZ is to interface and stabilize voltage-gated sodium channels, preventing the brain cell from achieving over-activated state (Benes et al. 1999). Singh et al. studied the effect of CBZ on cultured dorsal root ganglion neurons. The neurons significantly depressed Na^+ currents related to inhibiting the neurotransmitter release by CBZ (Singh et al. 2009). This compound plays a role in depressing polysynaptic reflexes and blocking post-tetanic potentiation. In clinical studies, auto-induction of 3–5 weeks is needed after drug intake. About 72% of metabolites (including 3% of unchanged CBZ) can be detected in urine and 28% in feces. The lowest known lethal dose of human being ranges from 1.6 (3-year-old female) to 3.2 g (24-year-old female) (Novartis 2018). CBZ's persistent properties prevent it from biodegradation, and it is not efficiently eliminated during wastewater treatment processes based on chlorination (Nakada et al. 2006). However, the most successful method for the removal (about 93%) of CBZ was UV treatment (Kosjek et al. 2009). Similarly, ozonation (0.5 mg/L) was shown to reduce more than 90% of CBZ (Ternes et al. (2002). Although CBZ has low acute toxicity to aquatic organisms, chronic sediment exposure experimental results revealed significant and specific effect in *Chironomus riparius*. Therefore, wild benthic insects may have a risk of negative health effects by this drug (Oetken et al. (2005). Although most pharmaceutical drugs are tested for human safety before putting into market, the potential hazard to non-target organisms/people in low environmental concentrations is not clear. Earlier studies have shown that intact CBZ as well as its metabolites enter the environment as excreta (Matamoros et al. 2007; Nakada et al. 2008; Kosjek et al. 2009; Novartis 2018). Also improper disposal of expired drugs by residents, pharmacies, drug manufacturers, and hospitals contributes to environmental contamination. Currently, very little is known on CBZ contamination levels in our regional waters. Understanding current levels of CBZ is key in identifying pollutant sources, risk assessment, and development of preventive measures.

Murray and Mayfield, Kentucky, are home to several pharmacies, hospitals, and private clinics. Prescriptions, misuse, and improper disposal of this drug may contribute to environmental contamination. Considering the nature of population in this region of western Kentucky including the elderly (retirement communities) and university students, the use of prescription CBZ is highly possible. Wastewater from houses and local hospitals is known to carry pharmaceutical residues to the wastewater treatment plant (Loganathan et al. 2009). Further, baseline screening studies conducted in western Kentucky watershed revealed occurrence of CBZ in this regional waters (Peng and Loganathan 2011). Based on the background of population in this region, especially Murray and Mayfield, and the persistent properties of CBZ (environmental half-life of about 100 days (Andreozzi et al. 2003)), it is hypothesized that detectable quantities of CBZ may be found in western Kentucky water resources.

The objectives of this study were to (i) determine the concentrations of CBZ in wastewater and surface water samples including effluent from Murray Wastewater Treatment Plant, Bee Creek (upstream and downstream of Murray Wastewater Treatment Plant), Clarks River at Squire Holland Road bridge and KY-94 bridge, and Red Duck Creek, Mayfield, KY; (ii) track possible source(s) of carbamazepine to these water resources; and (iii) determine spatial and temporal differences in concentrations of carbamazepine in this watershed and (iv) preliminary loading estimates of carbamazepine into water resources and per capita use of this drug in this small community.

2 Materials and Methods

2.1 *Sampling Locations and Samples*

In Murray, the following sampling points were chosen for collection:

Site 1. Effluent from Murray Wastewater Treatment Plant (MWWTP).
Site 2. Bee Creek – upstream of MWWTP.
Site 3. Bee Creek – downstream of MWWTP.
Site 4. Clarks River at KY 94 bridge.
Site 5. Clarks River at Squire Holland Road.

2.1.1 Details of Sampling Locations (Fig. 2) and Sampling Strategies

MWTTP was built in 1984 and is located near Bee Creek (Sanitary Sewer System 2011). This wastewater treatment plant has a capacity to process 20 megaliters of wastewater per day (2010 Census Data). The combined wastewater originates from homes, a hospital, university dormitories, and a small fraction of commercial and industrial sewage. This town has a local population (Calloway County) of approximately 37,200, including 17,741 people in the city of Murray (2010 US Census). A considerable portion of which are retirees and then an influx of university students (about 10,000 during academic year mid-August to mid-May). Significant population fluctuations (about 30%) occur during a calendar year, especially during winter and summer breaks, during which the student population is at its minimum. Although MWWTP has a capacity of processing 20 megaliters of wastewater, it rarely operates at its full capacity. Considering the population fluctuations and volume of wastewater processed, this WWTP serves an average of approximately 20,000 people.

Bee Creek is a small creek that originates in the northwestern part of Murray and flows eastward approximately 3 miles. It receives discharges from some local businesses, storm water drainages, and treated water (effluents of MWWTP) before it joins the Clarks River. Site 2 is located prior (upstream) to MWWTP effluent input into the creek. Site 3 is located after the MWWTP effluent drained into the creek. Ultimately, Bee Creek drains into the Clarks River. The Clarks River watershed consists of East Fork Clarks River and West Fork Clarks River located in southwestern Kentucky. The Clarks River watershed within Calloway County is located in

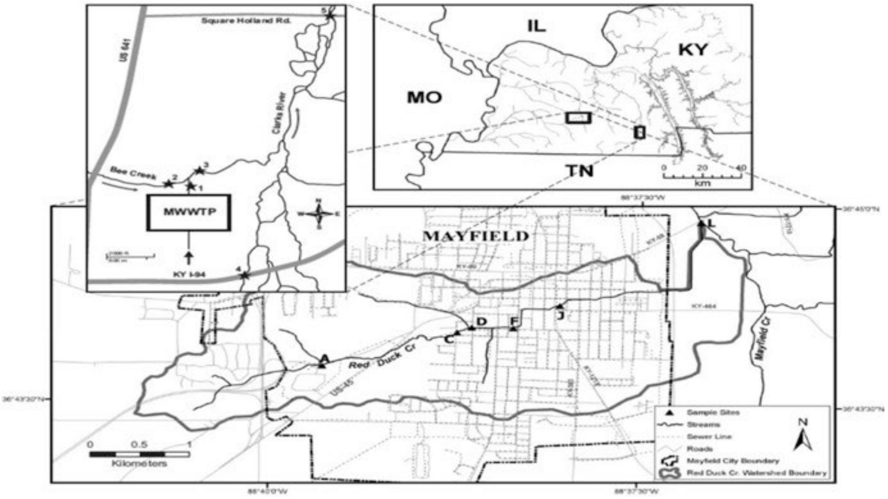

Fig. 2 Map showing sampling locations in Western Kentucky. ★ and ▲ indicate sampling locations in Murray and Mayfield, respectively

ecoregion 74b, the Mississippi Valley Loess Plains (Report- Jackson Purchase RC &d Foundation). This ecoregion is a productive agricultural area composed of rolling uplands, broad bottom lands, and terraces. Earlier studies have documented that agricultural activity contaminated the sediment and fish from the East Fork Clarks River (Kummarikunta 2010). In addition, local industries and the wastewater treatment plant also discharge their effluents into the East Fork Clarks River.

In order to compare CBZ levels in water samples originating from different population groups, Red Duck Creek in Mayfield, Kentucky, was selected, and the following sampling points were chosen to monitor CBZ in water samples:

Site A. Headwaters region of Red Duck Creek (RDC).
Site C. West of South 14th street behind Mayfield Grain.
Site D. Downstream of where Rodgers Branch enters RDC.
Site F. Downstream of south tenth stream ditch entrance to RDC.
Site J. Located behind AutoZone.
Site L. Region of RDC near where RDC drains into Mayfield Creek.

2.1.2 Details of Sampling Locations (Fig. 2) and Sampling Strategies

Red Duck Creek is an urban stream in Graves County that flows approximately 6.8 km before draining into Mayfield Creek. This creek receives drainages from approximately 3.7 square miles that includes a large portion of the city of Mayfield. Major land uses in the Red Duck Creek watershed include residential, agricultural, and some industrial uses in the upstream portion of watershed. Most residential areas in the watershed are within Mayfield city limits and have sewer lines available. However, in the upstream portions of the watershed, there are some residential areas that are located outside of city limits and have on-site sewage disposal systems such as septic systems. A few earlier studies conducted on this stream (Red Duck Creek) identified high bacteria counts associated with fecal contamination (Morgan 2004; Kentucky Watershed Watch (2014). However, no studies concerning pharmaceutical chemical contamination have been carried out in Red Duck Creek. In order to track sources as well as to discern temporal changes in CBZ input in Red Duck Creek, we selected six sampling locations along the course of the creek (Fig. 2).

Grab sampling procedure was followed to collect the water samples. Approximately 500 mL of water sample was collected using a pre-cleaned I-Chem glass bottle with Teflon-lined cap (Fisher brand, 500 mL). All samples were kept in a cooler with ice at approximately 4 °C until further processing. Water samples were thawed to room temperature and then filtered through a Millipore apparatus using pre-washed 0.45 μm filters (Millipore Corporation, Bedford, MA) under vacuum.

2.2 *Sample Extraction*

OASIS® C_{18}- Hydrophilic Lipophilic Balanced-Solid Phase Extraction (HLB-SPE) cartridges purchased from Waters Corporation (6 mL, 0.2 g, 30 μm, Milford, Massachusetts, USA) were used for sample extraction. The sorbent of HLB cartridges is a macroporous copolymer made with divinylbenzene and N-vinylpyrrolidone. The mechanism used is water-wettable reversed phase adsorption. HLB sorbent cartridges are known for their high retention and recovery rates, which allow them to isolate a wide range of compounds, even in extremely low concentrations. HLB cartridges are able to retain non-polar and polar compounds including CBZ which made them suitable for CBZ analysis in water samples (OASIS HLB1998, 2008). The cartridges were pre-conditioned using 6 mL methanol followed by 6 mL deionized water. About 200 mL of water samples were then passed through cartridges. Deionized water (200 mL) was used for blank analysis. An elution manifold was used to ensure a consistent extraction rate of 10 mL/min. An elution solvent was prepared by mixing methanol and acetic acid at 99:1 ratio. The CBZ were eluted by 4 × 5 mL solution using elution manifold. The eluents were evaporated to 1 mL using a gentle stream of nitrogen gas (ultra-high purity).

2.3 *Carbamazepine Analysis*

CBZ analysis was performed using enzyme-linked immunosorbent assay (ELISA). This is a highly sensitive, simple, inexpensive, and accurate method for determination of CBZ in water samples. Several studies have compared, validated, and employed this assay to monitor CBZ in a variety of matrices including surface water, groundwater, wastewater, etc. (Bahlmann et al. 2009, 2012; Calisto et al. 2011; ABRAXIS 2010a, b). A carbamazepine enzyme-linked immunosorbent assay (ELISA) kit containing standards, solutions, and microtiter plate was purchased from Abraxis LLC, PA, USA.

ELISA method is based on the identification of CBZ by mouse anti-carbamazepine antibodies and goat anti-mouse immobilized in microtiter plate. Standards, reagents, microtiter plates, and sample extracts (1 mL) were brought to room temperature prior to analysis. 75 μL each of the standard solutions (0.025, 0.05, 0.10, 0.25, 0.50, 2.5, 4.0 ppb) and water sample extracts was transferred into the wells of the test strips using micropipette. 50 μL of the CBZ enzyme conjugate and antibody solutions was added to the individual wells. Covering with parafilm, the plate was moved in a rapid circular motion to mix the contents. The reaction mixture was incubated for 90 minutes at 4 °C.

After incubation, the contents at the wells were removed. Using 1X washing buffer (phosphate) solution, the strips were washed and dried four times. 100 μL 3, 3', 5, 5'-Tetramethylbenzidine (TMB) was added as color solution to the dry wells. After 30 minutes, 50 μL sulfuric acid was added to end this reaction. Absorbance was measured using an Abraxis Model 6 PLUS_SPI 450 nm filter Mini Spectrophotometer. Duplicate analysis was performed for calibration standards. Mean absorbance values were used to draw the calibration curve. 7-point calibration with CBZ concentration range of 0.025 to 4.0 ppb was used. R^2 value obtained for the calibration curve was 0.984. CBZ concentrations of samples were calculated using a calibration equation from concentration vs. B/B_0 of absorbance. CBZ concentrations were expressed in ppt (ng/L).

3 Results

The recoveries of CBZ standards ranged from 66.8% to 144.7% (n = 7) with mean recovery of 102.7%. CBZ were detected in all 45 water samples analyzed. Tables 1 and 2 present the concentrations of CBZ in water samples collected from various locations including Clarks River, Bee Creek, and MWWTP effluents and Red Duck Creek from Mayfield KY. Concentrations of CBZ ranged from 11.4 ng/L (Site F in

Table 1 Concentrations of carbamazepine in water samples from Clarks River, Bee Creek, and Murray Wastewater Treatment Plant (MWWTP), Murray, KY

		MWTTP	Bee creek		Clarks River	
Survey no.	Date of sampling	effluent (ng/L)	upstream (ng/L)	Downstream (ng/L)	Sq. Holland (ng/L)	I-94 (ng/L)
1	10/21/2010	33.7	13.5	16.0	15.7	17.9
2	11/05/2010	29.4	14.6	15.4	17.4	17.6
3	03/11/2011	35.2	13.7	17.9	16.8	17.2
Mean		32.8	13.9	16.4	16.6	17.6

Table 2 Seasonal variation in concentrations of carbamazepine in water samples from Red Duck Creek, Mayfield, Kentucky

Survey no.	Date of sampling	Season	Site A (ng/L)	Site C (ng/L)	Site D (ng/L)	Site F (ng/L)	Site J (ng/L)	Site L (ng/L)	Avg. ng/L
1	10/30/2010	Fall	16.3	20.0	18.6	18.5	18.4	16.8	18.1
2	12/04/2010	Winter	18.7	14.7	17.9	17.0	15.9	15.7	16.7
3	02/13/2011	Winter	13.4	15.9	13.7	11.4	15.8	16.3	14.4
4	02/27/2011	Winter	16.6	17.2	14.3	13.9	14.7	13.6	15.1
5	03/05/2011	Spring	15.2	12.7	15.2	14.0	16.4	15.9	14.9
Mean			16.0	16.1	15.9	15.0	16.2	15.7	15.8

Red Duck Creek) to 35.2 ng/L (MWWTP effluent). In contrast to river waters and creek waters, effluents of MWWTP contained considerably higher concentrations of CBZ (range, 29.4–35.2 ng/L).

Three sampling events occurred in Bee Creek in October 2010 to March 2011. CBZ levels ranged from 13.5 ng/L to 17.9 ng/L. Although CBZ concentrations are in similar range in both upstream and downstream (Table 1) of WWTP, concentrations in downstream were consistently higher than in upstream samples. Statistical analysis comparing of upstream and downstream CBZ concentrations using a t-test revealed that CBZ levels in upstream were significantly lower ($p = <0.05$) than in downstream. The elevated levels of CBZ in downstream samples suggest that WWTP effluents contain considerable amount of CBZ and contribute to the contamination of Bee Creek downstream.

In Clarks River, two locations (KY 94 and at Squire Holland) were monitored for CBZ (Table 1). At KY 94 site, concentrations of CBZ were in the range of 17.2 ng/L to 17.9 ng/L. At Squire Holland site (downstream of all other sites in Murray), concentrations of CBZ were in the range of 15.7 ng/L to 17.4 ng/L with the mean value of 16.6 ng/L. CBZ concentrations in Clarks River at Squire Holland bridge were considerably lower than in WWTP effluents, however, relatively higher than upstream Bee Creek.

In Red Duck Creek, Mayfield, KY, the sampling events occurred from October 2010 to March 2011 (Fig. 2, Table 2). Six sample sites were selected along the course of the Creek in the city of Mayfield. CBZ levels were detected in all samples. CBZ concentrations ranged from 11.4 ng/L to 20.0 ng/L in Red Duck Creek. The results reveal that there exist no clear spatial and temporal variations in concentrations of CBZ in this creek during the sampling period (Table 2).

4 Discussion

Although many pharmaceutical chemicals are produced in large quantities similar to agricultural insecticides, relatively less research has been conducted dealing with the occurrence and fate of pharmaceutical chemicals in aquatic ecosystems

(Daughton and Ternes 1999). Since the pharmaceutical chemicals are designed to be lipophilic and biologically persistent, many of them, especially CBZ, are known to be persistent in the environment. One of the major pathways that this drug enters the environment is through municipal wastewaters. Further, many studies have shown that CBZ is not removed or degraded during wastewater treatment process; therefore, > 90% of this drug escape into effluent water and contaminate receiving waters during wastewater treatment processes (Matamoros et al. 2007; Kosjek et al. 2009; Skees et al. 2018).

In this study (Fig. 3), MWWTP effluent contained the highest concentration of CBZ (35.2 ng/L) than Bee Creek sites. Bee Creek sites at upstream and downstream of MWWTP contained relatively lower concentration of CBZ. Downstream site showed slightly higher concentrations of CBZ than upstream, indicating CBZ input from MWWTP effluent. Considering the CBZ concentrations found in downstream site, it appears that dilution of effluent occurred significantly. However, the magnitude of decline in CBZ concentrations in Bee Creek at downstream of MWWTP was unexpected, since the upstream flow was comparatively smaller than the flow from the MWWTP effluent. Therefore, considerable decline in CBZ concentrations in the downstream site may be attributable not only to dilution by the flow from upstream, but also CBZ might have adsorbed to sediments/suspended particulate matter. Future studies involving analysis of CBZ in dissolved phase as well as particulate phase (sediments/suspended particulate matters) will reveal partitioning behavior of this compound. Further, flow measurements of upstream Bee Creek will help understand magnitude of dilution of CBZ downstream.

Table 1 shows CBZ concentrations in the Clarks River sites, including upstream (at KY 94) and downstream (at Squire Holland bridge) sites which are located close to the downtown of Murray and away from the city of Murray, respectively. At KY

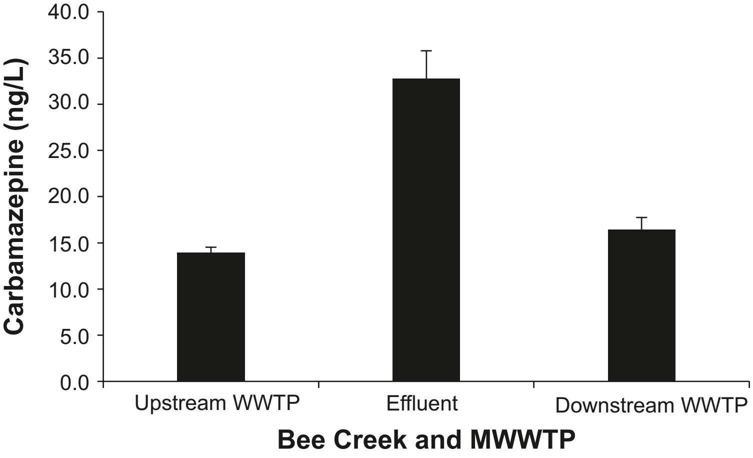

Fig. 3 Carbamazepine concentrations (ng/L) in Bee Creek and Murray Wastewater Treatment Plant effluent samples

94 site, CBZ concentrations ranged from 17.2 ng/L to 17.9 ng/L. This indicated contributions from some residential and commercial zones in this region. Although the Squire Holland site is located away from the city of Murray and receives discharges from various sources along the course of the river including agricultural drainages, a few industrial discharges, and the drainage from Bee Creek, CBZ concentrations were not influenced by these inputs. At the Squire Holland site, CBZ concentrations did not vary drastically. Slightly lower concentrations of CBZ in water samples at this site may be due to dilution or adsorption of this compound to sediments (Fig. 4).

As described in the earlier section, Red Duck Creek, Mayfield, receives drainages from different population groups. CBZ concentrations in various sites in Red Duck Creek are shown in Table 2. The concentration differences are not significant between each site. This suggests that none of these sites have any point source input for this compound. Comparing to sampling sites in Murray, CBZ concentrations in Red Duck Creek and Bee Creek are in similar range, both sites located within city limits, but slightly lower concentration than the upstream site in Clarks River which is located outside Murray. In terms of temporal variation in CBZ concentrations, it can be inferred that no distinct or significant change in concentration occurred during the three seasons sampled in this creek. Therefore, it may be surmised that CBZ is not a seasonal drug. However, further studies are needed with number of samples to make clear any seasonal pattern in CBZ levels in this creek.

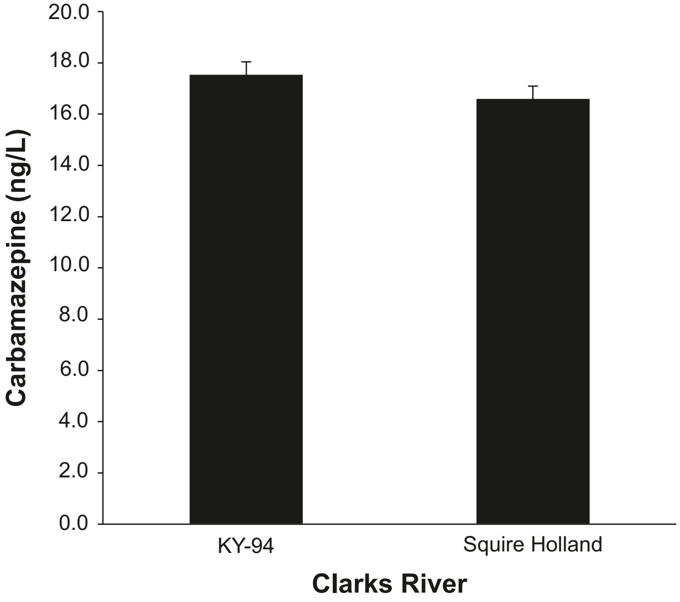

Fig. 4 Carbamazepine concentrations in Clarks River samples collected at KY 94 and at Squire Holland Road

Table 3 presents CBZ concentrations in wastewater treatment plant samples from various countries. Very high concentration (>3200 ng/L) was reported for effluent samples from Germany and the UK (3117 ng/L), followed by Cagliari, Italy (1318 ng/L), and downstream of Arc River-Aix-en-Provence, Italy (1150 ng/L). However, effluents of WWTPs from Naples, Varese Olona, and Palermo, Italy, contained CBZ concentrations less than 400 ng/L. CBZ concentrations in wastewater effluents from Seville, Spain, and Udupi, India, had a range of 400–800 ng/L. Earlier studies from US wastewater treatment plants showed CBZ concentrations in effluents ranged from 50 to 156 ng/L. Nakada et al. (2006) reported CBZ concentrations of <100 ng/L in effluents from Tokyo wastewater treatment plant (Table 3). In

Table 3 Concentrations (ng/L) of carbamazepine reported in wastewater treatment plant samples from various countries (Values in parenthesis indicate concentration range)

Samples/location	Carbamazepine (ng/L)	References
Murray WWTP (effluent)	32.8	Present study
Bee Creek (upstream)	13.9	Present study
Bee Creek (downstream)	16.4	Present study
Clarks River	17.1	Present study
Red Duck Creek	15.8	Present study
Murray WWTP (influent)	99.1 ± 26.0	Skees et al. (2018)
Murray WWTP (effluent)	99.7 ± 15.5	Skees et al. (2018)
Arc River-Aix en Provence, Italy (downstream)	1150	Comoretto and Chiron (2005)
Cagliari, Italy (effluent)	1318	Castiglioni et al. (2005)
Palermo, Italy (effluent)	<1.3	Castiglioni et al. (2005)
Naples, Italy (effluent)	382	Castiglioni et al. (2005)
Varese Olona, Italy (effluent)	179	Castiglioni et al. (2005)
Seville, Spain (influent)	500 ± 100	Weigel et al. (2004)
Sevile, Spain (effluent)	480 ± 60	Santos et al. (2005)
Tromso/Norway (Asgard sewer effluent)	270	Weigel et al. (2004)
STPs, Germany (effluent)	3200	Zhang et al. (2008)
Tokyo Japan (effluent)	<100	Nakada et al. (2006)
S. Korea (effluent)	13,954[a]	Subedi et al. (2013)
Udupi, India (influent)	450 (240–750)	Subedi et al. (2017)
Udupi, India (effluent)	580 (450–770)	Subedi et al. (2017)
UK (influent)	950–2593	Petrie et al. (2015)
UK (effluent)	826–3117	Petrie et al. (2015)
USA (Mississippi) (influent)	137 (66–348)	Kwon and Rodriguez (2014)
USA (Mississippi) (effluent)	156 (66–270)	Kwon and Rodriguez (2014)
USA (New York) (influent)	100 ± 78	Benotti and Brownawell (2007)
USA (New York) (effluent)	65 ± 15	Benotti and Brownawell (2007)

[a] mg/day/WWTP

general, CBZ concentrations in MWWTP, Clarks River, and Bee Creek were relatively lower than effluent samples from other countries except the effluent sample from Palermo, Italy (<1.3 ng/L).

Considering its persistent nature and ubiquitous presence in the aquatic environment, CBZ has been proposed as a marker for anthropogenic input (ABRAXIS 2010a, b). Previous studies have used CBZ concentrations in wastewater effluent to calculate per capita and environmental emission rates (Subedi et al. 2013). As stated earlier, this small wastewater treatment facility processes approximately 20 megaliters of wastewater per day. Using an average CBZ concentration of 32.8 ng/L in effluent water and an average of 20 million liters of effluent water per day, we calculated environmental loading of 655 mg/day. Although some pharmaceuticals are removed significantly during wastewater treatment processes, CBZ was found to have very small percent removal occur during the treatment (Table 3) (Subedi et al. 2017). Assuming effluent water contains 90% of CBZ in influent, the wastewater treatment plant receives about 728 mg of CBZ from the Murray community. Considering a population of 20,000 is served by this WWTP, per capita contribution of CBZ via dissolved phase (effluent water) is estimated to be about 36.4 μg/capita/day. As indicated above, our study has some limitations, and, thus, our results should be interpreted within those confines. Further studies are needed to evaluate the community use, disposal, and environmental contamination levels of this drug.

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References

ABRAXIS (2010a) Carbamazepine plate, detailed ELISA procedure. In: Carbamazepine plate kit. ABRAXIS, LLC, Warminster

ABRAXIS (2010b) Carbamazepine ELISA (microtiter plate): enzyme-linked immunosorbent assay for the determination of carbamazepine in water samples. ABRAXIS Product No. 515585, pp 1–4

Andreozzi R, Raffaele M, Nicklas P (2003) Pharmaceuticals in STP effluents and their solar photodegradation in aquatic environment. Chemosphere 50:1319–1330

Bahlmann A, Weller M, Panne U, Schneider RJ (2009) Monitoring carbamazepine in surface and wastewaters by an immunoassay based on a monoclonal antibody. Anal Bioanal Chem 395:1809–1820

Bahlmann A, Carvalho JJ, Weller MG, Panne U, Schneider RJ (2012) Immunoassays as high-throughput tools: monitoring spatial and temporal variations of carbamazepine, caffeine and cetirizine in surface and wastewaters. Chemosphere 89:1278–1286

Benes J, Parada A, Figueiredo AA, Alves PC, Freitas AP, Learmonth DA, Cunha RA, Garrett J, Soares-da-Silva P (1999) Anticonvulsant and sodium channel-blocking properties of novel 10,11-dihydro-5H-dibenz[b,f]azepine-5-carboxamide derivatives. J Med Chem 42:2582–2587

Benotti MJ, Brownawell BG (2007) Distributions of pharmaceuticals in an urban estuary during both dry-and wet-weather conditions. Environ Sci Technol 41:5795–5802

Björlenius B, Ripszám M, Haglund P, Lindberg RH, Tysklind M, Fick J (2018) Pharmaceutical residues are widespread in Baltic Sea coastal and offshore waters – screening for pharmaceuticals and modelling of environmental concentrations of carbamazepine. Sci Total Environ 633:1496–1509

Calisto V, Bahlmann A, Schneider RJ, Esteves V (2011) Application of ELISA to the quantitation of carbamazepine in ground, surface, and wastewaters and validation with LC-MS-MS. Chemosphere 84:1708–1715

CAMH (2009) Understanding psychiatric medications: mood stabilizers. Centre for Addiction and Mental Health. CAMH foundation, a Pan American Health Organization / World Health Organization Collaborating Centre. University of Toronto

Carbamazepine. Retrieved April 28, 2011., from http://www.drugs.com/ingredient/carbamazepine.html

Castiglioni S, Bagnati R, Calamari D, Fanelli R, Zuccato E (2005) A multiresidue analytical method using solid phase extraction and high-pressure liquid chromatography tandem mass spectrometry to measure pharmaceuticals of different therapeutic classes in urban wastewaters. J Chromatogr A 1092:206–215

Census Data (2010) Retrieved April 1, 2011, from http://2010.census.gov/2010census/data/

Comoretto L, Chiron S (2005) Comparing pharmaceutical and pesticide loads into a small Mediterranean river. Sci Total Environ 349:201–210

Daughton CG, Ternes TA (1999) Pharmaceuticals and personal care products in the environment: agents of subtle change? Environ Health Perspect 107:907–938

European Commission (EC) (2012) Proposal for a Directive of the European Parliament and of the Council Amending Directives 2000/60/EC and 2008/105/EC as Regards Priority Substances in the Field of Water Policy. 2012

Jackson Purchase RC&D Foundation, Inc. (n.d.) Watershed based plan for Clarks River. Strand Associates, Inc. A Report

Jones-Lepp TL, Stevens R (2007) Pharmaceuticals in biosolids – the interface between analytical chemistry and regulation. Anal Bioanal Chem 387:1173–1183

Kentucky Watershed Watch. Basin success stories. A Report by Watershed Watch in Kentucky, Inc. 40 pp. September 30, 2014

Kolpin D, Furlong E, Meyer M, Thurman E, Zaugg S, Barber L, Buxton H (2002) Pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999–2000: a National Reconnaissance. Environ Sci Technol 36:1202–1211

Kosjek T, Andersen HR, Kompare B, Ledin A, Heath E (2009) Fate of carbamazepine during water treatment. Environ Sci Technol 43:6256–6261

Kummarikunta V (2010) Organohalogen pollutants in sediment and fish samples from the Clarks River, Kentucky. M. S. Thesis. Murray State University, pp 84

Kwon J-W, Rodriguez JM (2014) Occurrence and removal of selected pharmaceuticals and personal care products in three wastewater treatment plants. Arch Environ Contam Toxicol 66:538–548

Liu W, Dang L, Black S, Wei H (2008) Solubility of carbamazepine (form III) in different solvents from (275 to 343) K. J Chem Eng Data 53:2204–2206

Loganathan BG, Phillips M, Mowery H, Jones-Lepp TL (2009) Contamination profiles and mass loadings of macrolide antibiotics and illicit drugs from a small urban wastewater treatment plant. Chemosphere 75:70–77

Matamoros V, Arias C, Brix H, Bayona JM (2007) Removal of pharmaceuticals and personal care products (PPCPs) from urban wastewater in a pilot vertical flow constructed wetland and a sand filter. Environ Sci Technol 41(23):8171–8177

Miao X-S, Metcalfe CD (2003) Determination of carbamazepine and its metabolites in aqueous samples using liquid chromatography-electrospray tandem mass spectrometry. Anal Chem 75:3731–3738

Morgan M (2004) Fecal coliform in red Duck Creek and its tributaries. In: Four Rivers Basin project report. Annual FRWW Conference Report

Nakada N, Tanishima T, Shinohara H, Kiri K, Takada H (2006) Pharmaceutical chemicals and endocrine disrupters in municipal wastewater in Tokyo and their removal during activated sludge treatment. Water Res 40:3297–3303

Nakada N, Kiri K, Shinohara H, Harada A, Kuroda K, Takizawa S, Takada H (2008) Evaluation of pharmaceuticals and personal care products as water-soluble molecular marker of sewage. Environ Sci Technol 42(17):6347–6353

Novartis (2018) Tegretol medication guide. T2018-27/T2018-28, March 2018. Novartis Pharmaceutical Corporation, East Hanover

OASIS® HLB Certificate of Analysis: OASIS® HLB Extraction Cartridge. OASIS® Sample Extraction Products (2008) Waters corporation. Waters Corporation, Milford

Oetken M, Nentwig G, Lçffler D, Ternes T, Oehlmann J (2005) Effects of pharmaceuticals on aquatic invertebrates. Part I. the antiepileptic drug carbamazepine. Arch Environ Contam Toxicol 49:353–361

Okuma T, Kishimoto A (1998) A history of investigation on the mood stabilizing effect of carbamazepine in Japan. Psychiatry Clin Neurosci 52:3–12

Peng S, Loganathan BG (2011) Carbamazepine concentrations in western Kentucky watershed, USA. Organohalogen Compd 73:87–90

Petrie B, Barden R, Kasprzyk-Hordern B (2015) A review on emerging contaminants in wastewaters and the environment: current knowledge, understudied areas and recommendations for future monitoring. Water Res 72:3–27

Ramirez AJ, Brain RA, Usenko S, Mottaleb MA, O'Donnell JG, Stahl LL, Wathen JB, Snyder BD, Pitt JL, Perez-Hurtado P, Dobbins LL, Brooks BW, Chambliss K (2009) Occurrence of pharmaceuticals and personal care products in fish: results of a national pilot study in the United States. Environ Toxicol Chem 28:2587–2597

Sanitary Sewer System. Retrieved April 1, 2011., from http://www.murrayky.gov/publicworks/sewer/index.htm

Santos JL, Aparicio I, Alonso E, Callejon M (2005) Simultaneous determination of pharmaceutically active compounds in wastewater samples by solid phase extraction and high-performance liquid chromatography with diode array and fluorescence detectors. Anal Chim Acta 550:116–122

Schindler W (1960) New N-heterocyclic compounds. U.S. Patent Office. 2,948,718, 1960

Singh JN, Jain G, Ramarao P, Sharma SS (2009) Inhibition of sodium current by carbamazepine in dorsal root ganglion neurons in vitro. Indian J Physiol Pharmacol 53(2):147–154

Skees AJ, Foppe KS, Loganathan B, Subedi B (2018) Contamination profiles, mass loadings, and sewage epidemiology of neuropsychiatric and illicit drugs in wastewater and river waters from a community in the Midwestern United States. Sci Total Environ 631-632:1457–1464

Subedi B, Loganathan B (2016) Environmental emission of pharmaceuticals from wastewater treatment plants in the USA. In: Loganathan BG, Khim J-S, Kodavanti PRS, Masunaga S (eds) Persistent organic chemicals in the environment: status and trends in the Pacific Basin countries II temporal trends. ACS Symposium Series 1244; American Chemical Society, Washington DC, pp 181–202

Subedi B, Lee S, Moon H-B, Kannan K (2013) Psychoactive pharmaceuticals in sludge and their emission from wastewater treatment facilties in Korea. Enviorn Sci Technol 47:13321–13329

Subedi B, Balakrishna K, Joshua D.I, Kannan K (2017) Mass loading and removal of pharmaceuticals and personal care products including psychoactive, antihypertensives, and antibiotics in two sewage treatment plants in southern India. Chemosphere 167: 429–437

Ternes TA, Meisenheimer M, McDowell D, Sacher F, Brauch H-J, Haist-Gulde B, Preuss G, Wilme U, Zulei-Seibert N (2002) Removal of pharmaceuticals during drinking water treatment. Environ Sci Technol 36:3855–3863

Waters Corporation (1998) Setting new standards for solid-phase extraction (SPE) technology. OASISTM HLB sample extraction products. Waters Corporation, Milford

Weigel S, Berger U, Jensen E, Kollenborn R, Thorensen H, Huhnerfuss H (2004) Determination of selected pharmaceuticals and caffeine in sewage and seawater from Tromso/Norway with emphasis on ibuprofen and its metabolites. Chemosphere 56:583–592

Zhang Y, Geiben S-U, Gal C (2008) Carbamazepine and diclofenac: removal in wastewater treatment plants and occurrence in water bodies. Chemosphere 73:1151–1161

An overview on selected plasticizers in the aquatic environment of China and India

Moitraiyee Mukhopadhyay and Paromita Chakraborty

Abstract Asia holds the second largest share of freshwater (28%) in the world. The Asia-Pacific region is a hotspot for plastic pollution, mainly due to the mismanaged plastic wastes that find their way into the ocean. Hence, it is inevitable for widely used plasticizers such as phthalic acid esters (PAEs) to be present in the aquatic environment. Contamination of aquatic environment by xenoestrogenic compounds such as PAEs has been extensively reported from two major economies of Asia, viz., China and India. Hence, this chapter aims at presenting an overview of the of selected PAEs in the aquatic environment of China and India. Further, a brief review on the human health exposure of these compounds has been also discussed.

Keywords Phthalic acid esters · Asia · Freshwater

1 Introduction

Global production of plastic cumulatively reached 7 billion tons with more than 50% discarded as waste in 2015. In addition, 42% of the plastics entering the used phase stemmed from packaging industries, followed by building and construction industries (19%). Globally, 1.15 and 2.41 million tons of plastic is estimated to end up in to the oceans every year, (Lebreton et al. 2017). Lebreton et al. (2017) estimated that more than 90% of the top 20 polluting rivers in terms of plastic pollution are present in Asia carrying 67% of the global plastic input into the oceans.

Polymeric materials may contain various hazardous chemicals such as phthalic acid esters (PAEs), heavy metals, and other non-intentionally added substances

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(NIAS) during recycling. The International Union of Pure and Applied Chemistry (IUPAC) adopted the following definition of a plasticizer: “A plasticizer is a substance or material incorporated in a material (usually a plastic or elastomer) to increase its flexibility, workability, or distensibility” (Godwin 2017). Presently, there are close to 100 plasticizers produced worldwide with only 50 being commercially crucial with more than 90% of its application in PVC materials. PAEs are a type of general plasticizer and represent 65% of the worldwide plasticizer market with a significant contribution from bis-2-ethylhexyl phthalate (DEHP), diisobutyl phthalate (DiBP), and diisononyl phthalate (DINP). PAEs are used in plastic products up to 65% by weight mostly in polyvinyl chloride (PVC) material (Hahladakis et al. 2018). However, PAEs were quantified in 24 out of 25 samples of polyethylene, polystyrene, PVC, polyethylene laminates, as well as cellulose-based polymer samples (Shen 2005).

PAEs in plastics act as “lubricants” and retain their chemical properties due to weak van der Waals interaction between PAEs and the polymer material, making the former easy to migrate to the external environment (Keizer-Schrama et al. 2006). High molecular PAEs are mainly used in building materials, adhesives, packaging, medical devices, pharmaceuticals, textiles, and household products. On the other hand, low molecular PAEs, predominantly DMP, DEP, and DnBP, are used as industrial solvents, personal care products and insecticides. Furthermore, DMP and DEP help lengthen the duration of fragrances and are thus used in perfumes and other personal care products. (Net et al. 2015). PAEs have been ubiquitously present in all the environmental compartments (air, water, soil, and sediment) (Net et al. 2015). Significant sources of PAEs pollution in the aquatic environment are untreated wastewater discharge (Adeniyi et al. 2011), surface runoff (Müller et al. 2019), and disposal of plastic waste (Chakraborty et al. 2019). However, studies on the occurrence of PAEs in the aquatic environment are scarce, especially from Asia, although it ranks first among continents in mismanaged plastic waste.

Due to the growing concern regarding their endocrine-disrupting abilities of PAEs, six PAEs, DMP, DEP, DnBP, BBP, DEHP, and DnOP, are enlisted as priority pollutants by the European Union and United States Environmental Protection Agency (USEPA 2014). Furthermore, the US Center for Disease Control and Prevention released 276 compounds denoting them as hazardous substances, including DnBP, BBP, and DEHP (ATSDR 2019). Various authorities and countries have given the recommended limit for DEHP. For example, WHO recommends a maximum concentration of 8 μg/L in drinking water, and the USA, Australia, and New Zealand have recommended limits of 6 μg/L, 9 μg/L, and 10 μg/L, respectively. Due to their wide applications, several countries have raised concerns over the usage of PAEs in various daily use products. For example, the usage of PAEs in toys was banned by the USA, Canada, Argentina, Brazil, and Japan (Liang et al. 2021 and Jambeck et al. 2015).

Asia accounts for over 50% of the worldwide plastic production and China and India produces 44.79 and 14.17 MT of plastic resin respectively (Liang et al. 2021). The developing economies have serious problems associated with mismanagement of generated plastic waste ending up in the rivers or open oceans. More than 70% of the produced plastic in China and India are mismanaged (Jambeck et al. 2015).

Plastic litter is a major source of plasticizers like PAEs and their associated estrogenic impacts on the aquatic ecosystem (Chakraborty et al. 2021).

Hence, in this chapter, have reviewed the fate of six priority PAEs enlisted as endocrine disruptors and their distribution in surface water of China and India.

2 Materials and Methods

2.1 Target PAEs

According to the reported detection frequency in various environmental matrices, six priority phthalates (i.e., DnOP, DEHP, BBP, DnBP, DEP, and DMP) were selected as the target compounds in this study. The physicochemical properties are presented in Table 1.

2.2 Data Sources

The keywords “water,” “river,” “Asia,” “PAEs,” or “phthalates” were used to search for the relevant information on Web of Science, Scopus, and Google Scholar for 2008–2021.

3 Discussion

3.1 Properties and Application of PAEs

3.1.1 Physical State

PAEs derived from lower-molecular-weight alcohols such as dimethyl phthalate (DMP) and diethyl phthalate (DEP) have low viscosity and are colorless. However, viscosity increases with an increase in the alkyl side chains of PAEs. PAEs have melting points below −25 °C, low freezing points (<0 °C), and boiling points between 230 and 486 °C. Due to their low melting and high boiling point, PAEs are used as heat transfer fluids, carriers, and plasticizers.

3.1.2 Water Solubility

Aqueous solubility is the most influential property governing biodegradation, bioaccumulation, and environmental distribution of a chemical. The water solubility of PAEs varies inversely with the alkyl side chain and varies between 5220 mg/L for DMP and 2.4×10^{-3} mg/L for DEHP (Cousins and Mackay 2000).

3.1.3 Plasticization

A typical method for plasticization includes the heating and simultaneous mixing of the polymer resin with the plasticizer until complete solvation of the resin. Thorough mixing is required for the plasticizers to modify the resin's properties and get the desired final product.

During plasticization, no chemical bonding takes place to impart flexibility to the polymer material's effective movement of the plasticizers within the polymer matrix. For example, to understand the difference between the flexibility of a PVC incorporated with non-migrating DEHP and migrating DEHP, Navarro et al. (2016) studied the glass transition temperature (Tg) of both types of PVC composition. It was observed that Tg changed between −40 °C and PLUS_SPI 40 °C from non-migrating DEHP polymer system to migrating PVC system, thereby making the former a non-flexible, reasonably rigid plastic, which is brittle at room temperature.

Three classical theories can explain plasticization: gel, lubricity, and free volume theory (Marcilla and Beltran 2004). Lubricity theory states that the incorporation of plasticizers reduces the internal resistance so that when the polymer gets flexed, the molecule can slide over each other. The gel theory considers that the polymer forms a tridimensional honeycomb structure with solvation-desolvation and aggregation-deaggregation equilibria between the polymer and the plasticizer molecules. Unlike lubricity theory, in the gel theory, reduction in the intermolecular friction is incorporated by reducing the number of attachment points of the polymer to polymer. The free volume theory is based on the free volume present in the polymer at absolute zero and the selected temperature. The concept mainly states that polymer incorporated with plasticizers will have a higher free volume and flexibility than rigid plastic.

3.2 *Fate in the Aquatic Environment*

The behavior of individual PAE in various environmental matrices is defined by their inherent properties, thereby affecting their fate. The ubiquitous presence of PAEs coupled with their environmental and toxicological impacts has initiated numerous efforts by scientists in the last decade to understand the fate and transport of PAEs, depending on their key physicochemical properties. Table 1 shows the selected physicochemical parameters for the most abundant PAEs. Figure 1 shows the generalized sediment-water exchange process of PAEs.

3.2.1 Octanol/Water Partitioning

The octanol/water partition coefficient (K_{OW}) represents the distribution of a compound at equilibrium between water and octanol and is often used to predict the probable partitioning between water and lipid and water and sediment/soil. K_{OW} of PAEs is directly proportional to the increase in the molecular weight of the alcohol moiety, indicating an increase in hydrophobicity.

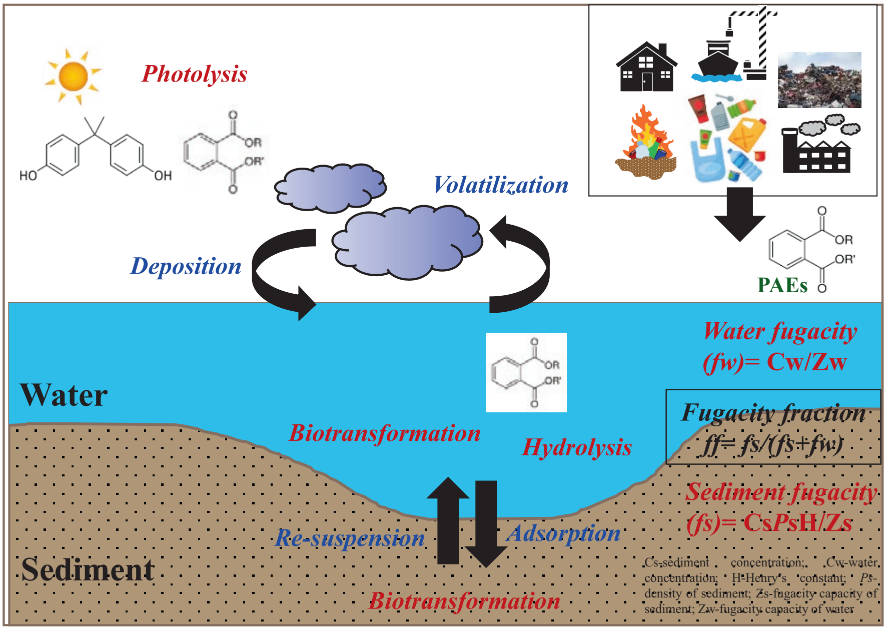


Fig. 1 Hypothetical schematic representation of sediment-water exchange process of PAEs

It is noteworthy that K_{OW} values of high-molecular-weight PAEs are due to a higher magnitude decrease per unit volume in a molar volume of water than that of octanol. Interestingly, the lipophilicity of PAEs is observed to increase with the slight increase in the alkyl side chain. Governed by the presence of free R–COOH group, low-molecular-weight PAEs such as DMP and DEP are more prone toward polar matrices. On the other hand, high-molecular-weight PAEs such as DEHP have a higher affinity toward non-polar matrices. With the increase in the K_{OW} of a chemical, the lipophilicity generally increases, indicating their bio-concentration in living organisms (Lyman 1990) (Table 2).

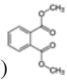
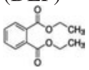
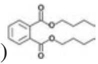
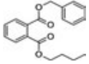
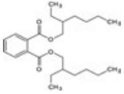
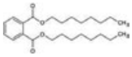
3.2.2 Octanol/Carbon Partitioning

Similar to K_{OW} values of PAEs, the octanol/carbon partitioning (K_{OC}) values of PAEs increase with an increase in the alkyl chain, indicating more propensity toward soil/sediment organic matter.

3.2.3 Vapor Pressure and Air/Water Partitioning

Similar to solubility, the vapor pressure of PAEs decreases with an increase in the alkyl side; however, the decrease is not very pronounced. Due to the high vapor pressure of low-molecular-weight PAEs, they tend to rapidly vaporize from a pure state; however, their low K_{AW} has been attributed to higher aqueous solubility.

Table 1 Physicochemical properties and application of priority phthalic acid esters (PAEs)

Compounds	Applications	Solubility (mg/L)	Vapor pressure (Pa)	H (Pa m^3/mol)	Log K_{OW}	Log K_{OA}	Log K_{AW}
Dimethyl phthalate  (DMP)	Insecticides, personal care products, fragrances, toys, lacquers, and paints	5220	0.263	0.00978	1.61	7.01	−5.4
Diethyl phthalate (DEP) 	Insecticides, fragrances, surface lubricants in food, solvents, pharmaceutical coatings, Plasticizers	591	6.48×10^{-2}	0.0244	2.54	7.55	−5.01
Di-n-butyl phthalate  (DnBP)	Cellulose acetate, plastics, cosmetics, solvents, fragrances, pharmaceutical coating	9.9	4.73×10^{-3}	0.133	4.27	8.54	−4.27
Butyl benzyl phthalate (BBP) 	Plasticizers in PVC products, vinyl flooring, food packaging, solvents, personal care products, toys, synthetic leather	3.8	2.49×10^{-3}	0.205	4.7	8.78	−4.08
Diethylhexyl phthalate (DEHP) 	PVC products, flooring, sanitary products, food packaging, dielectric fluids, solvents, toys, electrical equipment	2.49×10^{-3}	2.52×10^{-5}	3.95	7.73	10.53	−2.8
Di-n octyl phthalate (DnOP) 	Conveyor belts, bottle cap liners, flooring, taps, pool liners, and garden hose	2.49×10^{-3}	2.52×10^{-5}	3.95	7.73	10.53	−2.8

Aqueous solubility decreases with an increase in the alkyl chain of PAEs, thereby increasing their K_{AW} indicating high-molecular-weight PAEs will rapidly volatilize from water. However, this action is mitigated due to their affinity towards suspended matter in water. Although higher log K_{OA} and log K_{AW} values indicate partitioning of chemicals toward atmospheric particles and higher volatilization from water, due to the tendency of high-molecular-weight PAEs to sorb more toward suspended particles present in the aqueous environment, movement to air is drastically restricted.

Although DEHP can volatilize from seawater in the near-coast environment, global trends indicate that deposition dominates the air-sea exchange of PAEs (Xie et al. 2007). The aqueous environment was found with elevated levels of PAEs via wastewater discharge, leaching, and atmospheric deposition (Net et al. 2015). Once released in the aqueous environment, at neutral pH, the hydrolysis of PAEs is extremely low and can have half-lives up to 100 years. However, photolysis induced by UV-B directly or indirectly can substantially reduce the half-lives of PAEs. Another possible pathway for the degradation of PAEs in an aqueous environment is via aerobic or anaerobic biodegradation, which can reduce the half-lives up to a few hours. Biodegradation is suggested as the main pathway for the degradation of PAEs in sediment and depends on various factors, including pH, temperature, and aerobic/anaerobic conditions. Sediment has been found to act as a secondary emission source for low molecular PAEs and as a sink for high molecular PAEs (Mukhopadhyay and Chakraborty 2021).

3.3 PAEs in Surface Water

The highest share of ocean plastic pollution stems from Asia due to mismanaged plastic waste. Globally, the highest amount of mismanaged plastic waste comes from China (28%), followed by Indonesia (10%), Philippines, and Vietnam (6%). A recent study found that the top 4 plastic polluted rivers worldwide are from India and China (Lebreton et al. 2017). It is evident that with the enormous quantity of plastic waste, a massive load of plasticizers such as PAEs also finds its way through the rivers into the world's oceans. However, the study of PAEs in the aqueous environment of rivers from Asia is minimal with the majority of the studies from China followed by India. Table 2 shows the levels of six priority PAEs studied in various rivers from China and India.

China

China is the largest producer of plastics and represents one-fifth of the global consumption of PAEs. Given the high usage and presence of numerous non-point and point sources for the release of PAEs, the aquatic environment in China was evidenced with elevated PAEs (Liu et al. 2014). Comprehensive research has been carried out in China's longest river, the Yangtze River. In 2005, water samples were taken from 15 sites from mainstream, tributaries, and lakes of the Wuhan section of the Yangtze River to understand the pollution level of PAEs (Wang et al. 2008). In

Table 2 Level of priority phthalic acid esters in surface water from China and India

Compounds/concentration (μg/L)								
Site details		DMP	DEP	DnBP	BBP	DEHP	DnOP	References
Yangtze River, Wuhan, China	*High water period (mean)*							
	Zhuankou	ND	ND	0.023	-	0.011	ND	Wang et al. (2008)
	Baishazhou	0.031	0.032	0.041	-	0.016	ND	
	Wuhanguan	0.295	ND	0.134	-	0.026	ND	
	Left Yujiatou	ND	0.07	0.126	-	0.028	ND	
	Right Yujiatou	0.065	0.365	0.014	-	0.012	ND	
	Low water period (mean)							
	Jinkou	ND	ND	28.63	-	3.9	3.2	
	Zhuankou	ND	ND	10.33	-	30.26	0.07	
	Wuhanguan	0.1	ND	ND	-	43.01	0.51	
	Yangluo	ND	ND	35.65	-	54.73	0.84	
Yangtze River, Wanzhou County, China	*Range*	0.016 – 0.037	0.0086 – 0.057	0.135 – 0.801	0.0005 – 0.00135	0.073 – 0.261	0.0005 – 0.00106	He et al. (2020)
Yangtze River, Zhejiang section, China	Wet season *(range)*	0.02 – 1.55	0.01 – 2.65	0.38 – 12.58	-	1.26 – 10.21	0.03 – 1.05	Chen et al. (2019)
	Dry season *(range)*	0.01 – 0.07	0.03 – 1.10	0.33 – 10.59	-	0.96 – 9.65	0.06 – 1.22	

Pearl River Delta China	Mean (*range*, *n* = 7)	ND – 0.412	ND – 0.0183	0.099 – 0.203	0.003 – 0.0078	0.138 – 1.700	0.045 – 0.265	Weizhen et al. (2020)
	North River (*range*)	0.034 – 0.13	0.024 – 0.088	0.28 – 0.63	-	0.79 – 1.88	-	Li et al. (2017)
Jiulong River, China	West River (*range*)	0.028 – 0.23	0.029 – 0.22	0.33 – 2.40	-	0.91 – 3.63	-	
	Estuary (*range*)	0.033 – 0.11	0.021 – 0.12	0.31 – 0.97	-	1.13 – 10.9	-	
	Hai River (*median*)	0.068	-	1.02	0.023	1.95	-	
	Liao River (*median*)	0.069	0.043	-	-	0.27	-	
	Songhua River (*median*)	-	-	-	-		-	
Nationwide survey, China	Yellow River (*median*)	0.072	0.036	0.4	-	0.21	0.013	Liu et al. (2014)
	Yangtze River (*median*)	-	0.027	-	-	0.28	-	
	Pearl River (*median*)	0.062	0.026	0.22	-	-	-	
Songhua River, China	*Range*	2.5 (0.98 – 4.12)	2.35 (1.33 – 6.67)	5.12 (1.69 – 11.81)	2.49 (ND – 4.39)	7.01 (2.26 – 11.55)	2.37 (0.66 – 6.14)	Gao et al. (2014)
Kaveri River, India	*Range*	ND – 0.094	0.036 – 0.520	ND – 0.372	0.0054 – 0.145	ND – 0.822	ND – 0.085	Selvaraj et al. (2015)

(continued)

Table 2 (continued)

Compounds/concentration (μg/L)								
Site details		DMP	DEP	DnBP	BBP	DEHP	DnOP	References
Cochin estuary, India	*Range*	ND – 1.945	ND – 3.139	ND – 20.368	ND – 10.634	ND – 3.861	ND – 0.838	Ramzi et al. (2020)
Ganga River, India	*Range*	0.053	2.142	2.278	0.138	6.309	0.051	Chakraborty et al. (2021)
Sundarban River, India	*Range*	0.062	0.402	0.878	0.104	0.024	0.430	Chakraborty et al. (2021)
Hooghly River, India	*Maximum concentration*	0.770	0.041	0.078	0.118	0.032	0.600	Mukhopadhyay and Chakraborty (2021)

wthe mainstream, levels of six PAEs varied between 0.034 and 0.456 μg/L and from 35.73 to 91.22 μg/L in high and low water periods, respectively. While in its tributaries, the maximum concentration was an order magnitude higher both in high and low water periods and varied between 0.114 and 1.259 μg/L and 0.25 and 132.12 μg/L, respectively. Furthermore, a distinct increase in the mainstream level of PAEs was observed from upstream to downstream which was mainly attributed to the influx of PAEs from various tributaries downstream. DnBP and DEHP were the two major contributors of total PAEs and attributed to industrial and domestic discharge and surface runoff from agricultural and garbage land. In 2017, He et al. (2020) studied the levels of six priority PAEs and DiBP in Wanzhou County along the Yangtze River. The PAE levels in river water varied from 364 to 1300 ng/L, with a mean value of 599 ± 69 ng/L with a dominance of DnBP, DiBP, and DEHP. However, levels observed were lower than studies from other river regions which was attributed to lesser anthropogenic activities in this county. Chen et al. (2019) studied the distribution of five priority PAEs (DMP, DEP, DnBP, DEHP, DnOP) along with DiBP in water, particulate matter, and sediment from 45 sampling sites in the Zhejiang section of the Yangtze River Delta. DiBP, DnBP, and DEHP were the dominant PAEs observed in both the dissolved and particulate phases. However, in sediment, DiBP, DEHP and DnOP were the dominant congeners. Low-molecular-weight PAEs such as DMP and DEP showed significantly higher concentrations in wet periods than the dry period in the dissolved phase. In addition, a significantly higher concentration of DEP was observed in the particulate phase from the wet period than in the dry period. High aqueous solubility of DEP and DMP was suggested as the main cause for this seasonal variation. Calculated partition coefficient (K_{d1}) between particulate and dissolved phase derived from PAEs concentration indicated that both in a wet and dry period, high K_{d1} was obtained from high-molecular-weight PAEs such as DEHP and DnOP. It is, however, noteworthy that DMP, a low-molecular-weight PAE, also had higher K_{d1} during the wet period which might be due to the high water flow and resuspension from the sediment. Multivariate source apportionment indicated that industrial wastewater and intense shipping activities were the plausible reasons for DEHP, DnOP, DiBP, DnBP and domestic sewage discharge for DMP and DEP.

The Pearl River Delta is the largest urban area in the world in both size and population. Although numerous studies on other organic pollutants were done in this region, reports on PAEs contamination are hardly present. Weizhen et al. (2020) studied the levels of 14 PAEs in the riverine, estuarine, and reservoir regions of the delta in two seasons (wet and dry) from 2012 to 2014. Levels of Σ_{14}PAEs in the aqueous phase ranged from 465.53 ± 52.61 to 2825.35 ± 144.31 ng/L and were highly dependent on the population of the region, development model, the industrial level and the type of industry. Similar to other reports on PAEs in an aqueous environment, DnBP and DEHP were observed to be the dominant congeners. The riverine region had higher levels than the estuarine region and natural reservoirs indicating the source-specific contamination levels of PAEs. Furthermore, as observed in the Yangtze River, the dry period had higher levels than the wet period due to higher dilution in the latter.

Levels of sixteen PAEs were studied in the North and West Rivers from the Jiulong River Basin during 2014 (Li et al. 2017). The mean values of the Σ_6PAEs were 4.76 μg/L (North River), 6.09 μg/L (West River), and 7.50 μg/L (estuary). Similar to other reports, a dominance of DiBP, DnBP, and DEHP was also reported from Jiulong River in addition to the source-specific elevated concentrations. The riverine concentration of PAEs was observed to be influenced by the hydrodynamics of the river, the chemical constitution of SPM and the inherent properties of the PAE molecule. However, levels in the estuarine region were affected by mixing conditions of sea and river water, ballast discharge, and dredging.

A nationwide survey on the contamination level of six priority PAEs was addressed by Liu et al. (2014), where in water samples were taken from seven geographical zones of China between 2009 and 2012. The highest levels of DnBP, BBP, and DEHP were in Hai River, where as the highest levels of DMP and DnOP were in Liao River and DMP in Yangtze River Basin.

India

India generated 4.49 MT of plastic waste in 2010 with 85% of it being mismanaged. Apart from disposal of plastic waste, discharge of domestic and industrial wastewater and burning of dumped plastic waste and scrap recycling activities were evidenced as specific emission sources for PAEs in the riverine environment from India (Chakraborty et al. 2019). Similar to other Asian countries, reports on PAEs levels in surface water from India are also scarce. The concentration of $\sum_6$PAEs in surface water from River Kaveri, South India, varied between 0.3 and 4.6 μg/L with a dominance of DEHP followed by DEP and DnBP (Selvaraj et al. 2015). Specific source points were discussed in the above paper for the elevated levels of each PAE in surface water. For example, elevated levels of DEHP, BBP, and DEP at certain sites were reasoned with discharge from specific industries such as paper mills, leather, rubber, and chemicals. In addition, the elevated levels of DEP at an upstream site was mainly attributed to domestic discharge due to its pervasive usage in personal care products. Source for DMP was suggested as domestic wastewater along with agricultural runoff due to its use in insecticides.

The seasonal distribution of six priority PAEs along with their distribution between dissolved and particulate phases from Cochin Estuary was studied by Ramzi et al. (2020). Levels up to 27.99 μg/L were recorded in this study. Unlike other reports from China, the highest concentration was observed in the monsoonal period followed by the post-monsoon and the pre-monsoon. Furthermore, the average concentration of $\sum_6$PAEs was a magnitude higher in surface water than bottom water during monsoon; however, the average concentration of $\sum_6$PAEs remained approximately similar in surface and bottom water during post- and pre-monsoonal seasons. DnBP was dominant followed by BBP, DEHP, DEP, DMP, and DnOP. Similar to the dissolved phase, elevated levels of $\sum_6$PAEs were reported during monsoon season (321 μg/g) with a dominance of DEHP, DnBP, and BBP. A negative correlation between pH and salinity with $\sum_6$PAEs indicated freshwater discharge in the estuary as a possible source for plasticizers in surface water. Source apportionment using principal component analysis suggested that for low-molecular-weight PAEs, the dominant emission source might be their usage in personal care products, whereas, for mid- and high-molecular-weight PAEs, industrial discharge was identified as a potential source.

A comprehensive article focused on plastic additives and the associated estrogenicity on the entire stretch of River Ganga and the Sundarban delta was recently studied (Chakraborty et al. 2021). The study was divided into four stretches and the mean concentration of plasticizers was 1.73 ± 0.83, 2.08 ± 1.60, 0.90 ± 0.35, and 1.3 ± 0.4 μg/L, in the upper, middle, lower and wetland stretches respectively. Further, depending on the compositional profile and multivariate analysis of PAEs in various stretches of the rivers, specific sources were also identified. A higher proportion of DnBP over DEHP was associated with dumping mismanaged plastic waste, specifically single-use plastics and PET bottles. However, the study found that the dominance of DEHP over DnBP at certain sites was associated with their release via domestic and industrial wastewater leading to elevated estrogenic potential in those sites.

Consequently an in-depth study was done in the lower stretch of River Ganga i.e., the Hooghly river estuary on the distribution, sources, and fate of PAEs (Mukhopadhyay and Chakraborty 2021). Surface water and stormwater concentrations of seven plasticizers varied between 92.62 and 770 ng/L and 120.9 and 781.5 ng/L, respectively. It is noteworthy that with the increase in salinity, a decreasing trend for DEHP was evidenced and was associated with "salting out" effect. Like River Ganga, the main source of PAEs in River Hooghly was the unregulated disposal of plastic waste. Net diffusive flux based on fugacity fraction showed that sediment was acting as a sink for high-molecular-weight PAEs and a secondary source for low-molecular-weight PAEs.

4 Exposure and Toxicity

Many toxicity studies in laboratory animals have shown detrimental effects of PAEs on reproductive and developmental aspects (Foster 2006, Lapinskas et al. 2005). Furthermore, recent studies have also suggested a possible association between PAE exposure and adverse health effects on humans (Han et al. 2014, Wang et al. 2016). However, still, there is a dearth of knowledge on the toxicological studies of PAEs in humans. PAEs are known as xenoestrogens as they interact with the endocrine signalling as ligands of transcription factors residing in the nucleus. PAEs and their monoesters were observed to have stronger interactions with receptors than their natural agonists for xenobiotic metabolism (Sarath Josh et al. 2014). Consequently, the endocrine-disrupting effect of PAEs can lead to altered reproductive and neural development, sex anomalies, endometriosis, fertility issues, cancer, obesity, and insulin resistance (Benjamin et al. 2017). In addition, environmental quality standards for various PAEs were decided due to the ecotoxicological effect of PAEs on flora and fauna. The European Union has proposed 1.3 μg/L in the aquatic environment, including both freshwater and marine ecosystems (EU 2013). On the other hand, for 80% protection of freshwater species, Australia and New Zealand guidelines proposed a value of 5.1 mg/L for DMP, 1.3 mg/L for DEP, and 0.064 mg/L for DnBP and BBP (Australian and New Zealand Environment and

Conservation Council 2000). The environmental risk limit (ERL) for DnBP and DEHP is set at 1.82 mg/kg and 1 mg/kg for natural sediments (Wezel et al. 2000). While the no observed effect concentration (NOEC) for DnBP, BBP, DnOP, and DEHP is set at 2.2 mg/kg, 0.049 mg/kg, 0.58 mg/kg, and 0.47 mg/kg, respectively, in riverine sediments (Net et al. 2015). USEPA has also recommended reference doses for a few PAEs such as DEP (800 μg/kg bw/d), DnBP (100 μg/kg bw/d), DEHP (20 μg/kg bw/d), and BBP (200 μg/kg bw/d). (USEPA 1987a, 1987b, 1987c, 1989).

Major exposure routes for PAE exposure to humans are food (growth, processing, storage, and packaging) (Chakraborty et al., 2022; Yang et al. 2019), indoor air (Sakhi et al. 2019), drinking water (Amiridou and Voutsa 2011), and dermal contact due to personal care products (Gao and Kannan 2020). It is noteworthy that in developing economies, PET bottles made of recycled plastic can be a potential source of PAEs (Mukhopadhyay et al 2022). PAEs are chemically transformed into two distinct phases before elimination (urine, sweat, and feces). First, hydrophobic PAEs are hydrolyzed by esterase or lipase to form a more hydrophilic compound (monoesters) which is then subsequently transformed into sulpho- or gluco-conjugates and excreted (Kim and Park 2014, Latini et al. 2004). Biomonitoring of contaminants serves as an important tool to study exposure assessment. For PAEs, biomonitoring of urine, blood, milk, serum, and hair has been carried out so far. In the USA, levels of BBP and DEHP in hand wipe mass and dust had a significant correlation with their corresponding metabolites in children's urine (age 3–6 years). Significantly, higher PAE metabolites present in urine samples of humans residing in houses with vinyl flooring than those without vinyl flooring indicated, higher PAE exposure associated with flooring materials (Hammel et al. 2019). Furthermore, a study on biomonitoring of the Norwegian population of using urine as biomarker and exposure source, found that major routes for PAEs in adults were associated with personal care products (shower gel, hand cream, toothpaste, cream, and shaving products) in both male and female (Husøy et al. 2019). Blood has become the ideal matrix for biomonitoring since it comes in contact with every body organ. Phthalates level in blood serum and breast development in girls from Puerto Rica revealed significantly higher levels in serum, indicating possible adverse effects on human development (Colón et al. 2000). A study on the association of PAEs and blood pressure in the Chinese population revealed that higher DEHP exposure might be related to an increase in systolic blood pressure, whereas higher DMP might be related to increased cholesterol in blood serum (Zhang et al. 2018).

Similarly, elevated urinary level of DEHP was also associated with increased systolic blood pressure in children (Trasande and Attina 2015, Trasande et al. 2013). In addition, levels of eight PAE metabolites on blood and semen samples from a recent study in China varied between 2.7 and 55 and 0.99 and 17 ng/mL, respectively, with MEHP and MnOP being the predominant metabolites (Song et al. 2020). To study the effect of lifestyle choices on the body burden of PAEs, Kim et al. (2020) studied their association by using human breast milk as a biomonitoring tool. Metabolite of DnBP (MnBP), DiBP (MiBP), DEHP (MEHP), DEP (MEP), and BBP (MBP) in breast milk was associated with the usage of air freshener, recent purchase (<1 year) of furniture, regular fish consumption, and use of plastic food containers, respectively. Even though there have been studies on the adverse effect of PAE exposure, there still lies an immense gap in the rules and regulations pertaining to this compound.

5 Conclusion

Asia has 47% of the global average of freshwater per person and has 65% of the world's population. Asia has the fastest growing economy as well as the largest continental economy leading to widespread plastic usage and subsequent increase in pollution levels. Endocrine-disrupting compounds such as PAEs were found to be ubiquitous in the freshwater ecosystem of major Asian countries like India and China. Elevated levels of PAEs in aqueous environments have been found to be mainly associated with wastewater discharge and mismanaged plastic waste in both India and China. An overall dominance of DEHP and DnBP was seen in the surface water ecosystem of these countries based on other studies conducted previously. Despite having a higher number of source points in perennial river systems, the rain-fed rivers were seen with higher concentrations of PAEs which could be due tolesser dilution factors. Among the various rivers in the two countries, the Yangtze River in China was seen with the highest levels of PAEs. Coincidentally, the Yangtze River was termed as the most polluting river in Asia in terms of plastic input into oceans. Fugacity-based sediment-water fluxes indicated that for low-molecular-weight PAEs, sediment can act as a secondary emission source, whereas for high-molecular-weight PAEs, it acts as a sink. Further a host of adverse human health impacts were found to be arising out of an increased exposure to PAEs both in adults and children across the globe, highlighting the need for more intensive monitoring studies as well as stricter regulations on these chemicals in the future.

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References

Adeniyi AA, Okedeyi OO, Yusuf KA (2011) Flame ionization gas chromatographic determination of phthalate esters in water, surface sediments and fish species in the Ogun river catchments, Ketu, Lagos. Nigeria Environ Monitor Assess 172(1–4):561–569

Amiridou D, Voutsa D (2011) Alkylphenols and phthalates in bottled waters. J Hazard Mater 185(1):281–286

ATSDR (2019) Agency for toxic substances and disease registry, "ATSDR's Substance Priority List". Available at https://www.atsdr.cdc.gov/spl/index.html. Accessed 2 Aug 2021

Australian and New Zealand Guidelines for Fresh and Marine Water Quality. PAPER No.4, Volume 1, The Guidelines (Chapters 1−7), October 2000. Available at: https://www.waterquality.gov.au/sites/default/files/documents/anzecc-armcanz-2000-guidelinesvol1. pdf ; Accessed on 24th February 2022

Benjamin S, Masai E, Kamimura N, Takahashi K, Anderson RC, Faisal PA (2017) Phthalates impact human health: epidemiological evidences and plausible mechanism of action. J Hazard Mater 340:360–383

Chakraborty P, Mukhopadhyay M, Sampath S, Ramaswamy BR, Katsoyiannis A, Cincinelli A, Snow D (2019) Organic micropollutants in the surface riverine sediment along the lower stretch of the transboundary river Ganga: occurrences, sources and ecological risk assessment. Environ Pollut 249:1071–1080

Chakraborty P, Shappell NW, Mukhopadhyay M, Onanong S, Rex KR, Snow D (2021) Surveillance of plasticizers, bisphenol A, steroids and caffeine in surface water of River Ganga and Sundarban wetland along the Bay of Bengal: occurrence, sources, estrogenicity screening and ecotoxicological risk assessment. Water Res 190:116668

Chakraborty P, Bharat GK, Gaonkar O, Mukhopadhyay M, Chandra S, Steindal EH, Nizzetto L (2022) Endocrine-disrupting chemicals used as common plastic additives: Levels profiles and human dietary exposure from the Indian food basket. Sci Total Environ 810152200-10.1016/j.scitotenv.2021.152200

Chen H, Mao W, Shen Y, Feng W, Mao G, Zhao T, Yang L, Yang L, Meng C, Li Y (2019) Distribution, source, and environmental risk assessment of phthalate esters (PAEs) in water, suspended particulate matter, and sediment of a typical Yangtze River Delta City. China Environ Sci Pollut Res 26(24):24609–24619

Colón I, Caro D, Bourdony CJ, Rosario O (2000) Identification of phthalate esters in the serum of young Puerto Rican girls with premature breast development. Environ Health Perspect 108(9):895–900

Cousins I, Mackay D (2000) Correlating the physical–chemical properties of phthalate esters using the ‘three solubility’ approach. Chemosphere 41(9):1389–1399

EU 2013; DIRECTIVE 2013/39/UE DU PARLEMENT EUROPÉEN ET DU CONSEIL, Available at: https://eurlex. europa.eu/legal-content/fr/TXT/?uri=CELEX:32013L0039, Accessed on: 29th January 2022.

Foster PM (2006) Disruption of reproductive development in male rat offspring following in utero exposure to phthalate esters. Int J Androl 29(1):140–147

Gao D, Zhe L, Zhidan W, Nanqi R (2014) Occurrence and fate of phthalate esters in full-scale domestic wastewater treatment plants and their impact on receiving waters along the Songhua River in China. Chemosphere 9524-32 10.1016/j.chemosphere.2013.08.009

Gao C-J, Kannan K (2020) Phthalates, bisphenols, parabens, and triclocarban in feminine hygiene products from the United States and their implications for human exposure. Environ Int 136:105465

Godwin AD (2017) Applied plastics engineering handbook. Elsevier, pp 533–553

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

Hammel SC, Levasseur JL, Hoffman K, Phillips AL, Lorenzo AM, Calafat AM, Webster TF, Stapleton HM (2019) Children’s exposure to phthalates and non-phthalate plasticizers in the home: the TESIE study. Environ Int 132:105061

Han X, Cui Z, Zhou N, Ma M, Li L, Li Y, Lin H, Ao L, Shu W, Liu J (2014) Urinary phthalate metabolites and male reproductive function parameters in Chongqing general population, China. Int J Hyg Environ Health 217(2–3):271–278

He M-J, Lu J-F, Wang J, Wei S-Q, Hageman KJ (2020) Phthalate esters in biota, air and water in an agricultural area of western China, with emphasis on bioaccumulation and human exposure. Sci Total Environ 698:134264

Husøy T, Andreassen M, Hjertholm H, Carlsen MH, Norberg N, Sprong C, Papadopoulou E, Sakhi AK, Sabaredzovic A, Dirven H (2019) The Norwegian biomonitoring study from the EU project EuroMix: levels of phenols and phthalates in 24-hour urine samples and exposure sources from food and personal care products. Environ Int 132:105103

Jambeck, J. R., Geyer, R., Wilcox, C., Siegler, T. R., Perryman, M., Andrady, A., & Law, K. L. (2015). Plastic waste inputs from land into the ocean. Science, 347(6223), 768–771.

Keizer-Schrama S, Main K, Swan S, Foster P, Jensen A (2006) Possible impact of phthalates on infant reproductive health-discussion, Blackwell Publishing 9600 Garsington Rd, Oxford OX4 2DQ, Oxon, England

Kim SH, Park MJ (2014) Phthalate exposure and childhood obesity. Annal Pediatr Endocrinol & Metab 19(2):69

Kim JH, Kim D, Moon S-M, Yang EJ (2020) Associations of lifestyle factors with phthalate metabolites, bisphenol A, parabens, and triclosan concentrations in breast milk of Korean mothers. Chemosphere 249:126149

Lapinskas PJ, Brown S, Leesnitzer LM, Blanchard S, Swanson C, Cattley RC, Corton JC (2005) Role of PPARα in mediating the effects of phthalates and metabolites in the liver. Toxicology 207(1):149–163

Latini G, Verrotti A, De Felice C (2004) Di-2-ethylhexyl phthalate and endocrine disruption: a review. Curr Drug Target-Immune Endocr & Metab Disorder 4(1):37–40

Lebreton LC, Van Der Zwet J, Damsteeg J-W, Slat B, Andrady A, Reisser J (2017) River plastic emissions to the world's oceans. Nat Commun 8:15611

Li R, Liang J, Gong Z, Zhang N, Duan H (2017) Occurrence, spatial distribution, historical trend and ecological risk of phthalate esters in the Jiulong River, Southeast China. Sci Total Environ 580:388–397

Liang, Y., Tan, Q., Song, Q., & Li, J. (2021). An analysis of the plastic waste trade and management in Asia. Waste Management, 119, 242–253. doi:10.1016/j.wasman.2020.09.049

Liu X, Shi J, Bo T, Zhang H, Wu W, Chen Q, Zhan X (2014) Occurrence of phthalic acid esters in source waters: a nationwide survey in China during the period of 2009–2012. Environ Pollut 184:262–270

Lyman W (1990) Octanol/water partition coefficient. In: Handbook of chemical property estimation methods: environmental behavior of organic compounds. American Chemical Society, Washington, DC. 1990. p 1. 1–1. 54. 1 fig, 11 tab, 48 ref.

Marcilla A, Beltran M (2004) Mechanisms of plasticizers action. Handbook of Plasticizers:107–120

Mukhopadhyay M, Chakraborty P (2021) Plasticizers and bisphenol A: emerging organic pollutants along the lower stretch of River Ganga, north-east coast of the Bay of Bengal. Environ Pollut 276:116697

Mukhopadhyay M, Jalal M, Vignesh G, Ziauddin M, Sampath S, Bharat GK, Nizetto L, Chakraborty P (2022) Migration of Plasticizers from Polyethylene Terephthalate and Low-Density Polyethylene Casing into Bottled Water: A Case Study From India ; In Press - Bulletin of Environmental Contamination and Toxicology

Müller A, Österlund H, Nordqvist K, Marsalek J, Viklander M (2019) Building surface materials as sources of micropollutants in building runoff: a pilot study. Sci Total Environ 680:190–197

Navarro R, Perrino MP, García C, Elvira C, Gallardo A, Reinecke H (2016) Opening new gates for the modification of PVC or other PVC derivatives: synthetic strategies for the covalent binding of molecules to PVC. Polymers 8(4):152

Net S, Delmont A, Sempéré R, Paluselli A, Ouddane B (2015) Reliable quantification of phthalates in environmental matrices (air, water, sludge, sediment and soil): a review. Sci Total Environ 515:162–180

Ramzi A, Gireeshkumar T, Rahman KH, Balachandran K, Shameem K, Chacko J, Chandramohanakumar N (2020) Phthalic acid esters – a grave ecological hazard in Cochin estuary. India Mar Pollut Bull 152:110899

Sakhi AK, Cequier E, Becher R, Bølling AK, Borgen AR, Schlabach M, Schmidbauer N, Becher G, Schwarze P, Thomsen C (2019) Concentrations of selected chemicals in indoor air from Norwegian homes and schools. Sci Total Environ 674:1–8

Sarath Josh M, Pradeep S, Adarsh V, Vijayalekshmi Amma K, Sudha Devi R, Balachandran S, Sreejith M, Abdul Jaleel U, Benjamin S (2014) In silico evidences for the binding of phthalates onto human estrogen receptor α, β subtypes and human estrogen-related receptor γ. Mol Simul 40(5):408–417

Selvaraj KK, Sundaramoorthy G, Ravichandran PK, Girijan GK, Sampath S, Ramaswamy BR (2015) Phthalate esters in water and sediments of the Kaveri River, India: environmental levels and ecotoxicological evaluations. Environ Geochem Health 37(1):83–96

Shen H-Y (2005) Simultaneous screening and determination eight phthalates in plastic products for food use by sonication-assisted extraction/GC–MS methods. Talanta 66(3):734–739

Song X, Zhuo Q, Tang S, Xie T, Chen Z, Zang Z, Zhang Y, Niu X, Yin H, Zeng F (2020) Concentrations of phthalates metabolites in blood and semen and the potential effects on semen concentration and motility among residents of the Pearl River Delta region in China. Emerg Contam 6:39–43

Trasande L, Attina TM (2015) Association of exposure to di-2-ethylhexylphthalate replacements with increased blood pressure in children and adolescents. Hypertension 66(2):301–308

Trasande L, Sathyanarayana S, Spanier AJ, Trachtman H, Attina TM, Urbina EM (2013) Urinary phthalates are associated with higher blood pressure in childhood. J Pediatr 163(3):747-753. e741

USEPA, 2014. Risk Management for Phthalates. United States Environmental Protection Agency Available at: https://www.epa.gov/assessing-and-managing-chemicals-undertsca/ risk-management-phthalates. (Accessed 7 November 2021).

USEPA (1987a) Di(2-ethylhexyl)phthalate (DEHP); CASRN 117-81-7; Available at: https://cfpub.epa.gov/ncea/iris2/chemicalLanding.cfm?substance_nmbr=14; Accessed on: 24th February 2022. Integrated Risk Information System (IRIS), U.S. Environmental Protection Agency.

USEPA (1987b) Dibutyl phthalate; CASRN 84-74-2; Available at: https://iris.epa.gov/ChemicalLanding/substance_nmbr=38; Accessed on: 24th February 2022. Integrated Risk Information System (IRIS), U.S. Environmental Protection Agency.

USEPA (1987c) Diethyl phthalate; CASRN 84-66-2, Available at: https://cfpub.epa.gov/ncea/iris2/chemicalLanding.cfm? substance_nmbr=226; Accessed on: 24th February 2022. Integrated Risk Information System (IRIS), U.S. Environmental Protection Agency.

USEPA (1989) Butyl benzyl phthalate; CASRN 85-68-7; Available at: https://cfpub.epa.gov/ncea/iris2/chemicalLanding.cfm? substance_nmbr=293; Accessed on: 29th January 2022. Integrated Risk Information System (IRIS), U.S. Environmental Protection Agency.

Wang F, Xia X, Sha Y (2008) Distribution of phthalic acid esters in Wuhan section of the Yangtze River. China J Hazard Mater 154(1–3):317–324

Wang Y-X, Zeng Q, Sun Y, You L, Wang P, Li M, Yang P, Li J, Huang Z, Wang C (2016) Phthalate exposure in association with serum hormone levels, sperm DNA damage and spermatozoa apoptosis: a cross-sectional study in China. Environ Res 150:557–565

Weizhen Z, Xiaowei Z, Peng G, Ning W, Zini L, Jian H, Zheng Z (2020) Distribution and risk assessment of phthalates in water and sediment of the Pearl River Delta. Environ Sci Pollut Res:1–16

Wezel, Van A. P.; Van Vlaardingen, P.; Posthumus, R.; Crommentuijn, G. H.; Sijm, D. T. H. M. Environmental risk limits for two phthalates, with special emphasis on endocrine disruptive properties. Ecotoxicol. Environ. Saf. 2000, 46 , 305−321

Xie Z, Ebinghaus R, Temme C, Lohmann R, Caba A, Ruck W (2007) Occurrence and air–sea exchange of phthalates in the Arctic. Environ Sci Technol 41(13):4555–4560

Yang J, Song W, Wang X, Li Y, Sun J, Gong W, Sun C (2019) Migration of phthalates from plastic packages to convenience foods and its cumulative health risk assessments. Food Additi & Contam: Part B 12(3):151–158

Zhang S-H, Shen Y-X, Li L, Fan T-T, Wang Y, Wei N (2018) Phthalate exposure and high blood pressure in adults: a cross-sectional study in China. Environ Sci Pollut Res 25(16):15934–15942

Optical Techniques for Monitoring Persistent Organic Pollutants in Water and Wastewater

Prachi Rajput, Paromita Chakraborty, and Pooja Devi

Abstract Persistent organic pollutants (POPs) are a class of pollutants which possess characteristics like long-range transport leading to global pollution, non-biodegradability, and most importantly lipophilicity. They get deposited in the fatty tissues in the living organisms and are thus reported to have high levels in the food chain. Stockholm Convention initially listed 12 pollutants as POPs categorized under pesticides (chlordane, DDT, dieldrin, endrin, heptachlor, hexachlorobenzene (HCB), mirex and toxaphene), industrial chemicals (hexachlorobenzene and polychlorinated biphenyls (PCBs)), and by-products (HCB, polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/PCDF), and PCBs) on the basis of their origin. Further, 18 more new POPs have been added to the Stockholm Convention list including polybrominated diphenyl ethers (PBDEs), hexachlorocyclohexane, lindane, etc. In order to handle these harmful pollutants, their detection is a vital step, for which various analytical techniques have been developed. The current chapter mainly deploys the information about the various optical techniques such as surface-enhanced Raman scattering (SERS), fluorescence, absorbance, etc., which have found their applications in POP detection in water and wastewater. This chapter will also discuss about the implementation of these techniques for quantification of POPs in wastewater streams and e-waste recycling sites.

Keywords POPs · Water · Wastewater · Optical techniques · Detection of POPs · GC-MS · HPLC · SERS · Fluorescence · Photochemical · Fiber-optic sensor

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1 Introduction to Persistent Organic Pollutants

The upsurge of organic and inorganic pollutants in the environment including soil, water, and air has raised a global concern. Among them, there are certain chemical pollutants which are able to stay in the environment for long time and are therefore termed as persistent organic pollutants (POPs) (Peng et al. 2018). POPs are identified to be of anthropogenic origin due to agricultural (pesticides, herbicides, fungicides, etc.) and industrial (flame retardants, preserving agents, etc.) activities (Peng et al. 2018). They resist chemical, photolytic, and biological degradation and hence can remain intact for exceedingly longer periods of time in the environment (El-Shahawi et al. 2010). Due to long persistent characteristics and bio-accumulating behavior, POPs are also contemplated as silent killers. They can be found in every segment of the environment affecting animals, plants, and human beings.

POPs are mainly classified under four categories (Fig. 1) including polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), polybrominated diphenyl ethers (PBDEs), and organochlorine pesticides (OCPs) (Liu et al. 2017a). The source of PBDEs is generally expected to be originated from commercial deca-BDE mixtures widely used as flame retardants, whereas PAHs were expected to originate from pyrolytic sources with small portion of petrogenic origin and have high molecular weight. Although OCPs are banned by WHO, their presence can be known to originate from historical use and is mainly of industrial origin (Liu et al. 2017a).

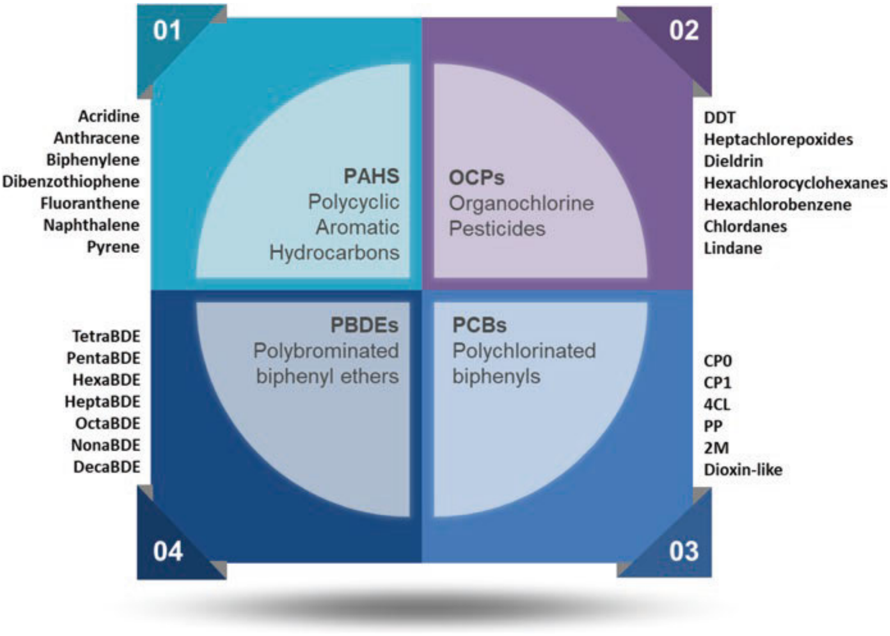

Fig. 1 Classification of POPs

In PCB category, there are a total of 209 PCB congeners named on the basis of the number of chlorine substituents present in the molecule in ascending order (USEPA 2003). The subcategories of the congeners comprise of co-planar, 4CL, PP, 2 M, and dioxin-like. The 68 co-planar congeners can be divided into 20 CP0 congeners having non-ortho-chlorine substitution and 48 CP1 congeners having mono-ortho-chlorine substitution. Further, there are 169 4CL congeners which have a total of four or more chlorine substituents regardless of position. PP congeners are 54 in number and classified on the basis of the chlorination on both para positions. The 140 2 M congeners have the chlorination at two or more of the meta positions. Those congeners that display all the four descriptors (CP0/CP1, 4CL, PP, and 2 M) are termed to be dioxin-like and are 12 in number (USEPA 2003).

Likewise, PBDEs are the class of POPs that differ in the position and number of bromine atoms attached ($n = 1–10$) but comprise an identical base structure (UNEP 2012; NRC 1983). They are generally synthetically produced mixtures and have ten congeners groups and total of 209 individual congeners, namely, monoBDE (3), diBDE (12), triBDE (24), tetraBDE (42), pentaBDE (46), hexaBDE (42), heptaBDE (24), octaBDE (12), nonaBDE (3), and decaBDE (1) (UNEP 2012; NRC 1983). PCBs, PBDEs, PAHs, and OCPs can further be classified on the basis of their origin/application. The OCPs are basically insecticides, herbicides, rodenticides, bactericides, fungicides, and larvicides used in agricultural applications in preventing insects, plants, rats, bacteria, fungi, and larvae, respectively. PCBs and PBDEs are industrial chemicals where PCBs are often utilized as heat exchange fluids in capacitors and electric transformers and also as protective coatings, whereas PBDEs are the commercial chemicals used as flame retardants. PCBs and PBDEs mostly enter the environmental matrix on burning constituent material and dismantling e-waste which is a major source. On the contrary, PAHs have a natural origin and are present in wood and fuel oil. But they enter the environment only on incomplete burning of these source materials (Haffner and Schecter 2014).

These POPs have found their ways into water bodies through direct or indirect discharge (Barletta et al. 2019). Among natural aquifers, estuaries are one of the most affected habitats which can inflict lasting modifications in the environment. The estuarine pollution leads to alterations in nutrient loads and increased consumption of dissolved oxygen (Barletta et al. 2019). Among various POPs, pesticide residues have a massive contribution in the environmental pollution, which is due to the excessive use of pesticides in the agricultural industry (Yadav et al. 2015). But recently, the most prominent one that is making their presence in water resources are POPs emitted from e-waste recycling sites. E-waste disposal and management has become a great challenge currently by virtue of frequent technological development. The major production of POPs takes place when the illegal and improper recycling of the e-waste is done (Jamieson et al. 2017). During the recycling, the waste is either burnt or undergoes acid bath treatment for extracting the precious metals from the circuits and other required parts of it. As a result, POPs released in this process make their way into water, soil, and air. POPs released into the environment are mostly a result of anthropogenic activities, and their influence is evident even in the remote and inaccessible habitats on earth. Their level is considerably high, and these have pervaded to the depth of the oceans (Jamieson et al. 2017). POPs are present even in the snow from European high mountain areas and also in the gas phase of the atmosphere (Carrera et al. 2001). For example, POPs like PCB and hexachlorohexanes (HCH) were found in much higher concentration than the detection limit of the method applied, and the less chlorinated PCBs congeners were found to be predominantly distributed in the studied European high mountain snow areas (Carrera et al. 2001). Distribution studies of PAHs and PCBs in freshwater systems have revealed that their distribution depends extremely on their physicochemical properties (Rabodonirina et al. 2015). PAHs with low molecular weights were found in dissolved state, and those with high molecular weight preferentially accumulated in the suspended solid matter. The presence of the PCB congener in freshwater systems showed that the occurrence of these pollutants was predominantly from combustion processes (Rabodonirina et al. 2015). Moreover, e-waste recycling or disassembly also highly accounts for the bio-transfer of POPs (Zhao et al. 2006). The studies of river water, paddy soil, groundwater, river sediment, fish, rice seeds, hen eggs, newborn meconium, and umbilical cord blood collected from e-waste recycling sites found the presence of toxic PCBs and organochlorine pesticides (OCPs). The preliminary studies also disclosed that these wastes can be a major source of emission of POPs into the local environment through evaporation, leakage, leaching, and runoffs (Zhao et al. 2006). Several pesticides were also found in higher concentration in European groundwater samples which also exceeded the European quality standard for groundwater value of 0.1 μg/L for pesticides (Loos et al. 2010).

1.1 Health Impacts of POPs

Owing to the persistent nature of POPs, they exhibit high ecological toxicity (Alharbi et al. 2018). Long-term exposure of POPs can give rise to various health hazards such as cancer, diabetes, endocrine disturbance, obesity, and reproductive and cardiovascular problems (Alharbi et al. 2018). For example, PCB congeners are associated with different health issues in adults and prenatal and postnatal infant growth (Iszatt et al. 2015). The higher chlorinated PCBs are involved in the increased abdominal obesity in seniors, whereas an inverse relation is shown by the lower chlorinated PCBs. Although there is no significant involvement of PCBs with the prenatal infant growth, it could cause impaired postnatal growth in breastfed infants (Iszatt et al. 2015).

Also, PAHs are one of the highly toxic classes of POPs and mostly exhibit carcinogenic activities. Nearly 85 PAHs compounds and their close chemical relatives have been reported (UNEP 2012; NRC 1983). Moreover, in a survey conducted by the European commission, it was found that some compounds like bisphenol A (BPA) and nonylphenol were found in groundwater samples in un-attenuated form. BPA and nonylphenol are not technically considered as POPs due to their short half-lives, but these are moderately bio-accumulative and do not readily get degraded

(Haffner and Schecter 2014). These chemicals are endocrine disruptors and are oftentimes grouped together with other POPs because of their prevalent presence in the environment (Haffner and Schecter 2014).

2 Monitoring of POPs

To protect humankind and environment from POPs, the Stockholm Convention has set up a range of measures with the aim of reducing and eliminating their release into the environment (Magulova and Priceputu 2016). For this, Article 16 sets the basics for the assessment of the effectiveness of its implementation worldwide, and the major pillar for this is monitoring the data received from the Global Monitoring Plan for POPs (Magulova and Priceputu 2016). Hence, the environmental monitoring of these POPs is of prime importance. To conduct this monitoring, various detection techniques are required. The detection techniques already existing for the monitoring of POPs are gas chromatography (GC), liquid chromatography (LC), mass spectrometry (MS), and various other techniques. In this chapter, we will discuss all the techniques for POPs monitoring, and the emphasis will be given on the optical techniques in the POP detection such as Raman spectroscopy, fluorescence, etc.

2.1 Challenges in POP Detection/Monitoring

The detection of POPs is challenging due to their complex structure and similarity (Čajka et al. 2005). For example, brominated flame retardants (BFRs) are chemicals which are extensively utilized in products such as plastics, upholstery, and textiles to prevent fire hazard. However, these PBDEs have structural similarity with PCBs; as a result, they possess similarity in the chemical properties, which in turn makes it difficult to detect them specifically. Thus, the sensitive detection of these pollutants sometimes needs a trade-off between signal intensity and acquisition speed settings in mass spectroscopy (Čajka et al. 2005). Another, most challenging job for an analytical technique is the chiral separation of enantiomers, since several POPs are chiral and they undergo the enantiomeric composition alterations as quickly as they are released into the environment (Eljarrat et al. 2008). The enantiomeric detection of these chiral POPs stands extreme importance as these compounds hold biological activity differences (Eljarrat et al. 2008). The challenge in the monitoring of these pollutants also arises from the reason that the analysis and sampling methods are not synchronized (Geissen et al. 2015). Also, the detection limits of the mostly existing techniques are very high, whereas the toxicity of these compounds is too much even at trace levels. Thus, there is an extreme requirement of highly sensitive analytical techniques for monitoring these pollutants to determine their fate in the environment (Geissen et al. 2015). Due to the absence of proper and extensive emission inventory of these POPs, it becomes challenging to develop controlling and monitoring strategies (Lohmann et al. 2007). The monitoring of POPs having more diverse usage pattern and lifecycle further makes their emission prediction more challenging (Lohmann et al. 2007). Therefore, the increment in the number of the compounds included in the existing monitoring plans is required along with their sensitive and enlarged detection (Focant 2012). Furthermore, due to lack of standard reference materials for POP analysis in water, it is quite a challenging matrix for monitoring network (Muir and Lohmann 2013). Since POPs are found to occur in trace amounts in water bodies, therefore, to reach the desired quantification, it is forced to work with high sample volumes, and this in turn is a time-consuming process (Lorenzo et al. 2018). Thus, the conventional analytical techniques have challenges associated with them for trace level detection of POPs in particular in water matrix (Lorenzo et al. 2018).

3 Analytical Techniques for POP Detection

Environmental monitoring of POPs is a crucial aspect to be taken. Stockholm Convention has implied a regular monitoring of the environment globally by evaluating the monitoring data from different countries across the world. This section presents the various conventional methods and processes employed in the detection and analysis of POPs (Fig. 2).

3.1 Detection of POPs Using Gas Chromatography (GC)/Mass Spectrometry (MS)

GC has been a preferred technique of choice for environmental sample analysis because of its excellent accuracy, precision, favorable combination of high resolution, selectivity, high sensitivity, and wide dynamic concentration range (Pitarch et al. 2007). Water analysis by GC and MS has been successfully reported using linear quadrupoles. This was the first time when GC-MS with triple quadrupole (QqQ) analyzer was explored in water analysis for various organic pollutants at low concentration levels. In addition to reducing the chemical noise in chromatograms, it is also adequate for the determination of analytes in sub-ppb levels (Pitarch et al. 2007). In this line, a multi-residue process known as stir bar sorptive extraction coupled with thermal desorption GC-MS (SBSE-TD-GC-MS) is developed to quantify 49 organic pollutants including PAHs, nonylphenol, OCPs, polybrominated biphenyl ethers, and PCBs (Sánchez-Avila et al. 2010). The application of this method finds place in the determination of the targeted pollutants in seawater, ports, desalination plant feed water, and coastal areas. It manifests a good linearity with a recovery in between 86% and 118% and standard deviation of 2% and 24% in case

Fig. 2 Various analytical techniques for POP analysis

of all compounds with a sample water volume of 100 ml. The method also provides a LOD between 0.011 and 2.5 ng/L for the pollutants, which is lower than the fixed Environmental Quality Standards (EQS) by the European Commission's Directive 2008/105/EC (Sánchez-Avila et al. 2010). Another such multi-residue method has been testified using pressurized liquid extraction (PLE), thermal desorption, and GC-triple quadrupole MS coupled with stir bar sorptive extraction (SBSE) (Camino-Sánchez et al. 2011). The list of compounds analyzed by this method consists of PCBs, PAHs, PBDEs, OCPs, organophosphorus, and other pesticides like triazines and urons. This is an efficient method having the capabilities of high efficiency and throughput rate due to PLE and exhibits excellent sensitivity by virtue of SBSE along with multi-residual analysis ability. The detection limit of this method is below pg/g (Camino-Sánchez et al. 2011). In order to increase the yield, GC-MS was employed with low-density ultrasound-assisted emulsification microextraction (USAEME) technique for measuring selected PCBs (Yurdakok-Dikmen et al. 2016). The list of PCBs analyzed includes congeners 28, 52, 101, 118, 138, 153, and 180. Different solvents were also tested for their respective yields such as chloroform, hexane, cyclohexane, and isooctane, where 200 μl isooctane validated highest yield for a sample volume of 10 ml. The LOD achieved with the combination was 3–12 ng/l (Yurdakok-Dikmen et al. 2016). Again, a liquid-phase microextraction (LPME) in combination with dual-gauge microsyringe along hollow-fiber membrane (LPME/DGM-HF) is reported in combination with GC/ion trap mass spectrometry (GC/ITMS) (Yan and Wu 2004). This combination provides the advantages of low solvent and sample consumption, ease of use, simplicity, and speed. The viability of this method was tested for the 5 OCPs, namely, 4,4′-DDT, 2,4′-DDD, 4,4′-DDD, Aldrin, and Deldrin (Yan and Wu 2004).

Gas chromatography-electron capture detector (GC-ECD) method is also utilized in evaluating various POPs such as OCPs, PCBs, HCHs, and PBDEs (Ballesteros et al. 2014). The limit of detection of the method for the pollutants in the lake water was between 0.03 and 0.05 ng/ml for HCHs and 0.08 and 0.33 ng/ml for other chlorinated compounds (Ballesteros et al. 2014). A method of magnetic matrix solid-phase dispersion for PCB determination by GC-ECD is also proposed (Diao et al. 2016). The magnetic solid in the method was bamboo charcoal, and the complete separation of the solid magnetic charcoal was obtained by using a permanent magnet. It demonstrated good linearity in 0.006–5.0 μg/l range with a LOD from 0.001 to 0.003 μg/l and a signal-to-noise ratio (SNR) of 3 (Diao et al. 2016). As mentioned earlier in this section that GC is the preferred choice of technique due to its high resolution, several other developments have also been made to improve its efficiency (Van Leeuwen and De Boer 2008). In comparison to the conventional single-column GC, a comprehensive two-dimensional GC gives more information owing to the large volume injection, which in turn improves the detection limits as well. Extraction, sample clean up, and fractionation are very important before performing GC in order to prevent unreliable results; hence, the recent development of PLE is an efficient solution to this. Although the reference materials for PCDD/Fs and PCBs are well established, there is requirement for this to improve in case of BFRs, etc. (Van Leeuwen and De Boer 2008).

3.2 Detection of POPs Using Liquid Chromatography (LC)/High-Pressure Liquid Chromatography (HPLC)/Mass Spectrometry (MS)

The combination of a linear stationary phase and the mobile phase that is liquid chromatography with their evident MS/MS transitions allows the full resolution of most of the isomers (Benskin et al. 2007). A method developed based on this theory of LC-MS/MS demonstrated the separation and detection of perfluorinated acids (PFAs) and their precursor isomers. The linear perfluorooctyl stationary phase and the acidified mobile phase induced elevated separation efficiency (Benskin et al. 2007). In a powerful analytical approach, a combination of LC-QTOF MS and GC-(Q) TOF MS was applied for testing of nearly 1500 organic compounds in ground- and surface water (Pitarch et al. 2016). Nearly 71% of compounds were identified. TOF MS-based approach provided a potential for screening a huge variety of pollutants with different physicochemical characteristics (Pitarch et al. 2016). In SBSE-based method, two stir bar coatings were examined for the simultaneous extraction of polar and non-polar compounds, namely, ethylene glycol-modified silicone (EG-silicone) and polydimethylsiloxane (PDMS) (Aparicio et al. 2017). The method successfully determined 48 target molecules including various preservatives, plasticizers, per fluorinated compounds, flame retardants, and pesticides. The detection was carried out for tap and surface water samples (Aparicio et al. 2017). As perfluorinated compounds don't get completely removed from the wastewater during treatment, they can be easily found in freshwater ecosystems (Mirasole et al. 2016). Owing to their water solubility and poor degradability, they keep on accumulating and contaminating the water systems. As the expected level of these compounds is very low, therefore, a highly sensitive and selective method of detection should be developed. A liquid chromatography-electrospray ionization tandem mass spectrometry (LC-ESI-MS/MS) method has been demonstrated for determination of such pollutants. This method is capable of the chromatographic separation of analytes in less than 6 minutes of time. The level of measurements of the compounds was achieved at ng/l (Mirasole et al. 2016). A new and rapid detection method for DDT is also described for environmental water samples (Zhou et al. 2009). This method is based on dispersive liquid liquid microextraction (DLLME) and HPLC in combination with ultraviolet detector. This method has several beneficial characteristics such as low cost, ease of operation, sensitivity, and high enrichment factor. The proposed method exhibited the detection in the range of 0.32–0.51 μg/l (Zhou et al. 2009).

3.3 Other Techniques for Detection of POPs

There are several additional steps or methods which when added to the existing methods can incorporate improvements in detection of POPs. Various such techniques are being discussed in the following section. Techniques such as adsorption, micromotors, and solvent extraction can be utilized as pre-concentration or pretreatment methods.

(a) **Adsorption**

In the adsorption of pesticides, distribution coefficient (K_{OW}) has a decisive action among all the important physical properties such as vapor pressure, solubility, Henry's constant, etc. (Ratola et al. 2003). Activated carbon has been used as an efficient adsorbent for a long time. In order to replace activated carbon in removal of OCPs such as lindane and heptachlor, a natural adsorbent such as the pine bark is utilized. The average removal efficiency obtained was 80.6% for lindane and 93.6% for heptachlor (Ratola et al. 2003). Floating marine plastic debris also functions as a solid-phase extraction media and adsorbs pollutants out of water (Rios et al. 2010). This debris was analyzed for various POPs like 36 PCBs, 17 OCPs, and 16 PAHs, where the range of concentration of these pollutants was observed to be a few ppb to thousands of ppb. Most plastic particles found were polyethylene as these are resistant to degradation and remained on or near ocean surfaces (Rios et al. 2010). Magnetic nanoparticles are one of the most important nanoparticle groups which have 7 times higher capacity of pollutants' removal in comparison to the coarse-grained counterparts (Ul-Islam et al. 2017).

Nanoparticles have extended applications in various fields and analytical techniques due to their versatile properties (Liu et al. 2011). They have emerged as important materials in detection and remediation of environmental pollutants. They possess unique features like high surface area, small size, absorptivity, photocatalytic, and photoelectronic properties (Liu et al. 2011). Therefore, multi-walled carbon nanotubes have been utilized as solid-phase extraction (SPE) adsorbents for the pollutant's pre-concentration (Zhou et al. 2006). These were examined for DDT, DDE, and DDD at trace level and received an extraordinarily high recovery of 89.7% to 115.5%; hence, they could serve as an excellent coupling material with HPLC for routine monitoring of DDT and its metabolites (Zhou et al. 2006). 3-D porous single crystalline ZnO nanosheets were utilized for the detection of POP stimulants by coupling with chromatography column. The separation of Furan and chlorobenzene was easily carried by this experimental apparatus (Hou et al. 2015).

(b) **Micromotors**

Micro/nanomotors are self-propelled synthetic machines, which are capable of converting varied energy sources into motion simultaneously (Ying and Pumera 2019). They can also serve ingenious environmental applications. These micromotors can carry out water purification by their catalytic or chemical surface to mitigate the pollutants faster by rapidly zooming through the solution (Ying and Pumera 2019). For example, reduced graphene oxide (rGO)-coated Silica (SiO_2)-Pt Janus magnetic micromotors were applied for the disposition of PBDEs and triclosan (Orozco et al. 2016). These magnetic micromotors rapidly moved in the contaminated solution and adsorbed POPs in a very short span of time. These can be considered as outstanding materials for effective environmental remediation of such toxic contaminants (Orozco et al. 2016). Likewise, novel Mg/Au Janus micromotors were employed in the degradation of diphenyl phthalate (Rojas et al. 2016). These micromotors increase fluid transport; by the virtue of which, the analytical signal dramatically improves while increasing the sensitivity and lowering the detection potential. This approach exhibits a recovery of ~100% and is very fast (~5 min). The micromotors-based technology provides additional advantages of portability, disposability, and possibility of carrying multiple analyses simultaneously (Rojas et al. 2016). Various improvements and developments have been attempted in micromotor applications in the context of improved speed, better material, efficiency, sensitivity, reusability, and inexpensiveness (Zarei and Zarei 2018). Several materials have been utilized in micromotors for their applications in POP remediation, decontamination, degradation, or disposition such as Pd/Ti/Fe/Cr, rGO/γ-Fe_2O_3/SiO_2-Pt, activated carbon/Pt, polymer/Pt, and Ag/Fe_3O_4/TiO_2. This method provides various benefits and requires a lot of developments for effective environmental remediation and monitoring (Zarei and Zarei 2018).

(c) **Solvent Extraction**

In environmental monitoring, modern clean up procedures and passive sampler technology are widely used in combination with analytical techniques (Wenzel et al. 2004). Dialysis method has its application on both of these areas. As dialysis is very long and a time-taking method, thus, the implementation of pressurized liquid extraction (PLE) has been implemented for achieving remarkable results. Accelerated solvent extraction (ASE) is one type of PLE and has been internationally utilized for about the last two decades (Wenzel et al. 2004). A simple and novel microwave-assisted solvent extraction (MASE) and liquid-phase microextraction (LPME) using hollow-fiber membrane analytical method for POP quantification has also been developed (Basheer et al. 2005). The detection limit for each of the POPs (OCPs and PCBs) by utilizing this method was in the range of 0.07–0.70 ng/g. This study included analysis of eight PCBs (PCB 1, 5, 29, 47, 98, 154, 171, and 200), congeners, and 12 OCPs (α-HCH, lindane, β-HCH, heptachlor, aldrin, dieldrin, endrin, endosulfan, *p,p'*-DDD, *p,p'*-DDT, endrin aldehyde, and methoxychlor) (Basheer et al. 2005).

4 Optical Techniques for POP Detection

The increasing number of pollutants has raised a demand of innovative analytical devices for field usage (Long et al. 2013). These techniques need to meet the requirements such as precision, sensitivity, specificity, rapidity, robustness, and easy usage. Optical techniques are seen as a strong alternative to the conventional analytical techniques. These techniques provide advantages over the conventional ones such as high-frequency monitoring, high sensitivity, and real-time monitoring and involve no tedious sample preparation (Long et al. 2013). For broad spatial synoptic coverage in monitoring aquatic habitats like ocean surfaces, etc., there is requirement of remote sensing techniques (Zielinski et al. 2009). These remote sensing (RS) methods are usually constructed on electronic, optical, or chemical techniques. There are a lot of improvements employed and yet to be implied for overcoming the different limitations of optical techniques currently in action. Remote sensing is also difficult when the pollutant is present in trace amount. The implication of the particular optical technique depends on the optical properties of the respective analyte. The optical techniques involved in water quality monitoring can be fluorescence based, photochemical techniques, and surface-enhanced Raman scattering (SERS) (Zielinski et al. 2009). Recently, developments in optical components have created application of new techniques like plasmonic sensors (Patrizi et al. 2019). These sensors exhibit good selectivity and sensitivity with a shorter detection time period. Among all the optical techniques, SERS is one of the most employed techniques providing highly sensitive detection (Patrizi et al. 2019).

Optical techniques are the techniques which predominantly utilize light to probe or control matter. This section specifically describes the different optical techniques which manifest their applications in the detection and analysis of the POPs (Fig. 3). The aspects of these techniques including their required developments are being discussed in this section.

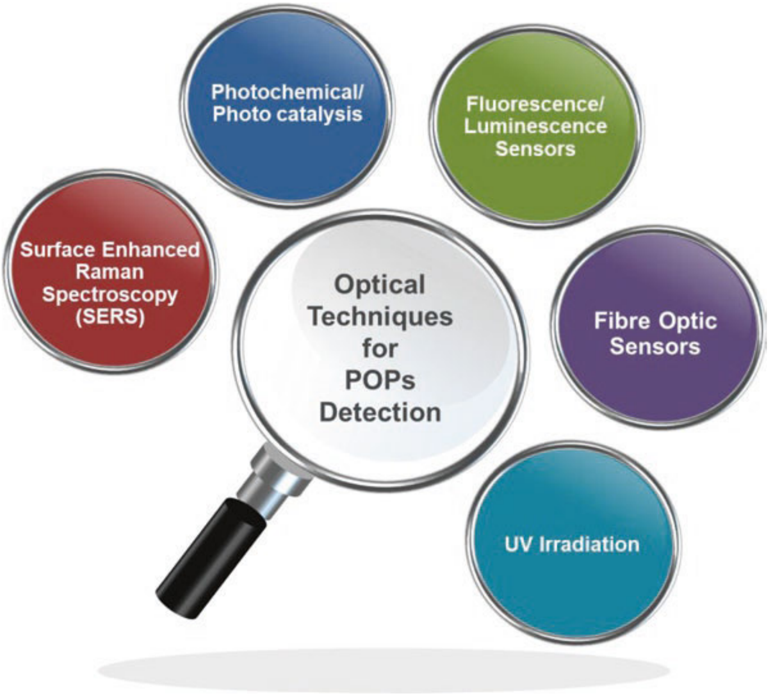

Fig. 3 Various optical techniques for detection/analysis of POPs

4.1 Surface-Enhanced Raman Spectroscopy (SERS)

SERS has attracted a lot of attention in the area of chemical analysis and environmental monitoring for the past two decades. The limit of detection with SERS has reached single molecule proving it to be a highly sensitive technique. Ag nanoparticle-modified Fe_3O_4@carbon shell microspheres were fabricated for the detection of pentachlorophenol (PCP), trinitrotoluene (TNT), and diethylhexyl phthalate (DEHP) (An et al. 2012). These POP compounds represent typically low SERS activities. The application of the aforementioned SERS substrate contributed to the pre-concentration of the analyte molecules near Ag-NP surface and enabled their efficient detection (An et al. 2012). Another label-free and sensitive method combining SERS and magnetomotive enrichment was proposed for the detection of PCB77 and 2,4,6-trinitrotoluene (Bao et al. 2014). The ferromagnetic Fe_3O_4 microspheres modulate optical property of AgNPs by controlling the geometric arrangement on the surface of the fabricated substrate by exerting external magnetic field. The limit of detection for both POP compounds was estimated to be 10^{-7} M (Bao et al. 2014). The detection of OCPs (endosulfan) was attempted for the first time by using SERS utilizing AgNPs functionalized with bis-acridinium lucigenin (LG) as substrate (Guerrini et al. 2008). This bis-acridinium lucigenin (LG) acts as a molecular assembler. The comparative study of this bare substrate and bis-acridinium lucigenin (LG) with the AgNPs functionalized by viologen LG demonstrated that the latter was more efficient. It is observed that the concentration seen with viologen LG-modified AgNPs was 10^{-6} M, which corresponds to a limit of detection of 20 ppb (Guerrini et al. 2008). For enhanced SERS hotspots, a novel SERS substrate utilizing Ag nanodendrites deposited at the end of optical fiber is reported (Pham et al. 2019). The as prepared substrate proved a great potential in rapid and direct detection of permethrin with detection limit of 0.0035 ppm (Pham et al. 2019).

Lately, a lot of substrates are being prepared mimicking the naturally occurring structures to achieve increased hot spot density (Wu et al. 2018). A gyroid-structured Au SERS substrate (Fig. 4) demonstrated the detection of bis(2-ethylhexyl) phthalate with a remarkably low detection limit of 1 fM. The as prepared substrate had high density 3D hotspots and illustrated an enhancement factor of 10^9 along with the features such as sensitivity, uniformity, and reproducibility (Wu et al. 2018). Gold nanoparticles (AuNPs) have also been utilized for SERS enhancement as they are also very stable in comparison to AgNPs (Liu et al. 2017b). A SERS substrate based on AuNPs is synthesized by ferroelectric-assisted assembly of AuNPS array using periodically poled $LiNbO_3$(PPLN) single crystal template. The reported substrate is employed for the detection of Rhodamine 6G. A strong Raman enhancement of 10^9 orders was observed at 561 nm laser. The substrate was also reported to be reproducible with less than 7% of intensity variation (Liu et al. 2017b). Likewise, gold nanostars (AuNS) are demonstrated to have a high sensitivity when tested for Rhodamine 6G and attained a detection level as low as 10^{-11} M (Shan et al. 2017). This substrate displayed plenty of hotspots, which led to fluorescence free detection of the analyte (Shan et al. 2017). A de-alloyed gold-based metallic glass ribbon was investigated to detect p-aminothiophenol (Chao et al. 2017). The field emission

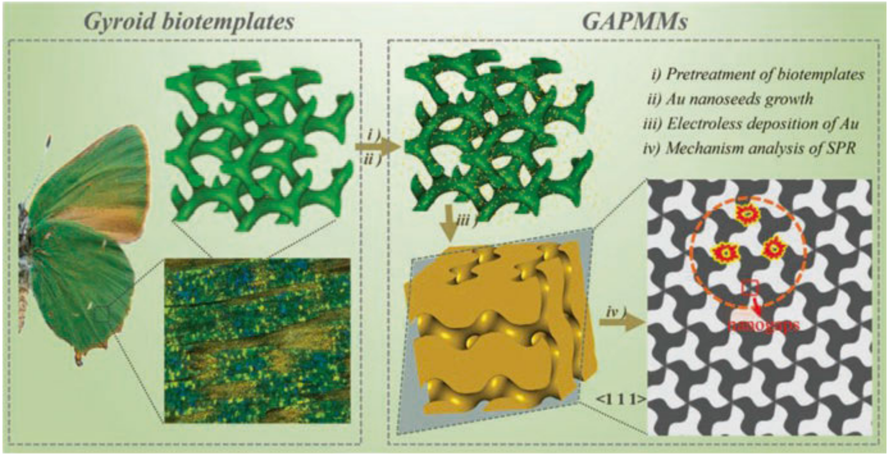

Fig. 4 Schematic illustration of fabrication of gyroid-structured Au periodic metallic materials (Wu et al. 2018)

scanning electron microscopy (FE-SEM) image shows that the de-alloyed gold-based glass ribbon had a bunch of nanostructures with protruding micro-islands producing hotspots. This substrate provided a large surface area and a large number of fine interstices producing hotspots for the enhancement. This gold-based metallic glass ribbon demonstrated an enhancement of 2 factor higher than the flat gold film (Chao et al. 2017). Gold silica hybrid microspheres are reported for detection of crystal violet (Son et al. 2017). The mesoporous polymer microspheres were used as a template and were further modified by polydopamine-mediated silicification to obtain hybrid microspheres. The detection limit with these mesoporous particles was found to be 10^{-8} M. These hybrid microspheres provided structural stability to gold nanoparticles and hence introduced a reusability factor (Son et al. 2017).

4.2 Photochemical/Photocatalytic Sensing

Photoelectrochemical (PEC) sensor is a somewhat newly introduced analytical method. This method is based on PEC oxidation and has wide application on the quantification of various analytes including several POPs. A PEC sensor was reported based on single crystalline molecular imprinted TiO_2nano rods ((SC, MI) TiO_2NRs) with properties of high sensitivity and selectivity for PCB 101 (Shi et al. 2016). The selectivity for PCB 101 was induced by the integration of molecular imprinting technique which reduced the interference from the other PCBs like PCB 77 and 126 below 37%. To observe the comparative response of SC TiO_2 NRs and (SC, MI) TiO_2 NR photoanode, the photocurrent response was recorded using 1 nM PCB 101 solution (Fig. 5) (Shi et al. 2016). Again, a novel probe made by molecular imprinting technique was developed for the detection of perfluorooctanoic acid (PFOA) (Gong et al. 2015). The probe was made of molecularly imprinted polymer (MIP) fabricated AgI nanoparticles-BiOI nanoflake arrays (MIP@AgI-BiOINFs). It is a photoactive electrode developed via a facile successive ionic layer adsorption and reaction (SILAR) approach. This PEC sensor manifests high selectivity and sensitivity for PFOA. The linear concentration range was 0.02 to 1000 ppb, and the detection limit was as low as 0.01 ppb. This cost-effective sensor was also proven efficient in real water samples (Gong et al. 2015). Another sensor using molecularly imprinted TiO_2 nanorods (NRs) was introduced for a novel cathodic PEC sensing method (Shi et al. 2018). The efficient reduction of PCB 101 on the cathode surface made it suitable for the selective detection of this pollutant. With an increase in the concentration of PCB 101, a sensitive cathodic photocurrent is produced under a negative bias potential. This gives rise to the very low detection limit for PCB 101 of 5×10^{-14} mol. L^{-1}. This particular sensor beholds an excellent selectivity even with the 100-fold excess of other pollutants coexisting with PCB 101 along with other PCB congeners, heavy metals, etc. The as prepared sensor was also tested successfully for real water and soil samples (Shi et al. 2018).

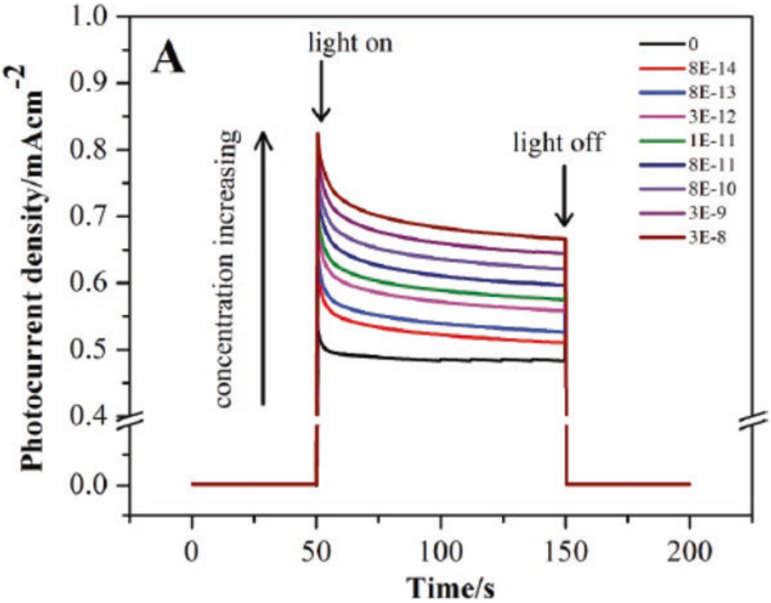

Fig. 5 Photocurrent response of (SC, MI) TiO_2 NRs photoanode for PCB 101 (Shi et al. 2016)

4.3 *Fluorescence/Luminescence Sensors*

A cyclodextrin promoted energy transfer is reported for the selective array-based detection of 30 POPs (Serio et al. 2015). In this study, three different fluorophores were used where the signals of energy transfer from aromatic POPs (aromatic analyte) to high quantum yield fluorophores were detected. γ-Cyclodextrin acting as a platform imposes the energy donor (aromatic analyte) to transfer energy to the acceptor in the proximity (fluorophore). This energy transfer creates unique signal for every analyte and fluorophore combination. Hence, the selective identification of each analyte can be carried out using that corresponding signal (Serio et al. 2015). Also, fluorescent nitrogen-doped graphene quantum dots (N-GQDs) are reported for the detection of 2,4,6-trinitrophenol (TNP) (Kaur et al. 2017). N-CQD detects TNP by selective and sensitive quenching of its fluorescence induced by TNP. The LOD of this green synthesized and simple detector is 420 nM (Kaur et al. 2017). Similarly, a luminescent lanthanide metal organic framework (Ln-MOF) having strong red luminescence was synthesized and demonstrated for PCB (1,2,4-TCB (trichlorobenzene)) detection (Fig. 6). This shows a very efficient detection of PCBs by quenching behavior that can easily indicate the concentration of the analyte (Wang et al. 2017).

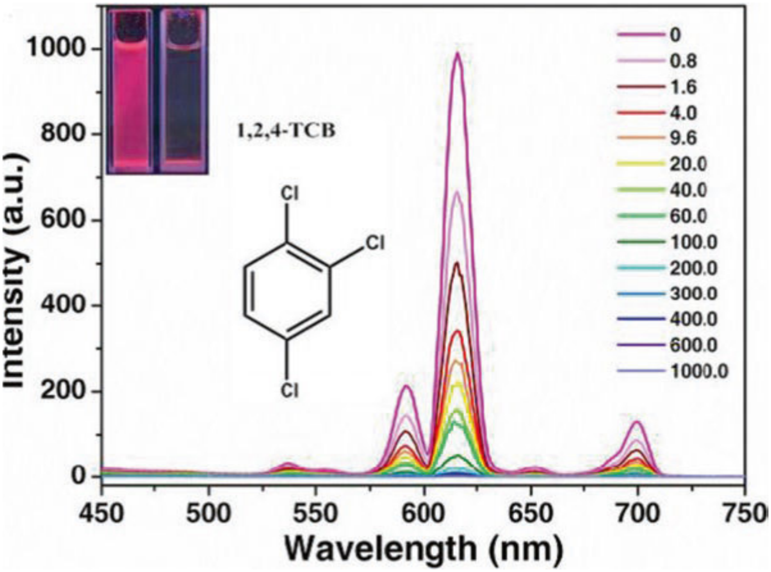

Fig. 6 Sensing behavior of luminescent Ln-MOF for varied concentration of 1,2,4- TCB, the luminescent spectra of Ln-MOF (inset: luminescence change in absence and presence of 1,2,4-TCB under 254 nm UV light) (Wang et al. 2017)

4.4 *Fiber-Optic Sensor*

Fiber optic is cylindrical light waveguide media for light transmission and can be employed as a sensor or sensing device (Prasetyo et al. 2017). A biochemical fiber sensor (BFS) can be fabricated by polishing cladding and later can be used for interaction to biochemical compounds. Due to the absorption of these compounds, a change in the light output spectrum is taken as a basis for the detection of targeted analyte, lindane in this case. Light from the halogen lamp (light source) interacts with the POP in sensing area where adsorption evanescent occurs. The spectrum by spectrophotometer is displayed for the wavelength of light that propagates through the fiber sensor. The experimental setup and sensor scheme has been demonstrated in Fig. 7. The evanescent absorption is proportional to the concentration of the POP compound in the sample (Prasetyo et al. 2017).

5 Future Outlook

An extensive research has already been done on the development and advancement of the conventional techniques for POP detection, but still, there is scope of improvement in terms of selectivity and sensitivity. POP monitoring in the environmental

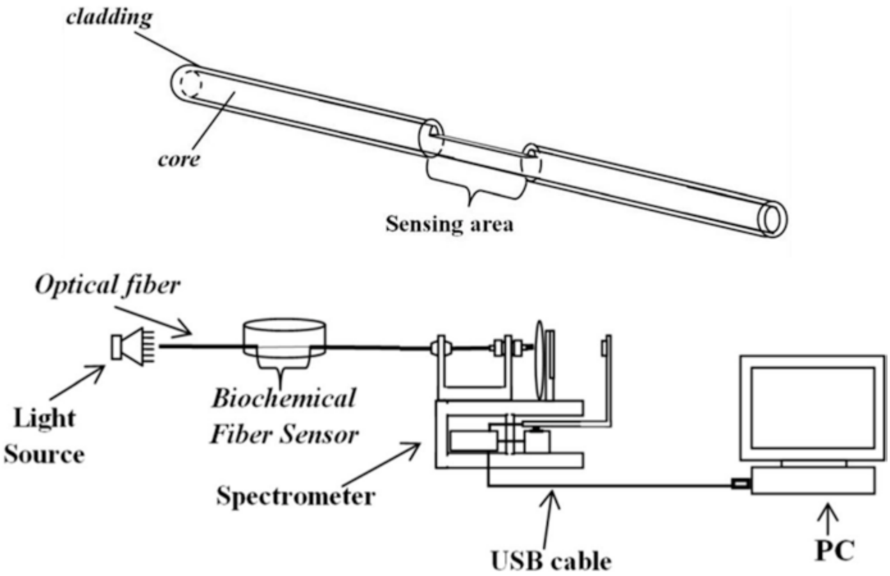

Fig. 7 Fiber sensor scheme and experimental setup (Prasetyo et al. 2017)

matrices especially water has become a crucial requirement; thus, there is a necessity of field-usable analytical techniques. As the natural matrix is complex, the technique must be capable of providing clear results for targeted analyte by overcoming the interference caused by the other molecules. Along with these features, a good analytical technique must also be inexpensive and reproducible while retaining satisfactorily unaltered structure as well as response. SERS is a potential technique; however, it has not been fully explored for POP detection in water. There is need of materials development having good enhancement factor and nontoxicity in the matrix used. Thus, possible green route obtained eco-friendly materials can be explored as potential SERS substrate. There are miles to go for developing and adapting POP extraction to ongoing eco-friendly trends of green methods.

To fulfill the requirement of extensive monitoring of POPs, it is required that highly effective, efficient, sensitive, specific, inexpensive, and preferably green methods of analysis, detection, and monitoring should be developed. Besides, the sensor material should be affordable, easily available, and reproducible. In addition to these characteristics, in order to develop an excellent optical detection technique, various supplementary features must be incorporated. One such attribute is signal-to-noise ratio. The detector involved should be capable of producing results with low signal-to-noise ratio. Also, the optical source must have a short response time and sufficiently large bandwidth. It must have a good stability with the changing operational conditions. A ubiquitous method can be developed by the integration of appropriate technology for detection on chip. A lab-on-a-chip approach could prove to be a robust and cost-effective one and also a solution to various existing sensors with certain drawbacks. The method involved must be highly feasible and valid for the detection of the POPs which could also be portable. There is high demand for the technique which can be effectively utilized in the real-time analysis of POPs to foster advanced and efficient environmental monitoring and remediation.

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References

Alharbi OM, Khattab RA, Ali I (2018) Health and environmental effects of persistent organic pollutants. J Mol Liq 263:442–453

An Q et al (2012) Silver-coated magnetite–carbon core–shell microspheres as substrate-enhanced SERS probes for detection of trace persistent organic pollutants. Nanoscale 4(16):5210–5216

Aparicio I et al (2017) Stir bar sorptive extraction and liquid chromatography–tandem mass spectrometry determination of polar and non-polar emerging and priority pollutants in environmental waters. J Chromatogr A 1500:43–52

Ballesteros ML et al (2014) Multimatrix measurement of persistent organic pollutants in Mar Chiquita, a continental saline shallow lake. Sci Total Environ 490:73–80

Bao ZY et al (2014) Quantitative SERS detection of low-concentration aromatic polychlorinated biphenyl-77 and 2, 4, 6-trinitrotoluene. J Hazard Mater 280:706–712

Barletta M, Lima AR, Costa MF (2019) Distribution, sources and consequences of nutrients, persistent organic pollutants, metals and microplastics in South American estuaries. Sci Total Environ 651:1199–1218

Basheer C, Obbard JP, Lee HK (2005) Analysis of persistent organic pollutants in marine sediments using a novel microwave assisted solvent extraction and liquid-phase microextraction technique. J Chromatogr A 1068(2):221–228

Benskin JP, Bataineh M, Martin JW (2007) Simultaneous characterization of perfluoroalkyl carboxylate, sulfonate, and sulfonamide isomers by liquid chromatography– tandem mass spectrometry. Anal Chem 79(17):6455–6464

Čajka T et al (2005) Challenges of gas chromatography–high-resolution time-of-flight mass spectrometry for simultaneous analysis of polybrominated diphenyl ethers and other halogenated persistent organic pollutants in environmental samples. J Sep Sci 28(7):601–611

Camino-Sánchez F et al (2011) Validation of a GC–MS/MS method for simultaneous determination of 86 persistent organic pollutants in marine sediments by pressurized liquid extraction followed by stir bar sorptive extraction. Chemosphere 84(7):869–881

Carrera G et al (2001) Persistent organic pollutants in snow from European high mountain areas. Atmos Environ 35(2):245–254

Chao B-K et al (2017) Gold-rich ligament nanostructure by dealloying Au-based metallic glass ribbon for surface-enhanced Raman scattering. Sci Rep 7(1):1–7

Diao CP et al (2016) Evaluation of magnetic matrix solid-phase dispersion for the determination of polychlorinated biphenyls in water samples by gas chromatography with electron capture detection. J Sep Sci 39(10):1926–1934

Eljarrat E, Guerra P, Barceló D (2008) Enantiomeric determination of chiral persistent organic pollutants and their metabolites. TrAC Trends Anal Chem 27(10):847–861

El-Shahawi M et al (2010) An overview on the accumulation, distribution, transformations, toxicity and analytical methods for the monitoring of persistent organic pollutants. Talanta 80(5):1587–1597

Focant J-F (2012) Dioxin food crises and new POPs: challenges in analysis. Anal Bioanal Chem 403(10):2797–2800

Geissen V et al (2015) Emerging pollutants in the environment: a challenge for water resource management. Int Soil Water Conserv Res 3(1):57–65

Gong J et al (2015) A highly sensitive photoelectrochemical detection of perfluorooctanic acid with molecularly imprinted polymer-functionalized nanoarchitectured hybrid of AgI–BiOI composite. Biosens Bioelectron 73:256–263

Guerrini L et al (2008) Functionalization of Ag nanoparticles with the bis-acridinium lucigenin as a chemical assembler in the detection of persistent organic pollutants by surface-enhanced Raman scattering. Anal Chim Acta 624(2):286–293

Haffner D, Schecter A (2014) Persistent organic pollutants (POPs): a primer for practicing clinicians. Curr Environ Health Report 1(2):123–131

Hou N et al (2015) New strategy for rapid detection of the simulants of persistent organic pollutants using gas sensor based on 3-D porous single-crystalline ZnO nanosheets. IEEE Sensors J 15(7):3668–3674

UNEP 2012, United Nation Environment Programme, Report of the Persistent Organic Pollutants Review Committeeon the work of its eighth meeting, Available at: http://chm.pops.int/Portals/0/Repository/poprc_subAnnexF_2008/UNEP-POPS-POPRC-SUBM-F08-OBDE-CAN-A3.English.PDF

USEPA 2003, United Nation Environmental Protection Agency, Table of Polychlorinated Biphenyl (PCB) Congeners, Available at: https://www.epa.gov/pcbs/table-polychlorinated-biphenyl-pcb-congeners

NRC 1983, National Research Council, Polycyclic aromatic hydrocarbons: evaluation of sources and effects. Available at:https://www.ncbi.nlm.nih.gov/books/NBK217760/

Iszatt N et al (2015) Prenatal and postnatal exposure to persistent organic pollutants and infant growth: a pooled analysis of seven European birth cohorts. Environ Health Perspect 123(7):730–736

Jamieson AJ et al (2017) Bioaccumulation of persistent organic pollutants in the deepest ocean fauna. Nat Ecol & Evol 1(3):1–4

Kaur M, Mehta SK, Kansal SK (2017) Nitrogen doped graphene quantum dots: efficient fluorescent chemosensor for the selective and sensitive detection of 2, 4, 6-trinitrophenol. Sens Actuators B 245:938–945

Liu Y et al (2011) Nanoparticle-based strategies for detection and remediation of environmental pollutants. Analyst 136(5):872–877

Liu C et al (2017a) Temporal occurrence and sources of persistent organic pollutants in suspended particulate matter from the most heavily polluted river mouth of Lake Chaohu, China. Chemosphere 174:39–45

Liu X et al (2017b) Ferroelectric-assisted gold nanoparticles array for centimeter-scale highly reproducible SERS substrates. Sci Rep 7(1):1–8

Lohmann R et al (2007) Global fate of POPs: current and future research directions. Environ Pollut 150(1):150–165

Long F, Zhu A, Shi H (2013) Recent advances in optical biosensors for environmental monitoring and early warning. Sensors (Basel) 13(10):13928–13948

Loos R et al (2010) Pan-European survey on the occurrence of selected polar organic persistent pollutants in ground water. Water Res 44(14):4115–4126

Lorenzo M, Campo J, Picó Y (2018) Analytical challenges to determine emerging persistent organic pollutants in aquatic ecosystems. TrAC Trends Anal Chem 103:137–155

Magulova K, Priceputu A (2016) Global monitoring plan for persistent organic pollutants (POPs) under the Stockholm convention: triggering, streamlining and catalyzing global POPs monitoring. Environ Pollut 217:82–84

Mirasole C et al (2016) Liquid chromatography–tandem mass spectrometry and passive sampling: powerful tools for the determination of emerging pollutants in water for human consumption. J Mass Spectrom 51(9):814–820

Muir D, Lohmann R (2013) Water as a new matrix for global assessment of hydrophilic POPs. TrAC Trends Anal Chem 46:162–172

Orozco J et al (2016) Graphene-based Janus micromotors for the dynamic removal of pollutants. J Mater Chem A 4(9):3371–3378

Patrizi B et al (2019) Dioxin and related compound detection: perspectives for optical monitoring. Int J Mol Sci 20(11):2671

Peng Y et al (2018) Screening hundreds of emerging organic pollutants (EOPs) in surface water from the Yangtze River Delta (YRD): occurrence, distribution, ecological risk. Environ Pollut 241:484–493

Pham TB et al (2019) Detection of permethrin pesticide using silver nano-dendrites SERS on optical fibre fabricated by laser-assisted photochemical method. Sci Rep 9(1):1–10

Pitarch E et al (2007) Determination of priority organic micro-pollutants in water by gas chromatography coupled to triple quadrupole mass spectrometry. Anal Chim Acta 583(2):246–258

Pitarch E et al (2016) Comprehensive monitoring of organic micro-pollutants in surface and groundwater in the surrounding of a solid-waste treatment plant of Castellón, Spain. Sci Total Environ 548:211–220

Prasetyo E et al (2017) Biochemical fiber sensor based on evanescent field for detection persistent organic pollutants (POPs). In: Journal of physics: conference series. IOP Publishing

Rabodonirina S et al (2015) Distribution of persistent organic pollutants (PAHs, Me-PAHs, PCBs) in dissolved, particulate and sedimentary phases in freshwater systems. Environ Pollut 206:38–48

Ratola N, Botelho C, Alves A (2003) The use of pine bark as a natural adsorbent for persistent organic pollutants–study of lindane and heptachlor adsorption. J Chem Technol Biotech: Int Res Proc Environ Clean Technol 78(2–3):347–351

Rios LM et al (2010) Quantitation of persistent organic pollutants adsorbed on plastic debris from the Northern Pacific Gyre's "eastern garbage patch". J Environ Monit 12(12):2226–2236

Rojas D, Jurado-Sánchez B, Escarpa A (2016) "Shoot and sense" Janus micromotors-based strategy for the simultaneous degradation and detection of persistent organic pollutants in food and biological samples. Anal Chem 88(7):4153–4160

Sánchez-Avila J et al (2010) Stir bar sorptive extraction-thermal desorption-gas chromatography–mass spectrometry: an effective tool for determining persistent organic pollutants and nonylphenol in coastal waters in compliance with existing directives. Mar Pollut Bull 60(1):103–112

Serio N et al (2015) Array-based detection of persistent organic pollutants via cyclodextrin promoted energy transfer. Chem Commun 51(58):11615–11618

Shan F et al (2017) Investigation of simultaneously existed Raman scattering enhancement and inhibiting fluorescence using surface modified gold nanostars as SERS probes. Sci Rep 7(1):1–10

Shi H et al (2016) A highly selective and picomolar level photoelectrochemical sensor for PCB 101 detection in environmental water samples. Biosens Bioelectron 81:503–509

Shi H et al (2018) Cathodic photoelectrochemical detection of PCB101 in environmental samples with high sensitivity and selectivity. J Hazard Mater 342:131–138

Son HY et al (2017) Bioinspired synthesis of mesoporous gold-silica hybrid microspheres as recyclable colloidal SERS substrates. Sci Rep 7(1):1–13

Ul-Islam M et al (2017) Current advancements of magnetic nanoparticles in adsorption and degradation of organic pollutants. Environ Sci Pollut Res 24(14):12713–12722

Van Leeuwen S, De Boer J (2008) Advances in the gas chromatographic determination of persistent organic pollutants in the aquatic environment. J Chromatogr A 1186(1–2):161–182

Wang L et al (2017) Detection of persistent organic pollutants of polychlorinated benzenes by a lanthanide metal-organic framework luminescent sensor. J Mater Chem A 11:5541–5549

Wenzel KD et al (2004) Dialysis of persistent organic pollutants and polycyclic aromatic hydrocarbons from semipermeable membranes. A procedure using an accelerated solvent extraction device. Anal Chem 76(18):5503–5509

Wu L et al (2018) Highly sensitive, reproducible and uniform SERS substrates with a high density of three-dimensionally distributed hotspots: gyroid-structured Au periodic metallic materials. NPG Asia Material 10(1):e462–e462

Yadav IC et al (2015) Current status of persistent organic pesticides residues in air, water, and soil, and their possible effect on neighboring countries: a comprehensive review of India. Sci Total Environ 511:123–137

Yan CH, Wu HF (2004) A liquid-phase microextraction method, combining a dual gauge micro-syringe with a hollow fiber membrane, for the determination of organochlorine pesticides in aqueous solution by gas chromatography/ion trap mass spectrometry. Rapid Commun Mass Spectrom 18(24):3015–3018

Ying Y, Pumera M (2019) Micro/nanomotors for water purification. Chem A Eur J 25(1):106–121

Yurdakok-Dikmen B et al (2016) Measurement of selected polychlorinated biphenyls (PCBs) in water via ultrasound assisted emulsification–microextraction (USAEME) using low-density organic solvents. J Water Health 14(2):214–222

Zarei M, Zarei M (2018) Self-propelled micro/nanomotors for sensing and environmental remediation. Small 14(30):e1800912

Zhao G et al (2006) Biotransfer of persistent organic pollutants from a large site in China used for the disassembly of electronic and electrical waste. Environ Geochem Health 28(4):341–351

Zhou Q, Xiao J, Wang W (2006) Using multi-walled carbon nanotubes as solid phase extraction adsorbents to determine dichlorodiphenyltrichloroethane and its metabolites at trace level in water samples by high performance liquid chromatography with UV detection. J Chromatogr A 1125(2):152–158

Zhou Q, Pang L, Xiao J (2009) Trace determination of dichlorodiphenyltrichloroethane and its main metabolites in environmental water samples with dispersive liquid–liquid microextraction in combination with high performance liquid chromatography and ultraviolet detector. J Chromatogr A 1216(39):6680–6684

Zielinski O et al (2009) Detecting marine hazardous substances and organisms: sensors for pollutants, toxins, and pathogens. Ocean Sci 5(3):329–349

Part III

Current Approaches for Remediation of Organic Micropollutants

Emerging Contaminants in Water and Remedial Techniques

Smita Chaudhry and Shivani Garg

Abstract Emerging contaminants (ECs) occur in extremely small concentrations; have a broad distribution, especially in water bodies; and have been identified to cause potential environmental and health risks. ECs comprise of chemical and biological micro-pollutants such as fertilizers and pesticides, pharmaceuticals, cosmeceuticals, nutraceuticals and other personal care products (PCPs), disinfectants, plastics, polycyclic aromatic hydrocarbons (PAH), dioxins, etc. that even in minor concentrations cause serious environmental threats and risks to the associated flora and fauna. The treatment of these ECs poses a major challenge to researchers, engineers and academicians. This chapter hence describes the types of ECs; the hazards associated with their widespread distribution in various fresh water bodies, groundwater and industrial wastewater; and also the associated modern remedial techniques. In order to tackle the bio-geo-environmental threats, various research efforts have been made to increase the efficiency of remediation techniques. Aerobic and anaerobic treatments, adsorption processes with activated carbon and clay minerals, hydrothermal carbonization of biomass, coagulation- flocculation, ozonation, advanced oxidation process (AOPs), UV irradiation, ultrafiltration (UF) membrane treatments, nanofiltration (NF), etc. are some effective treatment techniques for emerging contaminants in water and wastewater.

Keywords Emerging contaminants · Micro-pollutants · Remedial techniques · Advanced treatments · Adsorption · Nanofiltration · Activated carbon · Dioxins · Clay minerals · Personal care products · Polychlorinated biphenyls · Polycyclic aromatic hydrocarbons

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Abbreviations

PCPs	Personal care products
PACs	Polycyclic aromatic contaminants
EDCs	Endocrine disruptors contaminants
CBZ	Carbamazepine
CNTs	Carbon nanotubes
CW	Constructed wetland
UF	Ultrafiltration

1 Introduction

As the living standards have become higher and consumer demands become greater, environmental pollution concerns have been exaggerated, such as the increase in concentrations of greenhouse gases (GHGs), non-biodegradable pesticides, fertilizers, etc. (Rasheed et al. 2019). Emerging contaminants (ECs) also known as micro-pollutants are the range of extensively used anthropogenic/synthetic compounds such as cosmetics, pharmaceuticals, steroid hormones, pesticides, personal care products, etc. present in water (Gomes et al. 2018; Luo et al. 2014). WHO (2011) has considered ECs of utmost environmental concern as these are detected and monitored in ground-, drinking and surface water. ECs are not monitored and regulated in the environment and drinking water (Oviedo and Aga 2016). Important amongst these are pharmaceutical-based ECs that affect the aquatic body and environment (Patrie et al. 2013). These were not a big concern in wastewater and surface water in the 1970s since their concentrations were quite low at that time (Hignite and Azanoff 1977). Similarly, many contaminants are added into surface water during discharge of wastewater from treatment plants due to lack of capability of their complete removal and contaminants such as stimulants, cocaine and hallucinogen 3,4- methylenedioxy-*N*-methylamphetamine (MDMA) and are also found in river water (Baker and Kasprzyk-Hordern 2013). There has been a huge gap between the knowledge and techniques of treatment about emerging contaminants in the past, and investigations have seen a rise only recently, after development of modern biotechnological techniques. The limited sources of drinking water and increasing impacts of climate change have led to scarcity of fresh water supply. This further leads to increase in the recycling of water which is also a major concern about emerging contaminants. The unsatisfactory identification and development of methods for treatment and also the low knowledge of nature of emerging contaminants have made these the top area of research for scientists so as to assure the safe use of drinking water (Rodriguez-Narvaez et al. 2017).

Hence, the presence of ECs in wastewater and their nature during treatment of wastewater and drinking water are of special concern. Figure 1 gives the broad idea

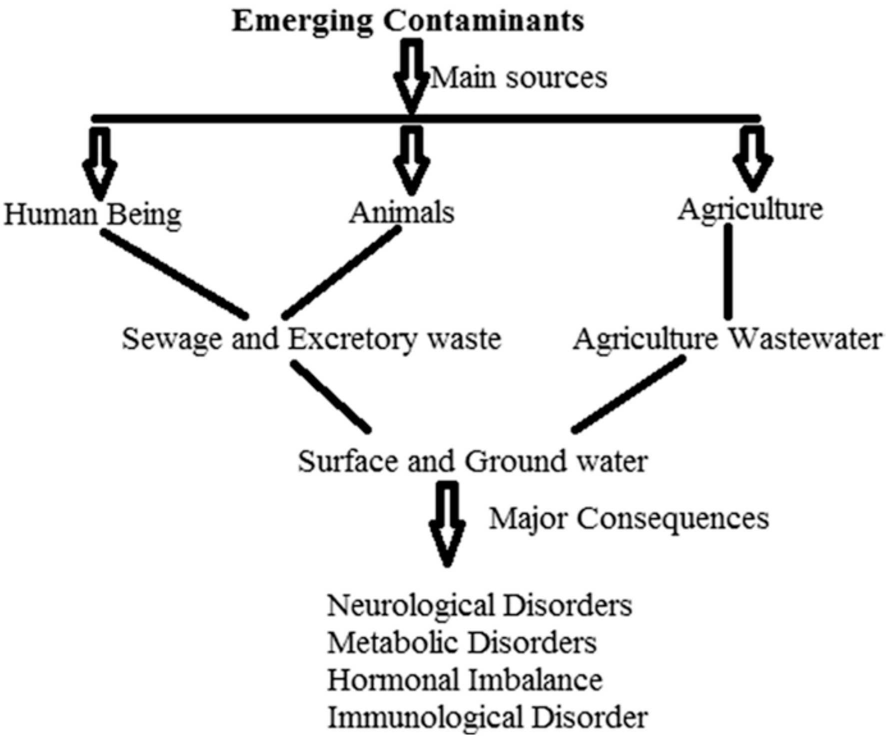

Fig. 1 Sources of emerging contaminants in water and their major impacts

of main sources of emerging contaminants, their occurrence pathway in surface and groundwater and major consequences for humans (certain physiological and neurological disorders), animals and the environment.

2 Categories and Health Impacts of Emerging Contaminants

Emerging contaminants are categorized on the basis of risk to environment and human health (US EPA 2012). ECs include a variety of synthetic and natural compounds which cause potential hazards. These include agricultural micro-pollutants, pharmaceuticals, personal care products, hormones, industrial additives, nanomaterials, etc. (Fig 2). Emerging contaminants, pharmaceuticals and PCPs are examples of contaminants in surface water. Due to increase in chemical industries, the variety of emerging contaminants discharged in the environment has also increased (Cassani and Gramatica 2015). The concentration of emerging contaminants in surface water ranges within less than ng/l to thousands of µg/l level.

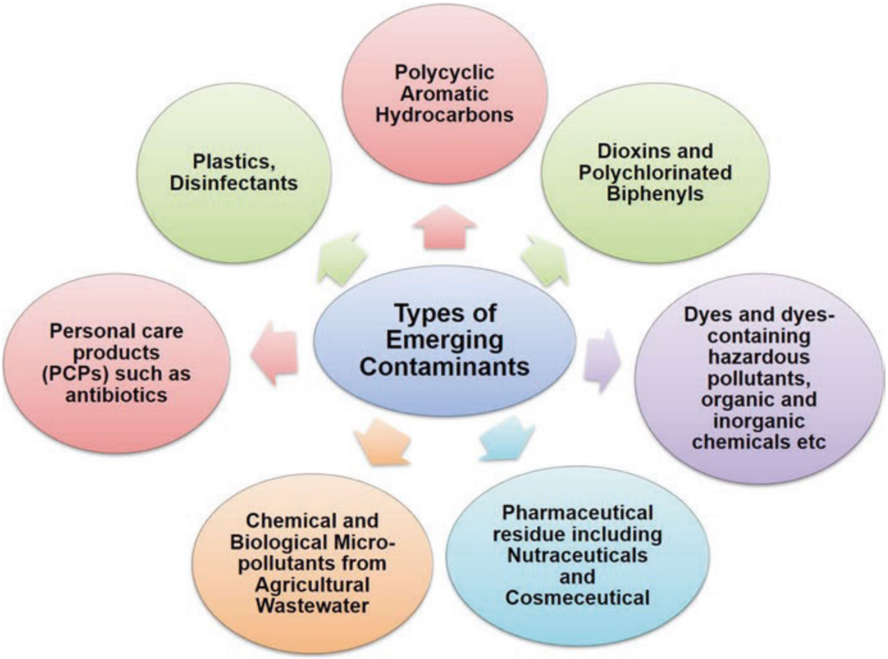

Fig. 2 Different categories of emerging contaminants in water

2.1 *Emerging Chemical and Biological Micro-Pollutants from Agricultural Wastewater: Biocides and Pesticides*

Pesticides are chemicals used to remove pests in agriculture. Extensive use of pesticides and fertilizers for agricultural use causes organic contamination in wastewater and affects human health (Houtman 2010). Biocides including penicillin, cephalosporin, nitroimidazole, macrolide and sulphonamide are used in urban environments for weed control, roof sealing and grass control in gardens (Margot et al. 2015). With the increasing population demand to produce more food and other crops for survival, more pesticides and fertilizers are being used in fields. With water drainage or runoff, these fertilizers and pesticides reach water bodies and cause water pollution. This leads to the contamination of surface- and groundwater bodies during rain events and eutrophication (Comber et al. 2015). According to the Environmental Agency (2010), those metaldehyde pesticides are of special interest that are detected above EU drinking water limits of pesticides**,** e.g. atrazine, acetochlor, 2,4-4, glyphosate, dichloropropene, methyl bromide, etc. (Linhart et al. 2019). The permissible limit for pesticides in water is 0.02 mg/l (20 μg/l).

2.2 Pharmaceutical (PhACs) Residue Including Nutraceuticals and Cosmeceutical-Based ECs

Pharmaceuticals are an important group of contaminants that are increasingly being used in medication of humans and veterinary. Pharmaceuticals include antidiabetics, antibiotics, painkillers, antidepressants, contraceptives and beta-blockers (McGrane 2016). The main source of pharmaceutical contaminants is agricultural fields, animal feeds, human medicines, landfill leachate, etc. According to a study conducted between 1999 and 2000, 139 streams across 30 states were contaminated by hormonal, organic wastewater contaminants and pharmaceuticals (Kolpin et al. 2002). Pharmaceutical concentrations detected in drinking water are usually lower than 0.05 μg (WHO 2011). These contaminants hassle the growth of resistant genes against antibiotics in soil bacteria so that these bio-accumulate and cause ecosystem-level problems (Arnold et al., 2013). Anti-inflammatory drugs such as acetaminophen, diclofenac and ibuprofen; lipid regulators such as clofibric, metabolites, bezafibrate, etc.; and carbamazepine are highly harmful and toxic for aquatic flora and fauna (Bilal et al. 2019). The presence of these drugs in water affects the microbial activity and efficiency of wastewater treatment. For example, ciprofloxacin affects the nitrification process (Gonzalez-Martinez et al. 2014). More than 100 PhACs above the detection limit are found in water bodies in developed countries such as European countries and the USA and more than 30 PhACs in Latin America, Eastern and Western European countries and Caribbean States (Aus der Beek et al. 2016). According to Liu et al. (2013), these pose certain health risks such as chronic and estrogenic toxicity, and the detailed knowledge of these PhACs is yet to be explored.

2.3 Personal Care Products (PCPs)-Based ECs

Some contaminants originate from households and personal care products, such as synthetic hormones, shampoos, sunscreens, fragrances, disinfectants, insect repellents, antifungal agents, cosmetic materials, steroids, etc. (Pal et al. 2014). These products are for external use and are released in the environment through sewage runoff (Margot et al. 2015). In sunscreens and skin care products, UV filters (generally 2,4-dihydroxy benzophenone and benzophenone derivatives) are used to prevent the skin from sunlight (Campanha et al. 2015). These are active, non-degradable and inert in nature and enter into water sources through leaching and sewage runoff. Hormones such as synthetic androgens including nandrolone, oxandrolone, etc. and synthetic oestrogens such as diethylstilbestrol used as contraceptives and naturally, endogenous steroids such as sex hormones, phytoestrogens, etc. also reach water bodies from the human body by excreta (Stefanakis and Becker 2016). The concentration of PCPs in drinking water is usually on the level of ng/l.

2.4 Plastics, Disinfectants ECs

Plastics have been known as major pollutants for rivers (Balas et al. 2001). Plastic particles that have <5mm diameter are known as micro-plastics (MPs). MPs enter the environment in many ways such as wastewater treatment plant (WWTP) discharge, usage of PCPs, washing of clothes, usage of treated wastewater and biosolids from WWTPs in agricultural land (Nizzetto et al. 2016) or discharge from industrial products (Dris et al. 2018). Micro-plastic polystyrene particles (240 nm in diameter) are transportable through placental cells (Wick et al. 2010). Water disinfectants are the basic requirement of a potable water supply system. Disinfection methods to make water safe for drinking make use of UV light, chlorine, NH_2Cl and ozone. Elemental chlorine is most commonly used for disinfection. However, chlorine is harmful if used above the prescribed limit. According to the WHO guideline, the permissible limit for $CHCl_3$ in groundwater is 300µg/l. A disinfectant becomes a contaminant when it reacts with certain precursors, and generally carbon acts as organic precursor. According to a study, drinking water contains approximately 80% of this organic precursor (Karanfil et al. 2005).

2.5 Polycyclic Aromatic Hydrocarbon-Based ECs

Polycyclic aromatic contaminants (PACs) are contaminants having more than one aromatic ring with different structural arrangements. The main source of polycyclic aromatic hydrocarbon (PAH) is incomplete combustion and pyrolysis of fossil fuels and biomass (Abdel-Shafy and Mansour 2016). US Environmental Protection Agency (USEPA) studied different types of PACs, but only few are considered as contaminants (Banger et al. 2010), for example, naphthalene, chrysene, benz[a]anthracene, benzo[k]fluoranthene, benzo[b]fluoranthene, etc.. These contaminants due to presence of multiple aromatic rings are hydrophobic and volatile in nature. The volatile aromatic contaminants easily pollute the soil, air, water and also the food chain (Xiang et al. 2016). These contaminants enter into human metabolic system with smoking, breathing, ingestion and skin contact (Navarro et al. 2017). According to a study, these contaminants are carcinogenic and cause other health issues such as diabetes, poor fatal growth, infertility, cardiovascular diseases and oxidative stress (Ferguson et al. 2017).

2.6 Dioxins and Polychlorinated Biphenyl (PCB)-Based ECs

Dioxins and PCBs are persistent chemicals that accumulate in the food chain and environment. The increase in body fat increases the half-life of these contaminants from weeks to months (Emond et al. 2005). Dioxins are the unintended by-products of combustion of industrial wastes, forest fires and waste incineration (McKay 2002). These are toxic and carcinogenic and cause behavioural changes, tumour promotion, cardiovascular diseases and perturbation of nervous and endocrine systems (Sany et al. 2015). The impact of dioxin-like (DL) compounds on environment depends on the interaction of receptors of aryl hydrocarbons (Emond et al. 2005). The non-DL compounds such as PCBs which do not bind with its receptors cause endocrine disruption, neurotoxicity and immune suppression (Hamer et al. 2011). These contaminants enter the human body through ingestion of fatty food. The contaminants dioxin and PCBs such as polychloro-sibenzo-p-dioxins, polychloro-dibenzofurans and polychlorinated biphenyls are present in suspended solid in wastewater as these are less soluble in water hence high octanol-water coefficient and low vapour pressure (Sany et al. 2015). PCB permissible limit in groundwater is 0.5 μg/L (USEPA 2012).

2.7 Industrial Wastewater ECs: Dyes, Organic and Inorganic Chemicals

Dye and dye-containing pollutants are generally discharged from textile industries. This industry uses huge amounts of water in different industrial processes, and the effluent generated from this industry is amongst the most polluting in industrial sectors. The main components of the textile industry effluent are recalcitrant organics, colorants, toxicants, surfactants and chlorinated compounds (Ben Mansour et al. 2012). Azo dyes are the most extensively used colorants that show toxic effects such as mutagenic and carcinogenic events (Pinheiro et al. 2004). Dye and dye-containing pollutants and other industrial pollutants are easily visible when effluents are discharged in the environment. The discharges of these dyes which are toxic and carcinogenic in water body cause an immense threat to human health and the environment (Bilal et al. 2017). These effluents affect the transparency and quality of water bodies such as rivers, ponds, lakes, etc. leading to the pollution and destruction of aquatic environments. As, Pb, Hg and Cd were enlisted as priority in WHO's list of chemicals of major health concern (WHO 2011). Arsenic used as alloy of Pb in car batteries constitutes about 1.5 ppm of the Earth's crust, but contamination or high concentration in water affects millions of people all over the world. The topmost producer of arsenic is China that accounts for almost 70% world share (Edelstein 2013). The provisional guideline value of arsenic in drinking water is 0.01 mg/l (10 μg/l). Some examples of industrial chemicals which can be considered as contaminants of emerging concern (CECs) are given in Table 1.

3 Environmental Impacts of Different Emerging Contaminants

The European Commission (2011) has documented the avoidance of utilization of endocrine disruptors in consumer products and beauty care products but does not set any permissible limits for concentrations of these contaminants in water,

Table 1 Some examples of industrial chemicals considered as emerging contaminants

Industrial chemical	Compound name
Volatile organic compounds (VOCs)	Benzene, CCl_4, 1,2-dichloroethane, 1,2-dichloroethene, dichloromethane, styrene, tetrachloroethene (PCE), toluene, $CHCl_3$, xylenes
Antioxidants	2,6-Di-*tert*-butylphenol
Polycyclic aromatic hydrocarbons (PAHs)	Naphthalene, benzo[*a*]pyrene
Antifouling compounds	Dibutyl tin ion, irgarol
Others	Polychlorinated biphenyl (PCBs), 2,4-dinitrophenol, pentachlorophenol, chloropicrin, pentachlorobenzene, hexabromocyclododecane

Table 2 Some studies on environmental impacts of emerging contaminants

Chemicals	Impacts	References
Antibiotics (penicillin, tetracyclines, etc.)	Alter microbial community structure and affect the food chain	Daughton and Ternes (1999)
Stimulant (caffeine)	Endocrine system disruption of goldfish	Li et al. (2012)
Blood lipid regulator (gemfibrozil) and antimicrobial (triclocarban, etc.)	Growth inhibition of algae	Rosal et al. (2009) Yang et al. (2008)
Preservatives (alkyl-p hydroxybenzoate)	Weak estrogenic activity	Routledge et al. (1998)
Disinfectants (triclosan)	Act as bio-acidic agent	McMurry et al. (1998)

wastewater and environment. Pesticides and fertilizers are added into the environment by agricultural runoff, mishandling, drainage, etc. This leads to bioaccumulation and biomagnification processes in the food chain and water bodies, respectively. Personal care product contaminants are generally found in urban wastewater (Margot et al. 2015). These contaminants make their way into the environment and human beings by drainage system and their disposal without treatment. Some studies on environmental impacts of emerging contaminants are listed in Table 2.

4 Remedial Techniques for ECs

Due to the presence of different types of contaminants in water and the need for treatment methods, remedial techniques have also improved. Major wastewater treatment methods are classified as physical, chemical and biological treatment technologies. Removal technologies and efficiency of EC removal mainly depend on chemical and biological natures of ECs. Table 3 summarizes the different

Table 3 Different techniques used for treatment of emerging contaminants

Name of techniques		Examples of contaminants removed by the techniques	Removal efficiency (%)	References
Conventional treatment	Coagulation-flocculation	Betaxolol, warfarin, hydrochlorothiazide, acetaminophen, diclofenac	<20%	Huerta-Fonntela et al. (2011) and Westerhoff et al. (2005)
Aerobic treatment	Activated sludge process	Cephalexin, ciprofloxacin	96 and 90%, respectively	Buttiglieri and Knepper (2007), Costanzo et al. (2005) and Zorita et al. (2009)
	Membrane technology	Progesterone and ethinylestradiol, ketoprofen, steriods pharmaceuticals	80–99%	Musson et al. (2010), Wintgens et al. (2003), Urase et al. (2005), Lesjean et al. (2005) and Carballa et al. (2007)
Natural aerobic process	Waste stabilization ponds (WSPs)	Pharmaceuticals and PCPs, exception of carbamazepine, e.g. galaxolide, caffeine, naproxen, tonalide, ibuprofen, triclosan	92–99%	Li et al. (2013) and Matamoros et al. (2016)
	Constructed wetlands	Oxytetracycline HCL, nadolol, cotinine and enrofloxacin, tetracycline, caffeine	94, 98–99%	Li et al. (2014) and Matamoros et al. (2007)
Phase-change treatment (adsorption assisted)	Activated carbon-assisted adsorption	Ciprofloxacin, carbamazepine, sulfamethoxazole	50–100%	Carabineiro et al. 2011 and Nguyen et al. 2016
	Biochar-assisted adsorption	Sulfamethoxazole	50–100%	Zheng et al. (2013)
	Clay minerals-assisted adsorption	Methylene blue		Olusegun et al. (2018)
	Nanomaterial-assisted adsorption	Antibiotics such as triclosan/ibuprofen		Zheng et al. (2013)

(continued)

Table 3 (continued)

Name of techniques		Examples of contaminants removed by the techniques	Removal efficiency (%)	References
Advanced treatment processes	Ozonation	Sulfamethoxazole, deprotonated amino acids, estrone, estradiol, estriol	98–99%	Dickenson et al. (2009) and Westerhoff et al. (2005)
	Ultraviolet (UV) irradiation	TOC and disinfection of *E. coli*, total coliform bacteria, sulphonamides	45–65%	Saggioro et al. (2019) and Kim et al. (2009)
	Nanofiltration	Ketorolac tromethamine, roxithromycin, azithromycin	>87%	Acero et al. (2010) and Liu et al. (2014)
	Advanced oxidation processes			
	Fenton reaction	Doxycycline	100%	Borghi et al. (2015)
	UV/ozone	Caffeine	>95%	Souza and Feris (2015)
	Ozone	Ethinylestradiol (EE2), naproxen (NPX)	80%	Vallejo-Rodríguez et al. (2014)
	Ozone/H_2O_2	Naproxen, piroxicam	96–98%	Feng et al. (2015)
	Photo-Fenton	Acetamiprid	70–90%	Carra et al. (2015)
	Sonochemical	Dicloxacillin	>99	Villegas-Guzman et al. (2015)

techniques used in various studies for treatment of emerging contaminants with examples. Many conventional and advanced methods including aerobic and anaerobic treatments such as filtration, coagulation, ozonation, screening, UV photolysis, wetland treatment, flocculation and sedimentation have been used to treat EC-contaminated water, but the removal rate of different processes is different for different types of ECs. Various processes may be coupled to remove ECs from water during treatment.

Amongst conventional treatment processes, coagulation is the process of conversion of colloidal particles of wastewater by chemicals (coagulants) causing aggregation to allow them to degrade with time. According to Huerta-Fonntela et al. (2011), aluminium sulphate has been used as coagulant for removal of 80% of betaxolol, warfarin and hydrochlorothiazide by coagulation-flocculation, combined with sand filtration. PCPs such as galaxolide and tonalide from wastewater of hospitals have also been removed by this process (Suarez et al. 2009). Many physico-chemical factors such as pH, temperature and coagulant quality and types affect the result of coagulation-flocculation process. Some hydrophobic pharmaceuticals such as doxazosin, warfarin, bromazepam, betaxolol, etc. could be removed efficiently with the help of aluminium sulphate as a coagulant (Huerta-Fontela et al. 2011). However, estrone and estradiol removal rate is reported to be <5% (Le-Minh et al. 2010). Coagulants (pre-hydrolysed) such as polyferric sulphate, polyaluminium chloride, etc. can remove dyes more effectively as compared to hydrolyzing metal salts (Verma et al. 2012).

4.1 Aerobic Processes

4.1.1 Activated Sludge Process

The biomass produced by microorganisms in the presence of oxygen in wastewater is known as activated sludge. The activated sludge process is the most common conventional wastewater treatment process applied in removal of many ECs. Mostly, ECs are removed from wastewater by the process of biodegradation (Liu et al. 2009). This process utilizes microorganisms (bacteria, protozoa) for treatment of wastewater with the help of biological floc and oxygen. This process converts organic matter into CO_2 and water with other inorganic compounds. Surfactants have been successfully removed by activated sludge process due to their susceptibility to microorganisms and the degrading nature of surfactants (Buttiglieri and Knepper 2007). Some oestrogens, testosterone, endocrine disruptors, octylphenol, etc. have been completely removed due to their relative binding structure and affinity by activated sludge process (Semblante et al. 2015). Also, the presence of oxygen plays an important role in removal of EDCs due to the high removal efficiency of activated sludge process in aerobic conditions (Furuichi et al. 2006). The activated sludge process is also suitable for the treatment of PCPs with removal efficiency approximately 78–90% (Buttiglieri and Knepper 2007). In Sweden, estrodenic EDCs are removed by activated sludge process using yeast oestrogen screen bioassay indicating high efficiency of 81% removal rate (Svenson et al. 2003). The significant degradation of oestrogens for a wide range of sludge retention time under mesophilic and thermophilic conditions has been observed (Carballa et al. 2006). During the treatment, the treatment facility exerts foul smell due to the formation of hydrogen sulphide and mercaptans.

4.1.2 Membrane Technology

Membranes are produced with the help of different materials according to pore size, hydrophilic nature and surface area and used as a phase-changing process for removal of ECs (Schäfer et al. 2011). Membrane filtration can be categorised as ultrafiltration, microfiltration, nanofiltration, reverse osmosis, etc. depending upon the pore size. Membrane processes use hydrostatic pressure to remove suspended solids from water. Microfiltration cannot remove contaminant solids of size less than 1 μm and hence is not considered useful for EC removal (Zhou et al. 2010). Ultrafiltration process is used for removal of ECs as the membrane pore size (in between 0.001 and 0.1 mm) is smaller than microfiltration (Lidén and Persson 2016). For example, polysulfone-made ultrafiltration (UF) membrane was able to remove ECs by 75%, whereas polyvinylidene-made ultrafiltration membrane removed 98% of experimental influent load (Melo-Guimarães et al. 2013). The nanofiltration (NF) process can also be used for removal of ECs due to its small pore size (in between 10 and 100 Å) membrane (Lidén and Persson 2016). Hence NF is considered as more efficient than UF for EC removal; for example, caffeine removal with UF was in the range of 2–21% as compared to NF which removed 46–84% of caffeine (Acero et al. 2010). Reverse and forward osmosis is used as a semi-permeable membrane to filter solids from water. Reverse osmosis (RO) has high removal efficiency of particle size 10 Å and colloidal particles (Malaeb and Ayoub 2011). Forward osmosis can remove carbamazepine and caffeine by the rate of 80–99%. There are very few ECs that have less than 50% removal efficiency rate by using reverse or forward osmosis such as acetaminophen (Vickers 2017).

4.2 *Natural Aerobic Processes*

4.2.1 Waste Stabilization Ponds (WSPs)

Waste stabilization ponds are artificially built to remove organic matter and pathogens from wastewater for the treatment process. According to one report, WSPs have higher efficiency in the removal of pharmaceuticals and PCPs with the exception of carbamazepine; and the removal efficiency rate for PCPs by lagoon systems is as high as 80–100% (Li et al. 2013). The removal efficiency for malathion, erythromycin and 17 beta-estradiol has been reported moderate (50–75%) and for aldrin, endosulfan, hexachlorocyclohexane and diclofenac as low i.e. <50% (Kumar and Kumar 2020). In favourable environmental conditions, algae bacteria in WSPs could remove approximately 94% of 17 beta-estradiol (Parlade et al. 2018). According to another report, the algae *Chlorella pyrenoidosa* removed triclosan by cellular uptake, and *Desmodesmus* sp. removed it by biotransformation (Wang et al. 2018).

4.2.2 Constructed Wetlands

Constructed wetlands are land-based, natural wastewater treatment systems which use floating and emerging rooted vegetation in shallow beds and ponds (Cole 1998). CWs are classified into two categories: vertical flow constructed wetlands (VFCW) and horizontal flow constructed wetlands (HFCW). HFCWs have been reported to attenuate the ecotoxicological effects of ECs on aquatic systems by 60% (Matamoros et al. 2017). It has been reported that in constructed wetlands, the removal rate of some ECs such as oxytetracycline HCL, nadolol, cotinine and enrofloxacin is 70% (Li et al., 2014). The removal of emerging contaminants in constructed wetland depends upon sorption interaction and oxygen availability. Endocrine-disrupting contaminants (steroids, oestrogens, bisphenol A, phthalates) can be removed approximately 75–100% by the constructed wetland treatment process (Chen and Zhou 2014). Surface flow constructed wetlands (SFCW) have been reported to remove pesticides and beta-blockers at a rate of 80–100% (Ahmed et al. 2017).

4.3 Anaerobic Treatments

The emerging contaminants during wastewater treatment are sorbed to suspended solids and found in the sludge of primary and secondary clarifiers (Stasinakis 2012). Anaerobic digestion process is a widely used method for stabilization of sludge that can be used for agricultural practices after treatment (Kelessidis and Stasinakis 2012). Degradation of sulphonamide sulfamerazine has been conducted by bench-scale upflow anaerobic sludge blanket (UASB) reactor with aerobic stirred tank reactor (Sponza and Demirden 2007). The removal of three natural hormones such as E1, E2 and E3 has been achieved by full-scale anaerobic digester with 65:35 ratio of primary and secondary sludge and removal efficiency in the range of 30–40% (Muller et al. 2010). The concentration of ECs such as perfluorinated compounds is higher in sludge than wastewater which indicates that the formation of these compounds occurs during precursor transformation of biological treatments (Schultz et al. 2006).

4.3.1 Anaerobic Membrane Bioreactor (AnMBR)

Anaerobic membrane bioreactor (AnMBR) is an advanced anaerobic digestion method, has high stability of system and abundance of microbial population and has higher EC biodegradation efficiency than conventional anaerobic digestion techniques (Ji et al. 2020). Sludge anaerobic digestion process for degradation of surfactant linear alkyl benzene sulphonates (LAS) has been reported by Angelidaki et al. (2004). Use of cellulose as primary substrate under anaerobic condition has been reported to remove metoprolol tartrate, progesterone and ethinylestradiol faster (Musson et al. 2010).

4.4 Phase-Changing Techniques

Modern techniques for treatment of wastewater are capable of changing contaminants from one phase to another phase. Adsorption processes such as activated carbon, biochar-assisted adsorption, etc. have been extensively studied for the removal of different emerging pollutants. The adsorption process consists of many steps of treatment such as (a) bulk adsorbate movement by static fluid film encompassing the adsorbent to transport solute, (b) film diffusion adsorbate transport across the film, (c) pore-adsorbate diffusion through permeable system to active sites and (d) interaction of porous fabric and adsorbate (Homem and Santos 2011).

4.4.1 Activated Carbon-Assisted Adsorption

Activated carbon acts as an effective contaminant remover due to its unique properties such as large surface area and high porosity (Rivera-Utrilla et al. 2013; Al-Othman et al. 2012). Several types of pharmaceutical ECs can be removed by using activated carbon adsorption (Le-Minh et al. 2010). Activated carbon lowers the concentration of emerging contaminants such as ciprofloxacin to its detection limit (Carabineiro et al. 2011). According to a study, activated carbon can remove 19 types of PPCPs and pharmaceutical compounds from effluents that have been already treated in an ETP (Yang et al. 2011). The rate of removal of tetracycline by activated carbon from different sources such as activated carbon from peanut hulls and sugar beet pulp removes more than 90% of tetracycline, whereas wood removes 75%, and coconut shell could lower the concentration by 30% (Torres-Perez et al. 2012). Activated carbon obtained from waste material gives significant results in removing ECs such as anti-inflammatory drugs (Bueno et al. 2012) and paracetamol (Mirasole et al. 2016). Activated carbon adsorption process with other treatment processes can be used for removal of a wide range of ECs from water, and the result of the treatment has been reported to be 84–88% (Acero et al. 2012). More studies are required to determine the effect of different parameters on the feasibility of the activated carbon adsorption process.

4.4.2 Biochar-Assisted Adsorption

Biochar is a charcoal-based substance used to improve soil properties. It is generally prepared with help of pyrolysis (heating of biomass at high temperature with no oxygen) of biomass (Xie et al. 2014). Biochar is used for removal of ECs, and efficiency of adsorption process depends upon pyrolysis process (Mitchell et al. 2015). The production of biochar using different thermal conditions in pyrolysis affects the efficiency of the adsorption process of sulfamethoxazole; for example, without thermal activation, biochar removes 35% and with thermal activation could remove only 16% (Zheng et al. 2013). The acid-base and hydrophilic-hydrophobic properties of biochar are affected by thermal activation which transforms to feedstock and in turn influences the removal efficiency by particle size and porosity (Rasheed et al. 2019). Biochar associated with treatment efficiency of ECs depends upon the feedstock. Wood feedstock-based biochar removes sulfamethoxazole in the range of 12%, sugarcane feedstock-based biochar by 21% and rice husk and rice straw feedstock-based biochar approximately 12%. The presence of phosphorus and nitrogen with carbon affects the treatment efficiency of biochar (Yao et al. 2012; Liu et al. 2012). Tylosin removal by biochar prepared from different feedstock at different thermal conditions has been reported up to 10%, and the reason of lowest removal of antibiotic is associated with chemical configuration of tylosin as it exhibits more oxidation state and shows higher water solubility, in comparison to other antibiotics (Jeong et al. 2012). Also, the study of Mitchell et al. (2015) suggests that biochar removes ECs more efficiently as compared to activated carbon and exhibits different selectivity.

4.4.3 Clay Mineral-Assisted Adsorption

Hydrous aluminium phyllosilicate, cations of alkali and alkaline earth metals, magnesium (Mg), iron (Fe) and cations of variable amounts subject to planetary surface form clay minerals which are used as adsorbent for ECs (Rasheed et al. 2019). The removal efficiency varies with the presence of nitrogen, Fe and other minerals (Rahardjo et al. 2011). The adsorption capacity of surface modified clay is higher than native clay due to physico-chemical properties (Liu 2007), and the capacity of raw clay can be improvised by spray drying a disperse solution with sodium dodecyl sulphate that assists removal of methylene blue by surface modification (Olusegun et al. 2018). The removal efficiency of clay is different if obtained from different places. The performance and selectivity can be improved by value of cation exchange capacity and specific surface area (Parolo et al. 2012). Guz et al. (2014) have studied the advanced oxidation systems applied in Fenton-type reactions where a catalyst with matrix, i.e. clay minerals, was used for degradation of contaminants, and the matrix was recovered after the reaction.

4.4.4 Nanomaterial-Assisted Adsorption

Carbon nanotubes (CNTs) are modified carbon allotropes which are subject to physico-chemical characteristics, diameter, internal geometry and degree of curl and have graphite-like configuration used for several adsorption properties (Kim et al. 2014). CNTs are of two types: single-walled nanotubes (SWNT) and multiwalled nanotubes (MWNT). MWNTs are prepared from SWNTs by chemical processes which result in enhanced removal efficiency of MWNT by increasing surface area and active sites (Cho et al. 2011). The efficiency of CNTs depends on the methods used for their production and surface area. The structure of CNTs also plays an important role in surface area development and alters the removal of the same contaminants; for example, tetracycline removal rate was 92% using SWNT, whereas it was 16% by using MSNT (Ji et al. 2010). The removal rate of triclosan/ibuprofen using MWNT was 100% (Zheng et al. 2013); likewise, SWNT has been used to remove norfloxacin with 100% removal rate (Peng et al. 2012). Further studies are required to employ the use of CNTs for EC removal as comparative studies of both types of CNTs give different results during the removal process for the same types of contaminants (Tian et al. 2013).

4.5 Advanced Treatment Processes

Different substances (approximately 3000) are estimated to be used as painkillers, antibiotics, beta-blockers, antidiabetics, contraceptives, antidepressants, lipid regulators and impotence drugs. Significant research has been undertaken for the development of advanced removal technologies of emerging pollutants (ECs) in water in recent years. Advanced wastewater treatment processes, as shown in Fig. 3, including ozonation, UV irradiation, photolysis, reverse osmosis, peroxidation (peroxide and UV) and ultrasound can generally accomplish a higher removal rate than conventional treatment. Some advanced wastewater treatment techniques are discussed below.

4.5.1 Ozonation

Ozone as a powerful oxidant reacts with aromatic rings and double bonds of emerging compounds with high electron density (Acero et al. 2015). Ozonation is an energy-intensive process that helps in enhancement of biodegradability of contaminants during treatment. Numerous studies have been done with ozone for

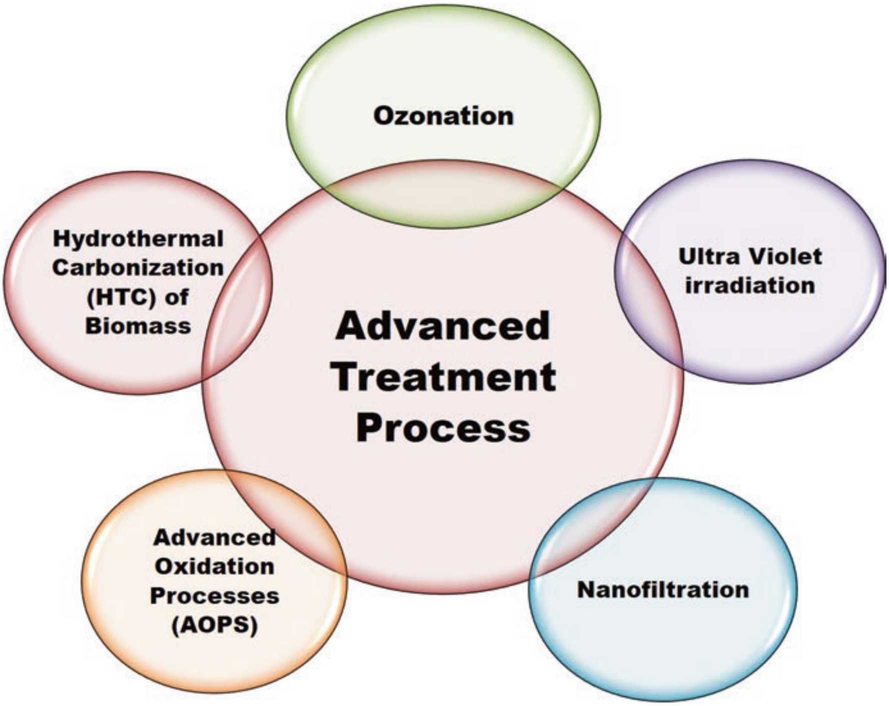

Fig. 3 Different types of advanced treatment processes

degradation of pharmaceuticals (Deegan et al. 2011). Removal of emerging contaminants is achieved by the most commonly used dark oxidation process known as ozonation (Esplugas et al. 2007). Some aromatic compounds e.g. sulfamethoxazole, deprotonated amino acids e.g. trimethoprim and non-aromatic alkenes, that are susceptible to oxidative reactions, are reported to show >90% contaminant removal efficiency (Dickenson et al. 2009). Ozone helps in deactivation of bactericidal property of antimicrobial chemicals by altering the functional groups such as N-etheroxime (Lange et al. 2006), aniline of sulphonamides (Huber et al. 2005), etc. The major problem with the ozonation process is formation of oxidative by-product, energy consumption and interference of radical scavengers (Luo et al. 2014).

4.5.2 Ultraviolet (UV) Irradiation

UV radiation can be used to degrade organic matter in water (Rosenfeldt and Liden 2004), and the process is based on quantum yield of compounds and the amount of UV used (Kim et al. 2009). UV radiations are used for wastewater disinfection as these have germicidal characteristics and also act as bactericide and virucide if the amount of UV dose is appropriate. The application of UV light can be extended with advanced oxidation processes of photolysis (degrade contaminants through absorption of photons and light exposure), since it is most commonly used for disinfection of water (Reynolds and Richards 1995; Metcalf & Eddy 2014). Various pharmaceuticals, EDCs and PCPs that have chromophores are transformed by UV radiation absorption (Gogoi et al. 2018). UV radiation use is limited for small-scale treatment as the cost of UV radiation lamp is very high (Prieto-Rodriguez et al. 2012). According to another study, the removal of ECs is more efficient by UV and chlorine AOPs (Rott et al. 2013).

4.5.3 Nanofiltration (NF)

The pore size of nanofilters ranges from 10 to 100A°, and these are used for treatment of wastewater in membrane bioreactors. Nanofilter membranes work on low pressure of water feed (Liden and Persson 2016). NF has been reported to be highly efficient as compared to UF for removal of ECs; for example, caffeine removal efficiency by UF was 2–21%, whereas by NF, it was 46–84% for ketorolac tromethamine (Acero et al. 2010). NF membranes can be used to remove pharmaceuticals by three processes such as electrostatic repulsion, adsorption and sieving (Dolara et al. 2012). Nanofiltration has been used for heavy metal removal and saline water and wastewater treatment; but using NF membranes has many challenges such as membrane fouling and disposal issues (Luo et al. 2014). For the removal and dispensing of pharmaceuticals, NF has been considered to be a promising option with an accomplishment of more than 90% removal rate (Bolong et al. 2009).

4.5.4 Advanced Oxidation Processes (AOPs)

AOPs are processes that help in generation of hydroxyl radicals by UV radiation and can be done by various methods including direct reaction of hydrogen peroxide (Rosenfeldt and Linden 2004) or by photocatalysis using titanium dioxide (Egerton et al. 2006). AOPs are very efficient techniques for water and wastewater treatment (Malato et al. 2009) and can be used for pre- or post-biological wastewater treatments. Bench-scale and pilot-scale utilized and accessed AOPs involve use of hydrogen peroxide (H_2O_2), ozone, photolysis using UV, semiconductors, Fenton reagents and sonolysis. Figure 4 shows the general process diagram of advanced oxidation process. Hydroxyl radical is an intense oxidizing agent used for organic matter oxidation (Litter 2005). Fenton processes are a type of AOPs that require iron to react with hydrogen peroxide to produce hydroxyl radical (Shemer et al. 2006). According to one study, photocatalytic ozonation (ozonation with titanium dioxide and solar photo Fenton using Fe (III) by solar heterogeneous photocatalysis) leads to higher degradation than photocatalytic oxidation (Gimeno et al. 2016). A significant factor for AOPs is hydroxyl radical production and the type of reaction required to produce it. The hydroxyl radical is a non-specific and intense oxidizing agent that attacks oxidizable organic compound at the rate of 106–109 M^{-1} S^{-1} (Andreozzi et al. 2003), for example, using UV photolysis for degradation of hydrogen peroxide (Sui et al. 2011) or using UV radiation for degradation of ozone (Ocampo-Pérez et al. 2012). A number of studies have shown that dicloxacillin is inert to UV radiation alone but highly sensitive to sonochemical conditions for degradation (Villegas-Guzman et al. 2015).

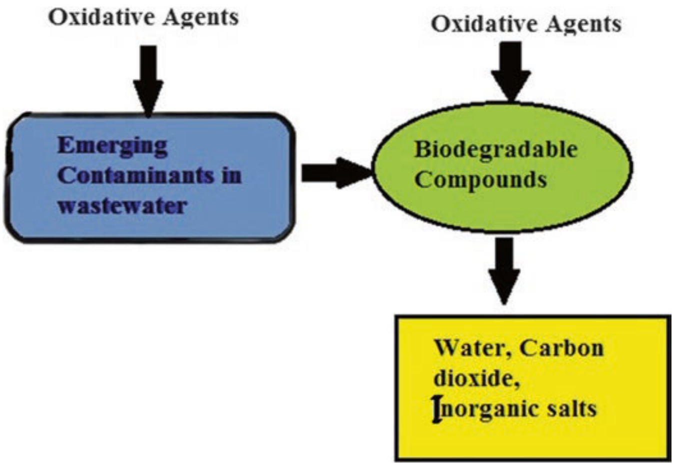

Fig. 4 General description of advanced oxidation process

4.5.5 Hydrothermal Carbonization (HTC) of Biomass

HTC is a simple process that reduces economical and energy cost (Fernandez et al. 2015) as this process heats biomass at temperatures in the range between 180 and 250 °C in water medium under saturated pressure for several hours. The biochar produced from this process has functional groups on the surface which act as good adsorbent (Roman et al. 2013). Many processes such as hydrolysis, dehydration, polymerization, etc. are applied to biomass, but their reactions to the treatment process are not common (Funke and Ziegler 2010). Agro-industrial wastes such as sunflower stems, walnut shell and olives (Roman et al. 2012), corn silage and poultry waste (Oliveira et al. 2013) and empty branches of palm (Parshetti et al. 2013) have been used as precursors to produce biochar.

5 Conclusion and Future Prospects

Emerging contaminants have been reported to cause potential environmental and health risks. In recent years, ECs have become a major concern for scientists trying to develop sustainable technologies for removal of water pollutants. A single remedial technique may not be suitable for the complete removal of ECs, as the physicochemical parameters may differ during different treatments. Hence, a combination of two or more advanced techniques is required along with the conventional wastewater treatment systems. Phase-change techniques are not considered effective for low concentrations but have been used for concentration pre-treatment with further treatments to degrade the ECs. However, advanced oxidation processes are considered as efficient solutions for ECs in many research studies. Further research in these areas should also include the evaluation of economical cost for using such advanced technology for pollutant treatment, as these techniques require additional energy and material. A wide range of molecules are removed by the aerobic metabolism of bacteria. However, the reutilization of the treated by product for different purposes requires more research so that these do not have any negative environmental impacts. The microorganisms and the chemicals (aerobic and anaerobic treatments) involved in the elimination of emerging contaminants do not have proper documentation; therefore, integrating such treatment technologies may help in the protection of the environment if the technologies are documented and experimented critically and the information is available for further use. Knowledge on the fate of emerging contaminants that are toxic to the environment after treatment is still lacking. The nature of ECs cannot be explained on the basis of laboratory tests as their reactions and behaviour in natural condition are different. So, to overcome the threat by ECs, further studies and research with natural environment are required. There is no single processes that can totally remove specific EC from water. The combination of different methods is required to achieve maximum removal efficiency. The cost and time consumption in multiple process cannot be avoided; hence, further research is required to optimize all treatment plan operations in a cost-effective manner.

References

Abdel-Shafy HI, Mansour MS (2016) A review on polycyclic aromatic hydrocarbons: source, environmental impact, effect on human health and remediation. Egypt J Pet 25(1):107–123

Acero JL, Benitez FJ, Teva F, Leal AI (2010) Retention of emerging micropollutants from UP water and a municipal secondary effluent by ultrafiltration and nanofiltration. Chem Eng J 163:264–272

Acero JL, Benitez FJ, Real FJ, Teva F (2012) Coupling of adsorption, coagulation, and ultrafiltration processes for the removal of emerging contaminants in a secondary effluent. Chem Eng J 210:1–8

Acero JL, Benitez FJ, Real FJ, Rodriguez E (2015) Elimination of selected emerging contaminants by the combination of membrane filtration and chemical oxidation processes. Water Air Soil Pollut 226(5):139

Ahmed MB, Zhou JL, Ngo HH, Guo W, Thomaidis NS, Xu J (2017) Progress in the biological and chemical treatment technologies for emerging contaminant removal from wastewater: a critical review. J Hazard Mater 323:274–298

Al-Othman ZA, Ali R, Naushad M (2012) Hexavalent chromium removal from aqueous medium by activated carbon prepared from peanut shell: adsorption kinetics, equilibrium and thermodynamic studies. Chem Eng J 184:238–247

Andreozzi R, Raffaele M, Nicklas P (2003) Pharmaceuticals in STP effluents and their solar photodegradation in aquatic environment. Chemosphere 50:1319–1330

Angelidaki I, Toräng L, Waul CM, Schmidt JE (2004) Anaerobic bioprocessing of sewage sludge, focusing on degradation of linear alkylbenzene sulfonates (LAS). Water Sci Technol 49(10):115–122

Arnold KE, Boxall ABA, Brown AR, Cuthbert RJ, Gaw S, Hutchinson TH, Jobling S, Madden JC, Metcalfe CD, Naidoo V, Shore RF, Smits JE, Taggart MA, Thompson HM (2013) Assessing the exposure risk and impacts of pharmaceuticals in the environment on individuals and ecosystems. Biol Lett 9

Aus der Beek T, Weber FA, Bergmann A, Hickmann S, Ebert I, Hein A, Küster A (2016) Pharmaceuticals in the environment—Global occurrences and perspectives. Environ Toxicol Chem 35(4):823–835

Baker DR, Kasprzyk-Hordern B (2013) Spatial and temporal occurrence of pharmaceuticals and illicit drugs in the aqueous environment and during wastewater treatment: new developments. Sci Total Environ 454:442–456

Balas CE, Williams AT, Simmons SL, Ergin A (2001) A statistical riverine litter propagation model. Mar Pollut Bull 42(11):1169–1176

Banger K, Toor GS, Chirenje T, Ma L (2010) Polycyclic aromatic hydrocarbons in urban soils of different land uses in Miami, Florida. Soil Sediment Contam 19(2):231–243

Ben Mansour H, Houas I, Montassar F, Ghedira K, Barillier D, Mosrati R, Chekir-Ghedira L (2012) Alteration of in vitro and acute in vivo toxicity of textile dyeing wastewater after chemical and biological remediation. Environ Sci Pollut Res Int 19:2634–2643. https://doi.org/10.1007/s11356-012-0802-7

Bilal M, Asgher M, Parra-Saldivar R, Hu H, Wang W, Zhang X, Iqbal HM (2017) Immobilized ligninolytic enzymes: an innovative and environmental responsive technology to tackle dye-based industrial pollutants – a review. Sci Total Environ 576:646–659

Bilal M, Adeel M, Rasheed T, Zhao Y, Iqbal HM (2019) Emerging contaminants of high concern and their enzyme-assisted biodegradation – a review. Environ Int 124:336–353

Bolong N, Ismail AF, Salim MR, Matsuura T (2009) A review of the effects of emerging contaminants in wastewater and options for their removal. Desalination 239:229–246

Borghi AA, Silva MF, Al Arni S, Converti A, Palma MS (2015) Doxycycline degradation by the oxidative Fenton process. J Chem 2015

Bueno MM, Gomez MJ, Herrera S, Hernando MD, Agüera A, Fernández-Alba AR (2012) Occurrence and persistence of organic emerging contaminants and priority pollutants in five sewage treatment plants of Spain: two years pilot survey monitoring. Environ Pollut 164:267–273

Buttiglieri G, Knepper TP (2007) Removal of emerging contaminants in wastewater treatment: conventional activated sludge treatment. In: Emerging Contaminants from Industrial and Municipal Waste. Springer, Berlin, Heidelberg, pp 1–35

Campanha MB, Awan AT, de Sousa DN, Grosseli GM, Mozeto AA, Fadini PS (2015) A 3-year study on occurrence of emerging contaminants in an urban stream of São Paulo State of Southeast Brazil. Environ Sci Pollut Res 22(10):7936–7947

Carabineiro SAC, Thavorn-Amornsri T, Pereira MFR, Figueiredo JL (2011) Adsorption of ciprofloxacin on surface-modified carbon materials. Water Res 45(15):4583–4591

Carballa M, Omil F, Alder AC, Lema JM (2006) Comparison between the conventional anaerobic digestion of sewage sludge and its combination with a chemical or thermal pre-treatment concerning the removal of pharmaceuticals and personal care products. Water Sci Technol 53(8):109–117

Carballa M, Omil F, Lema JM (2007) Calculation methods to perform mass balances of micropollutants in sewage treatment plants. Application to Pharmaceutical and Personal Care Products (PPCPs). Environ Sci Technol 41(3):884–890

Carra I, Pérez JAS, Malato S, Autin O, Jefferson B, Jarvis P (2015) Application of high intensity UVC-LED for the removal of acetamiprid with the photo-Fenton process. Chem Eng J 264:690–696

Cassani S, Gramatica P (2015) Identification of potential PBT behavior of personal care products by structural approaches. Sustain Chem Pharm 1:19–27

Chen K, Zhou JL (2014) Occurrence and behavior of antibiotics in water and sediments from the Huangpu River, Shanghai, China. Chemosphere 95:604–612

Cho HH, Huang H, Schwab K (2011) Effects of solution chemistry on the adsorption of ibuprofen and triclosan onto carbon nanotubes. Langmuir 27(21):12960–12967

Cole S (1998) The emergence of treatment wetlands. Environ Sci Technol 32(9):218A–223A

Comber S, Gardner M, Jones V, Ellor B (2015) Source apportionment of trace contaminants in urban sewer catchments. Environ Technol 36(5):573–587. https://doi.org/10.1080/09593330.2014.953599

Costanzo SD, Murby J, Bates J (2005) Ecosystem response to antibiotics entering the aquatic environment. Mar Pollut Bull 51(1-4):218–223

Daughton CG, Ternes AT (1999) Pharmaceuticals and personal care products in the environment: agents of subtle change? Environ Health Perspect 107(Suppl 6):S907–S938

Deegan AM, Shaik B, Nolan K, Urell K, Oelgemöller M, Tobin J, Morrissey A (2011) Treatment options for wastewater effluents from pharmaceutical companies. Int J Environ Sci & Technol 8(3):649–666

Dickenson ERV, Drewes JE, Sedlak DL, Wert EC, Snyder SA (2009) Applying surrogates and indicators to assess removal efficiency of trace organic chemicals during chemical oxidation of wastewaters. Environ Sci Technol 43:6242–6247

Dolara D, Gros M, Rodriguez-Mozaz S, Moreno J, Comas J, Rodriguez-Roda I, Barceló D (2012) Removal of emerging contaminants from municipal wastewater with an integrated membrane system, MBR–RO. J Hazard Mater 239–240:64–69

Dris R, Gasperi J, Tassin B (2018) Sources and fate of microplastics in urban areas: a focus on Paris Megacity. In Freshwater Microplastics. Springer, Cham, pp 69–83

Edelstein D (2013) Mineral Commodity Summaries 2016: Arsenic. Tech. Rep., U.S. Geological Survey (USGS), https://minerals.usgs.gov/minerals/pubs/commodity/arsenic/mcs-2016-arsen.pdf

Egerton TA, Christensen PA, Kosa SAM, Onoka B, Harper JC, Tinlin JR (2006) Photoelectrocatalysis by titanium dioxide for water treatment. Int J Environ Pollut 27(1–3)

Emond C, Michalek JE, Birnbaum LS, DeVito MJ (2005) Comparison of the use of a physiologically based pharmacokinetic model and a classical pharmacokinetic model for dioxin exposure assessments. Environ Health Perspect 113(12):1666

Environment Agency (2010) The Environment Agency's Position on Metaldehyde. Available from http://www.environmentagency.gov.uk/static/documents/Business/Metaldehyde_position_statement.doc-27.1.10.pdf

Esplugas S, Bila DM, Krause LGT, Dezotti M (2007) Ozonation and advanced oxidation technologies to remove endocrine disrupting chemicals (EDCs) and pharmaceuticals and personal care products (PPCPs) in water effluents. J Hazard Mater 149(3):631–642

European Commission (2011) Screening Report Iceland: Chapter 27. Environment European Commission, Brussels

Feng L, Watts MJ, Yeh D, Esposito G, van Hullebusch ED (2015) The efficacy of ozone/BAC treatment on non-steroidal anti-inflammatory drug removal from drinking water and surface water. Ozone Sci Eng 37(4):343–356

Ferguson KK, McElrath TF, Pace GG, Weller D, Zeng L, Pennathur S et al (2017) Urinary polycyclic aromatic hydrocarbon metabolite associations with biomarkers of inflammation, angiogenesis, and oxidative stress in pregnant women. Environ Sci Technol 51(8):4652–4660

Fernandez ME, Ledesma B, Roman S, Bonelli PR, Cukierman AL (2015) Development and characterization of activated hydrochars from orange peels as potential adsorbents for emerging organic contaminants. Bioresour Technol 183:221–228

Funke A, Ziegler F (2010) Hydrothermal carbonization of biomass: a summary and discussion of chemical mechanisms for process engineering. Biofuels Bioprod Biorefin 4:160–177

Furuichi T, Kannan K, Suzuki K, Tanaka S, Giesy JP, Masunaga S (2006) Occurrence of estrogenic compounds in and removal by a swine farm waste treatment plant. Environ Sci Technol 40(24):7896–7902

Gimeno O, Araya JFG, Beltran FJ, Rivas FJ, Espejo A (2016) Removal of emerging contaminants from a primary effluent of municipal wastewater by means of sequential biological degradation-solar photocatalytic oxidation process. Chem Eng J 290:12–20

Gogoi A, Mazumder P, Tyagi VK, Chaminda GT, An AK, Kumar M (2018) Occurrence and fate of emerging contaminants in water environment: a review. Groundw Sustain Dev 6:169–180

Gomes IB, Simões LC, Simões M (2018) The effects of emerging environmental contaminants on Stenotrophomonas maltophilia isolated from drinking water in planktonic and sessile states. Sci Total Environ 643:1348–1356

Gonzalez-Martinez A, Rodriguez-Sanchez A, Martinez-Toledo MV, Garcia-Ruiz MJ, Hontoria E, Osorio-Robles F, Gonzalez-Lopez J (2014) Effect of ciprofloxacin antibiotic on the partial-nitritation process and bacterial community structure of a submerged biofilter. Sci Total Environ 476:276–287

Guz L, Curutchet G, Sánchez RT, Candal R (2014) Adsorption of crystal violet on montmorillonite (or iron modified montmorillonite) followed by degradation through Fenton or photo-Fenton type reactions. J Environ Chem Eng 2(4):2344–2351

Hamers T, Kamstra JH, Cenijn PH, Pencikova K, Palkova L, Simeckova P, Vondracek J, Andersson PL, Stenberg M, Machala M (2011) In vitro toxicity profiling of ultrapure non–dioxin-like polychlorinated biphenyl congeners and their relative toxic contribution to PCB mixtures in humans. Toxicol Sci 121(1):88–100

Hignite C, Azarnoff DL (1977) Drugs and drug metabolites as environmental contaminants: chlorophenoxyisobutyrate and salicylic acid in sewage water effluent. Life Sci 20(2):337–341

Homem V, Santos L (2011) Degradation and removal methods of antibiotics from aqueous matrices – a review. J Environ Manage 92(10):2304–2347

Houtman CJ (2010) Emerging contaminants in surface waters and their relevance for the production of drinking water in Europe. J Integr Environ Sci 7(4):271–295

Huber MM, GÖbel A, Joss A, Hermann N, LÖffler D, McArdell CS, Ried A, Siegrist H, Ternes TA, von Gunten U (2005) Oxidation of pharmaceuticals during ozonation of municipal wastewater effluents: a pilot study. Environ Sci Technol 39(11):4290–4299

Huerta-Fontela M, Galceran MT, Ventura F (2011) Occurrence and removal of pharmaceuticals and hormones through drinking water treatment. Water Res 45:1432–1442

Jeong CY, Wang JJ, Dodla SK, Eberhardt TL, Groom L (2012) Effect of biochar amendment on tylosin adsorption–desorption and transport in two different soils. J Environ Qual 41(4):1185–1192

Ji L, Chen W, Bi J, Zheng S, Xu Z, Zhu D, Alvarez PJ (2010) Adsorption of tetracycline on single-walled and multi-walled carbon nanotubes as affected by aqueous solution chemistry. Environ Toxicol Chem 29(12):2713–2719

Ji J, Kakade A, Yu Z, Khan A, Liu P, Li X (2020) Anaerobic membrane bioreactors for treatment of emerging contaminants: A review. J Environ Manage 270:110913

Karanfil T, Erdogan I, Schlautman M (2005) The impact of filtrate turbidity on UV254 and SUVA254 determinations. J Am Water Works Ass 97(5):125–136

Kelessidis A, Stasinakis AS (2012) Comparative study of the methods used for treatment and final disposal of sewage sludge in European countries. Waste Manag 32(6):1186–1195

Kim I, Yamashita N, Tanaka H (2009) Performance of UV and UV/H_2O_2 processes for the removal of pharmaceuticals detected in secondary effluent of a sewage treatment plant in Japan. J Hazard Mater 166(2–3):1134–1140

Kim HJ, Choi K, Baek Y, Kim DG, Shim J, Yoon J, Lee JC (2014) High-performance reverse osmosis CNT/polyamide nanocomposite membrane by controlled interfacial interactions. ACS Appl Mater Interfaces 6(4):2819–2829

Kolpin DW, Furlong ET, Meyer MT, Thurman EM, Zaugg SD, Barber LB, Buxton HT (2002) Pharmaceuticals, hormones, and other organic wastewater contaminants in US streams, 1999–2000: a national reconnaissance. Environ Sci Technol 36(6):1202–1211

Kumar R, Kumar P (2020) Wastewater stabilisation ponds: removal of emerging contaminants. J Sustainable Develop Energy Water Environ Syst 8(2):344–359

Lange F, Cornelissen S, Kubac D, Sein MM, von Sonntag J, Hannich CB, Golloch A, Heipieper HJ, Moder M, von Sonntag C (2006) Degradation of macrolide antibiotics by ozone: A mechanistic case study with clarithromycin. Chemosphere 65:17–23

Le-Minh N, Khan JS, Drewes EJ, Stuetz MR (2010) Fate of antibiotics during municipal water recycling treatment processes. Water Res 44:4295–4323

Lesjean B, Gnirss R, Buisson H, Keller S, Tazi-Pain A, Luck F (2005) Outcomes of a 2-year investigation on enhanced biological nutrients removal and trace pollutants elimination in membrane bioreactor (MBR). Water Sci Technol 52(10–11):453–460

Li W, Nanaboina V, Zhou Q, Korshin VG (2012) Effects of Fenton treatment on the properties of effluent organic matter and their relationships with the degradation of pharmaceuticals and personal care products. Water Res 46(2):403–412

Li X, Zheng W, Kelly WR (2013) Occurrence and removal of pharmaceutical and hormone contaminants in rural wastewater treatment lagoons. Sci Total Environ 445:22–28

Li Y, Zhu G, Ng JW, Tan KS (2014) A review on removing pharmaceutical contaminants from wastewater by constructed wetlands: design, performance and mechanism. Sci Total Environ 468–469, 908–932

Lidén A, Persson KM (2016) Comparison between ultrafiltration and nanofiltration hollow-fiber membranes for removal of natural organic matter: a pilot study. J Water Suppl: Res Technol—AQUA 65(1):43–53

Linhart C, Niedrist GH, Nagler M, Nagrani R, Temml V, Bardelli T, Wilhalm T, Riedl A, Zaller JG, Clausing P, Hertoge K (2019) Pesticide contamination and associated risk factors at public playgrounds near intensively managed apple and wine orchards. Environ Sci Eu 31(1):28

Litter MI (2005) Introduction to photochemical advanced oxidation processes for water treatment. environmental photochemistry Part II, Volume 2M of the Series The Handbook of Environmental Chemistry, pp. 325–366.

Liu P (2007) Polymer modified clay minerals: a review. Appl Clay Sci 38(1–2):64–76

Liu ZH, Kanjo Y, Mizutani S (2009) Removal mechanisms for endocrine disrupting compounds (EDCs) in wastewater treatment—physical means, biodegradation, and chemical advanced oxidation: a review. Sci Total Environ 407(2):731–748

Liu P, Liu WJ, Jiang H, Chen JJ, Li WW, Yu HQ (2012) Modification of bio-char derived from fast pyrolysis of biomass and its application in removal of tetracycline from aqueous solution. Bioresour Technol 121:235–240

Liu A, Egodawatta P, Guan Y, Goonetilleke A (2013) Influence of rainfall and catchment characteristics on urban stormwater quality. Sci Total Environ 444:255–262

Liu XP, Zhang MH, Feng JY, Yang LF, Zhang PJ (2014) Removal of trace antibiotics from wastewater: a systematic study of nanofiltration combined with ozonebased advanced oxidation processes. Chem Eng J 240:211

Luo Y, Guo W, Ngo HH, Nghiem LD, Hai FI, Zhang J, Liang S, Wang XC (2014) A review on the occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment. Sci Total Environ 473:619–641

Malaeb L, Ayoub GM (2011) Reverse osmosis technology for water treatment: state of the art review. Desalination 267(1):1–8

Malato S, Fernandez-Ibanez P, Maldonado MI, Blanco J, Gernjak W (2009) Decontamination and disinfection of water by solar photocatalysis: recent overview and trends. Catal Today 147(1):1–59

Margot J, Rossi L, Barry DA, Holliger C (2015) A review of the fate of micropollutants in wastewater treatment plants. Wiley Interdiscip Rev Water 2(5):457–487

Matamoros V, Arias C, Brix H, Bayona JM (2007) Removal of pharmaceuticals and personal care products (PPCPs) from urban wastewater in a pilot vertical flow constructed wetland and a sand filter. Environ Sci Technol 41:8171–8177

Matamoros V, Rodriguez Y, Albaiges J (2016) A comparative assessment of intensive and extensive wastewater treatment technologies for removing emerging contaminants in small communities. Water Res 88:777–785

Matamoros V, Rodríguez Y, Bayona JM (2017) Mitigation of emerging contaminants by full-scale horizontal flow constructed wetlands fed with secondary treated wastewater. Ecol Eng 99:222–227

McGrane SJ (2016) Impacts of urbanisation on hydrological and water quality dynamics, and urban water management: a review. Hydrol Sci J 61(13):2295–2311

McKay G (2002) Dioxin characterisation, formation and minimisation during municipal solid waste (MSW) incineration. Chem Eng J 86(3):343–368

McMurry ML, Oethinger M, Levy BS (1998) Triclosan targets lipid synthesis. Nature 394:6693

Melo-Guimarães A, Torner-Morales FJ, Durán-Álvarez JC, Jiménez-Cisneros BE (2013) Removal and fate of emerging contaminants combining biological, flocculation and membrane treatments. Water Sci Technol 67(4):877–885

Metcalf & Eddy, Abu-Orf M, Bowden G, Burton FL, Pfrang W, Stensel HD, Tchobanoglous G, Tsuchihashi R, AECOM (Firm) (2014) Wastewater engineering: treatment and resource recovery. McGraw Hill Education

Mirasole C, Emond Di Carro M, Tanwar S, Magi E (2016) Liquid chromatography–tandem mass spectrometry and passive sampling: powerful tools for the determination of emerging pollutants in water for human consumption. J Mass Spectrom 51(9):814–820

Mitchell SM, Subbiah M, Ullman JL, Frear C, Call DR (2015) Evaluation of 27 different biochars for potential sequestration of antibiotic residues in food animal production environments. J Environ Chem Eng 3(1):162–169

Muller M, Combalbert S, Delgenes N, Bergheaud V, Rocher V, Benoit P, Delgens JP, Patureau D, Hernandez-Raquet G (2010) Occurrence of estrogens in sewage sludge and their fate during plant-scale anaerobic digestion. Chemosphere 81(1):65–71

Musson ES, Campo P, Tolaymat T, Suidan M, Townsend GT (2010) Assessment of the anaerobic degradation of six active pharmaceutical ingredients. Sci Total Environ 408:2068–2074

Navarro KM, Cisneros R, Noth EM, Balmes JR, Hammond SK (2017) Occupational exposure to polycyclic aromatic hydrocarbon of wildland firefighters at prescribed and wildland fires. Environ Sci Technol 51(11):6461–6469

Nizzetto L, Langaas S, Futter M (2016) Pollution: Do microplastics spill on to farm soils? Nature 537(7621):488–488

Nguyen NL, Van de Merwe PJ, Hai IF, Leusch LDF, Kang J, Price EW, Roddick F, Magram FS, Nghiem DL (2016) Laccase–syringaldehyde-mediated degradation of trace organic contaminants in an enzymatic membrane reactor: removal efficiency and effluent toxicity. Bioresour Technol 200:477–484

Ocampo-Pérez R, Rivera-Utrilla J, Gómez-Pacheco C, Sánchez-Polo M, López-Peñalver JJ (2012) Kinetic study of tetracycline adsorption on sludge-derived adsorbents in aqueous phase. Chem Eng J 213:88–96

Oliveira I, Blohse D, Ramke HG (2013) Hydrothermal carbonization of agricultural residues. Bioresour Technol 142:138–146

Olusegun SJ, de Sousa Lima LF, Mohallem NDS (2018) Enhancement of adsorption capacity of clay through spray drying and surface modification process for wastewater treatment. Chem Eng J 334:1719–1728

Oviedo KN, Aga DS (2016) Lessons learned from more than two decades of research on emerging contaminants in environment. J Hazard Mater 316:242–251

Pal A, He Y, Jekel M, Reinhard M, Gin KYH (2014) Emerging contaminants of public health significance as water quality indicator compounds in the urban water cycle. Environ Int 71:46–62

Parlade, E., Hom-Diaz, A., Blanquez, P., Martinez-Alonso, M., Vivent, T. And Gaju, N., 2018. Effect of Cultivation Conditions on B-Estradiol Removal in Laboratory and Pilot-Plant Photobioreactors by an Algal-Bacterial Consortium Treating Urban Wastewater, Water Res, Vol. 137, pp 86-96.

Parolo ME, Avena MJ, Pettinari GR, Baschini MT (2012) Influence of Ca2 PLUS_SPI on tetracycline adsorption on montmorillonite. J Colloid Interface Sci 368(1):420–426

Parshetti GK, Hoekman SK, Balasubramanian R (2013) Chemical, structural and combustion characteristics of carbonaceous products obtained by hydrothermal carbonization of palm empty fruit bunches. Bioresour Technol 135:683–689

Peng H, Pan B, Wu M, Liu Y, Zhang D, Xing B (2012) Adsorption of ofloxacin and norfloxacin on carbon nanotubes: hydrophobicity-and structure-controlled process. J Hazard Mater 233:89–96

Petrie B, McAdam EJ, Scrimshaw MD, Lester JN, Cartmell E (2013) Fate of drug during wastewater treatment. TrAC Trends Anal Chem 49:145–159

Pinheiro HM, Touraud E, Thomas O (2004) Aromatic amines from azo dye reduction: status review with emphasis on direct UV spectrophotometric detection in textile industry wastewaters. Dyes Pigment 61(2):121–139

Prieto-Rodriguez L, Miralles-Cuevas S, Oller I, Agüera A, Puma GL, Malato S (2012) Treatment of emerging contaminants in wastewater treatment plants (WWTP) effluents by solar photocatalysis using low TiO2 concentrations. J Hazard Mater 211:131–137

Rahardjo AK, Susanto MJJ, Kurniawan A, Indraswati N, Ismadji S (2011) Modified Ponorogo bentonite for the removal of ampicillin from wastewater. J Hazard Mater 190(1–3):1001–1008

Rasheed T, Bilal M, Nabeel F, Adeel M, Iqbal HM (2019) Environmentally- related contaminants of high concern: potential sources and analytical modalities for detection, quantification, and treatment. Environ Int. https://doi.org/10.1016/j.envint.2018.11.038. (In press)

Reynolds TD, Richards PAC (1995) Unit operations and processes in environmental engineering (No. 628.162 R333u Ej. 1). PWS Publishing Company

Rivera-Utrilla J, Sánchez-Polo M, Ferro-García MÁ, Prados-Joya G, Ocampo-Pérez R (2013) Pharmaceuticals as emerging contaminants and their removal from water. A review. Chemosphere 93(7):1268–1287

Rodriguez-Narvaez OM, Peralta-Hernandez JM, Goonetilleke A, Bandala ER (2017) Treatment technologies for emerging contaminants in water: a review. Chem Eng J.323:361–380

Roman S, Nabais JMV, Laginhas C, Ledesma B, Gonzalez JF (2012) Hydrothermal carbonization as an effective way of densifying the energy content of biomass. Fuel Process Technol 103:78–83

Roman S, Valente Nabais JM, Ledesma B, Gonzalez JF, Laginhas C, Titirici MM (2013) Production of low-cost adsorbents with tunable surface chemistry by conjunction of hydrothermal carbonization and activation processes. Microporous Mesoporous Mater 165:127–133

Rosal R, Rodea-Palomares I, Boltes K, Fernandez-Pinas F, Leganes F, Gonzalo S, Petre A (2009) Ecotoxicity assessment of lipid regulators in water and biologically treated wastewater using three aquatic organisms. Environ Sci Pollut Res 17:135–144

Rosenfeldt EJ, Linden KG (2004) Degradation of endocrine disrupting chemicals bisphenol A, ethinyl estradiol, and estradiol during UV photolysis and advanced oxidation processes. Environ Sci Technol 38(20):5476–5483

Rott E, Lange C, Kuch B, Minke R, Steinmetz H (2013) Elimination of emerging contaminants in wastewater treatment effluent using UV/chlorine advanced oxidation treatment. ISTANBUL3WCONGRESS 2013, p 525

Routledge JE, Parker J, Odum J, Ashby J, Sumpter JP (1998) Some alkyl hydroxy benzoate preservatives (parabens) are estrogenic. Toxicol Appl Pharmacol 153:12–19

Saggioro EM, Chaves FP, Felix LC, Gomes G, Bila DM (2019) Endocrine disruptor degradation by UV/chlorine and the impact of their removal on estrogenic activity and toxicity. Int J Photoenergy 2019

Sany SBT, Hashim R, Salleh A, Rezayi M, Karlen DJ, Razavizadeh BBM, Abouzari-lotf E (2015) Dioxin risk assessment: mechanisms of action and possible toxicity in human health. Environ Sci Pollut Res 22(24):19434–19450

Schäfer AI, Akanyeti I, Semião AJ (2011) Micropollutant sorption to membrane polymers: a review of mechanisms for estrogens. Adv Colloid Interface Sci 164(1-2):100–117

Schultz MM, Higgins CP, Huset CA, Luthy RG, Barofsky DF, Field JA (2006) Fluorochemical mass flows in a municipal wastewater treatment facility. Environ Sci Technol 40(23):7350–7357

Semblante GU, Hai FI, Huang X, Ball AS, Price WE, Nghiem LD (2015) Trace organic contaminants in biosolids: impact of conventional wastewater and sludge processing technologies and emerging alternatives. J Hazard Mater 300:1–17

Shemer H, Kunukcu YK, Linden KG (2006) Degradation of the pharmaceutical metronidazole via UV, Fenton and photo-Fenton processes. Chemosphere 63(2):269–276

Souza FS, Féris LA (2015) Degradation of caffeine by advanced oxidative processes: O3 and O3/UV. Ozone Sci Eng 37(4):379–384

Sponza DT, Demirden P (2007) Treatability of sulfamerazine in sequential upflow anaerobic sludge blanket reactor (UASB)/completely stirred tank reactor (CSTR) process. Sep Purif Technol 56(1):108–117

Stasinakis AS (2012) Review on the fate of emerging contaminants during sludge anaerobic digestion. Bioresour Technol 121:432–440

Stefanakis AI, Becker JA (2016) A review of emerging contaminants in water: classification, sources, and potential risks. In: Impact of water pollution on human health and environmental sustainability, pp 55–80

Sui Q, Huang J, Deng S, Chen W, Yu G (2011) Seasonal variation in the occurrence and removal of pharmaceuticals and personal care products in different biological wastewater treatment processes. Environ Sci Technol 45(8):3341–3348

Suarez S, Lema JM, Omil F (2009) Pre-treatment of hospital wastewater by coagulation–flocculation and flotation. Bioresour Technol 100(7):2138–2146

Svenson A, Allard A, Ek M (2003) Removal of estrogenicity in Swedish municipal sewage treatment plants. Water Res 37:4433–4443

Tian Y, Gao B, Morales VL, Chen H, Wang Y, Li H (2013) Removal of sulfamethoxazole and sulfapyridine by carbon nanotubes in fixed-bed columns. Chemosphere 90(10):2597–2605

Torres-Pérez J, Gérente C, Andrès Y (2012) Sustainable activated carbons from agricultural residues dedicated to antibiotic removal by adsorption. Chin J Chem Eng 20(3):524–529

Urase T, Kagawa C, Kikuta T (2005) Factors affecting removal of pharmaceutical substances and estrogens in membrane separation bioreactors. Desalination 178(1-3):107–113

US EPA (2012) Water: Contaminant Candidate List 3. US Environmental Protection Agency, Washington, DC

USEPA (2012) Guidelines for Water Reuse EPA/625/R-04/108. USEPA, Washington, D.C.

Vallejo-Rodríguez R, Murillo-Tovar M, Navarro-Laboulais J, León-Becerril E, López-López A (2014) Assessment of the kinetics of oxidation of some steroids and pharmaceutical compounds in water using ozone. J Environ Chem Eng 2(1):316–323

Verma AK, Dash RR, Bhunia P (2012) A review on chemical coagulation/flocculation technologies for removal of colour from textile wastewaters. J Environ Manage 93:154–168

Vickers NJ (2017) Animal communication: when i'm calling you, will you answer too? Curr Biol 27(14):R713–R715

Villegas-Guzman P, Silva-Agredo J, Giraldo-Aguirre AL, Flórez-Acosta O, Petrier C, Torres-Palma RA (2015) Enhancement and inhibition effects of water matrices during the sonochemical degradation of the antibiotic dicloxacillin. Ultrason Sonochem 22:211–219

Wang S, Poon K, Cai Z (2018) Removal and Metabolism of Triclosan by Three Different Microalgal Species in Aquatic Environment. J Hazard Mater 342:643–650

Westerhoff P, Yoon Y, Snyder SA, Wert E (2005) Fate of endocrine-disruptor, pharmaceutical, and personal care product chemicals during simulated drinking water treatment processes. Environ Sci Technol 39(17):6649–6663

WHO (2011) Pharmaceuticals in Drinking Water: Public Health and Environment Water, Sanitation, Hygiene and Health. World Health Organization, Geneva

Wick P, Malek A, Manser P, Meili D, Maeder-Althaus X, Diener L, Diener PA, Zisch A, Krug HF, von Mandach U (2010) Barrier capacity of human placenta for nanosized materials. Environ Health Perspect 118(3):432–436

Wintgens T, Gallenkemper M, Melin T (2003) Occurrence and removal of endocrine disrupters in landfill leachate treatment plants. Water Sci Technol 48(3):127–134

Xiang P, Liu RY, Sun HJ, Han YH, He RW, Cui XY, Ma LQ (2016) Molecular mechanisms of dust-induced toxicity in human corneal epithelial cells: water and organic extract of office and house dust. Environ Int 92:348–356

Xie M, Chen W, Xu Z, Zheng S, Zhu D (2014) Adsorption of sulfonamides to demineralised pine wood biochars prepared under different thermochemical conditions. Environ Pollut 186:187–194

Yang L, Yu LE, Ray MB (2008) Degradation of paracetamol in aqueous solutions by TiO2 photocatalysis. Water Res 42(3):3480–3488

Yang X, Flowers RC, Weinberg HS, Singer PC (2011) Occurrence and removal of pharmaceuticals and personal care products (PPCPs) in an advanced wastewater reclamation plant. Water Res 45(16):5218–5228

Yao Y, Gao B, Chen H, Jiang L, Inyang M, Zimmerman AR et al (2012) Adsorption of sulfamethoxazole on biochar and its impact on reclaimed water irrigation. J Hazard Mater 209:408–413

Zheng H, Wang Z, Zhao J, Herbert S, Xing B (2013) Sorption of antibiotic sulfamethoxazole varies with biochars produced at different temperatures. Environ Pollut 181:60–67

Zhou JE, Chang Q, Wang Y, Wang J, Meng G (2010) Separation of stable oil–water emulsion by the hydrophilic nano-sized ZrO2 modified Al2O3 microfiltration membrane. Sep Purif Technol 75(3):243–248

Zorita S, Martensson L, Mathiasson L (2009) Occurrence and removal of pharmaceuticals in a municipal sewage treatment system in the south of Sweden. Sci Total Environ 407(8):2760–2770

Emerging Contaminants in Wastewater and Associated Treatment Technologies

Akash Balakrishnan, Muthamilselvi Ponnuchamy, Ashish Kapoor, and Prabhakar Sivaraman

Abstract The expanding production base of agricultural and industrial products triggered by population growth and lifestyle changes has increased the demand for fresh water besides polluting the existing natural water bodies. Consequently, provision of safe drinking water has become a challenge due to newer contaminants arising from all the human activities leading to the expansion of water-stressed and water-scarce regions. Emerging pollutants are defined as synthetic or naturally occurring chemicals such as pharmaceuticals, personal care products, pesticides, flame retardants, etc. These compounds in the environment can enter the environment and cause ecological and (or) human health effects. The existence of these organic pollutants is detected in surface water. So, there is the need for wastewater treatment technology indeed to ensure the provision of a safe supply of water. Different methods like adsorption, bioremediation, membrane technology, advance oxidation process (photocatalysis, sonolysis), and other hybrid technologies are adopted for water treatment technology. Generally conventional wastewater treatment methods are not highly encouraged in removal of emerging contaminants due to poor efficiency, high sludge production, chemical requirements, and operating costs. Therefore, advanced oxidation process is adopted for water remediation processes for the complete mineralization of emerging contaminants. This chapter focuses on existing and hybrid wastewater treatment methods for the destruction of organic compounds.

Keywords Emerging contaminants (ECs) · Treatment techniques · Wastewater · Advance oxidation process (AOP) · Membrane technology

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1 Introduction

Increasing population and improving quality of life have escalated the demand for water in the last few decades. Even though natural water cycle is in perpetual operation, the precipitation has become skewed due to several factors including climatic changes and deforestation. With increasing demand for food as well as other lifestyle conveniences, synthetic substitutes such as fertilizers, pesticides in agriculture, synthetic cosmetics, etc. are increasingly produced. Consequently, many new products are developed with a variety of chemicals, some of them being toxic. Eventually, these products find their way into effluent streams after use or in small amounts during the manufacturing process as pollutants initially as liquid wastes slowly finding their way to water bodies through different means (Harrison 2011; Mansour et al. 2018).

Water is a common resource required by every act of human being encompassing different sectors like industries, agriculture, domestic activities, and transportation. The major sources other than seawater which is saline can be classified as surface water and underground water. Both require rainwater for replenishment. Overexploitation of water results in the presence of harmful contaminants such as heavy metals, arsenic, fluorides, etc. depending upon the source of aquifers; new contaminants do also emerge in these such as uranium, lead, etc., which are not normally present in water. These contaminants which owe their origin to the geological characteristics are termed as geogenic contaminants. Some of the long-known contaminants in this category include iron, arsenic, fluoride, nitrate, etc., while the emerging contaminant species include heavy metal ions such uranium, lead, etc.

The other category of contaminants classified as “anthropogenic” is the result of human activities including agricultural, industrial, pharmaceuticals, etc. The list of these contaminants is always growing and is called “emerging contaminants” (ECs) (Salimi et al. 2017). Different sources of ECs are illustrated in Fig. 1. US geological survey defined ECs as synthetic or naturally occurring chemicals or any microorganisms that are tracked in the environment which cause severe health and environmental impacts (USGS 2017). Most of these contaminants are difficult to remove and get carried by water in nano-quantities because of extremely low solubility in water. This in turn results in the generation of large quantities of wastewater containing trace levels of contaminants. The pollutants of emerging concern are a new group of contaminants seen in water bodies for years constituting a high-risk environmental issue being a potential health hazard (Bolong et al. 2009). It is reported that antibiotic resistance bacteria are also included as emerging contaminants and they exhibit long term ecological effects (Philip et al. 2018). Generally, ECs are substances with high concern due to bio-accumulation in fatty tissues, long range transportability, and high toxicity even at low dosages (Kumari et al. 2020).

Due to rapid usage of ECs, they are seen in all environmental matrices like soil, water, and air and resist biodegradation and eventually accumulate in the food chain

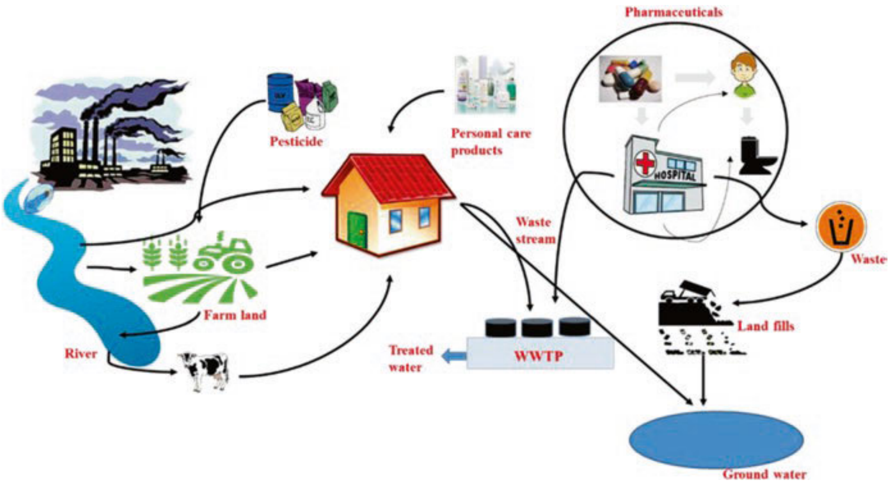


Fig. 1 Sources of different emerging contaminants

(Dhaka et al. 2019). The presence of these ECs is detected in micro- or nanoscale with different levels on toxicity and persistence creating severe effects on the ecosystem (Rodriguez-Narvaez et al. 2017). Major sources of ECs are pollutant stream from wastewater treatment plants, water runoff from farmlands, dumping of outdated chemicals to water bodies, direct discharge of industrial effluents, and landfill leaching (Balakrishnan et al. 2020).

Physical, chemical, or biological treatment methods are not capable of eliminating ECs due to its complex and complicated chemical structure, non-biodegradability, and low concentration (Salimi et al. 2017). Literature also emphasized that ECs are not eliminated through the conventional water treatment plants and wastewater treatment plants because of low concentration of ECs in microscale range (Yap et al. 2019). Therefore, an advanced oxidation process and a combination of AOPs with other treatment methods can be adopted for the mineralization of ECs from water bodies (Kanakaraju et al. 2018).

1.1 Emerging Contaminants

Emerging contaminants (ECs) is a term used to recognize the risk associated with the release of new toxic contaminants with severe damage to both humans and the environment. ECs include endocrine disruptors (EDCs), pesticides, fire retardants, artificial sweeteners, surfactants, pharmaceuticals, and personal care products (García et al. 2020). The presence of these harmful compounds may cause significant impact on livelihood of humans. It's evident that ECs cause severe long-term and short-term health effects like endocrine disruption, neurotoxicity, cancers, immunotoxicity, skin disorders, etc. (Sanchez and Egea 2018). Several techniques

Table 1 Commonly seen emerging pollutants in wastewater

ECs/class	Example	Maximum contaminant level ng/mL	Solubility mg/L
Pesticides			
Organophosphate	Chlorpyrifos	20	1.4 at 25 °C
	Malathion	100	143 at 20 °C
	Diazinon	0.6	60 at 20 °C
	Parathion	2.3	11 at 20 °C
	Methyl parathion	2	37.7 at 20 °C
Organochlorine	Endosulfan	42	0.53 at 25 °C
	2,4-Dichlorophenoxyacetic acid	70	677 at 25 °C
	Methoxychlor	40	0.040 at 24 °C
	Dieldrin	0.2	0.195 at 25 °C
Triazine	Atrazine	3	34.7 at 26 °C
	Cyanazine	1	170 at 25 °C
Pyrethroids	Cypermethrin	–	$4 * 10^{-3}$ at 20 °C
EDCs	Bisphenol-A	20	300 at 25 °C
	Diethyl phthalate	–	1000 at 25 °C
	Phthalic acid	–	6965 at 25 °C
	Phthalic acid diethyl ester		1080 at 25 °C
Artificial sweeteners	Aspartame	–	20 at 25 °C
Pharmaceuticals	Diclofenac	–	2.37 at 25 °C
	Ibuprofen	–	21 at 20 °C

USEPA (2017)

were reported for the redemption of organic pollutants such as physical, chemical, or biological methods. Commonly detected ECs with its maximum contaminant level (MCL) and solubility in water are depicted in Table 1.

2 Wastewater Treatment Technologies

In view of an environmental engineer, the need for treatment of water streams containing ECs is performed by adopting various physical, chemical, and biological treatment technologies (Paumo et al. 2020). Thus, elimination of ECs is conducted for complete separation and recovery of target compounds. Different treatment methods like coagulation, flocculation, bioremediation, ozonation, filtration, and sedimentation are used to eliminate toxic compounds (Patel et al. 2019). These traditional water treatment systems are only applicable for insoluble pollutants in water and therefore not popular due to its complexity, high installation cost, and

Table 2 Advantages and disadvantages of different treatment methods

Treatment method	Advantage	Disadvantage
Coagulation/ flocculation	Simple Economically feasible Reduce turbidity due to suspended organic and inorganic particles	Higher sludge production Requirement of higher coagulant
Biodegradation	Economically feasible	Maintenance of optimum operating and nutrition requirements
Chlorination	Generally eliminate reactive compounds	Produce toxic chlorinated by-products
MF/UF	High-quality effluent and no toxicity risk associated with ECs Remove pathogens and inorganic metals	Not fully effective in removal of ECs with larger pore size
NF	Effectively remove organic and inorganic pollutants	High operational cost High energy demand Prone to membrane fouling
RO	Reduce wastewater volume	High energy consumption Interference of radical scavengers
Adsorption	High efficiency Produce high-quality treated water	Regeneration is difficult
Membrane-based method	Produce good-quality treated water	Expensive Not suitable for treatment of higher volumes
Ion exchange	Ease in regeneration	High cost
Oxidation	Rapid and efficient process	High energy consumption Need for expensive chemical requirements
Ozonation	Selective oxidants favor disinfection	High energy consumption Formation of oxidative by-products
Fentons and photofentons	High removal percentage	Generate degradation by-products
AOPs (UV/H_2O_2, O_3/UV, etc.)	High removal percentage Short degradation rate	Operationally complex process High energy consumption, operating cost, and maintenance cost
Photocatalysis	Minimum sludge production Less chemical requirements	Economically unfeasible due to formation of by-products Inefficient to handle larger volume High energy demand and operational cost

difficulty in maintenance and handling where adsorption converts pollutants from one phase to other (Dong et al. 2015). So, most of these physical and chemical processes are not suitable in abatement of pollutants effectively. Thus, advanced treatment methods like photocatalysis, sonocatalysis, biological degradation, and hybrid systems are necessary in complete mineralization of pollutants seen in water (Balakrishnan et al. 2020). The key advantages of different treatment methods are highlighted in Table 2.

3 Conventional Treatment Methods

The coagulation/flocculation is a proficient method for elimination of ECs to a few extent as it requires large quantity of coagulants to neutralize ions and charged particles in suspension (Paumo et al. 2020). So, this approach leads to higher sludge production resulting in disposal and handling problems associated with different toxic compounds and their metabolites (Patel et al. 2019). Chemical precipitation involves transitions in the form of materials dissolved in water to solid particles. It's not highly accepted in treatment technology due to its high treatment cost, higher generation of waste product, and higher operational, maintenance, and power requirements (Crini and Lichtfouse 2019).

3.1 Adsorption

Adsorption is a surface phenomenon in which a group of compounds commonly called adsorbate is preferentially deposited on the solid adsorbent surface (Barczak et al. 2020; Gusain et al. 2020). Adsorption is a flexible and practiced methodology in redemption of EC due to its biodegradability, ease of handling, high efficiency, low cost, and ability to treat target pollutant molecules in lower concentrations (Chakraborty et al. 2020). A wide variety of materials are utilized as adsorbents for potential application in water treatment (Sophia and Lima 2018). Commonly seen adsorbent types are (Trivedi and Mandavgane 2018):

1. Adsorbents prepared from biomass.
2. Commercial activated carbon (granular activated carbon, surface-modified activated carbon, mesoporous activated carbon, etc.)
3. Synthetic materials (bentonites, zeolites, silica gel).

Activated carbon is the most commonly used and commercially available adsorbent (Hernández-Abreu et al. 2020). The development of further new cost-effective adsorbents is necessary to avoid problems related to reactivation for the adsorbents (de Bezerra et al. 2020). In recent days, locally available biomass is used as a source of preparation of adsorbents to address issues related to regeneration and mass loss along with contaminant disposal concern to a specific point (Jacob et al. 2020). Adsorbents like silica, clays, zeolites, biochar, and chitosan is used along with low-cost materials, such as sugar cane bagasse, wood pulp, vegetable waste, banana stalk, coffee waste, and maize cob, as alternatives for activated carbon in water technology (Sowmya and Meenakshi 2014; Tara et al. 2019; Chakraborty et al. 2020; Jacob et al. 2020; Xiang et al. 2020). Treatment technology based on adsorption is solely dependent on nature, selectivity of adsorbents along with potent availability, and minimum financial constraints (Gusain et al. 2020).

Many researchers explored different adsorbents for the adsorption of different ECs (Table 3). The conclusions drawn from these studies are that activated carbon

Table 3 Recently reported adsorbents for the treatment of ECs

Adsorbate	Adsorbent	Adsorption capacity (mg/g)	Reference
Bisphenol-A	Lignin-based AC Resorcinol formaldehyde hydrogel	220 78	Hernández-Abreu et al. (2020)
Oxytetracycline Glyphosate Cr (VI) Cd (II)	Graphitic nanobiochar	520 83 7.46 922	Ramanayaka et al. (2020)
4-bromophenol 4-Chloroaniline	Activated carbon derived from the shell of cashew of Para	488.2 552.5	Thue et al. (2020)
Tetracycline hydrochloride	Boron nitride nanosheets	1101	Chao et al. (2020)
Ciprofloxacin Amoxicillin	Activated carbon prepared from *Prosopis juliflora*	250 714	Chandrasekaran et al. (2020)
Diclofenac Sulfamethazine	Magnetic COF	109 113.2	Zhuang et al. (2020)
Amoxicillin Imipramine Diclofenac sodium Paracetamol	Ti-pillared montmorillonite clay	4.26 82.68 23.05 20.83	Chauhan et al. (2020)
Fluoxetine Nicotinic acid	Hydrochar-based adsorbents	44.1 90.1	Román et al. (2020)
Daidzein Coumestrol	Nanozeolitic beta modified with tetrasubstituted ammonium cation	40.74 42.87	Goyal et al. (2018)

and synthetic materials provide high surface area and adsorption capacity for elimination of EC like herbicides, EDCs, and pharmaceuticals (Trivedi and Mandavgane 2018; Singh et al. 2020). The main problems associated with these techniques are (i) high time requirements and (ii) problems associated with regeneration (Trivedi and Mandavgane 2018; Patel et al. 2019). Therefore, this technique is not highly favorable for the decomposition of emerging contaminants as it's not capable to completely detoxify chemical compounds rather than phase change (Gusain et al. 2020).

3.2 Microbial Bioremediation

Bioremediation process mediated through microorganisms is an effective alternative strategy to treat different emerging pollutants like pesticides, herbicides, pharmaceuticals, personal care products, chlorinated solvents, etc. (Ghangrekar et al. 2020). These biological degradation processes using microorganisms are versatile, less hazardous, cost-effective, and environmentally benign alternatives for pollutant abatement (Trivedi and Mandavgane 2018; Sutherland and Ralph 2019). In this process, harmful compounds are continuously and progressively converted to less toxic form for the replacement of pollutants using anaerobic or aerobic bacteria. Further bioremediation of emerging contaminants can be conducted using in situ and ex situ methods (Ghangrekar et al. 2020). In situ techniques like biosparging, bioventing, and bio-augmentation are used to treat polluted water and soil at on-site treatment with minimal influence of external parameters in terms of excavation (Niti et al. 2014). On the other hand, ex situ treatment method is suitable for treatment of groundwater or soil from a contaminated site at specific treatment plant with the support of physiochemical processes (Niti et al. 2014). The ex situ remediation method possesses limitations like large operating cost, transportation cost associated with pumping, and treatment cost, while in situ allows onsite remediation of ECs with minimum cost (Azubuike et al. 2016).

Literature explored utilization of different microbial strains (like *Pseudomonas putida* SM 1443, *Azotobacter* sp. Strain SSB81) from the soil for degradation of different emerging pollutants. However, microbial consortium showed a higher selectivity and biodegradation than a single selective strain because of its adaptability toward wide variety of stress (Trivedi and Mandavgane 2018). Bioremediation is highly influenced by pH of the solution, temperature, type of strain and its activity, concentration of ECs, and holding time inside the reactors, and dissolved oxygen played a crucial role in transformation of emerging contaminants to non-hazardous form (Niti et al. 2014).

Commonly used strains for biological decomposition of ECs are *Achromobacter* sp. *QXH*, *Streptomyces consortium*, *Pseudomonas putida* mt-2, and isolated bacterial consortium for the removal of ECs (Mansour et al. 2012). The merits of biological degradation processes are as follows: (i) they are eco-friendly in nature, and (ii) microorganisms like *Azotobacter* fix nitrogen in soil (Trivedi and Mandavgane 2018). This is temperature dependent and requires automated process control for the maintenance of operational parameters (Trivedi and Mandavgane 2018). However, hybrid bioremediation technologies for the treatment of wastewater containing ECs are necessary for scale up as it reduces the reaction time.

3.3 Membrane Technology

Membrane is a barrier which enables the preferential passage of a species selectively because of its specific property under an applied gradient, mechanical, thermal, electrical, or chemical. In wastewater treatment, only porous membranes are used, which operate under pressure gradient known as "pressure-driven membrane processes." Microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) are the commercially used membranes processes, particularly for separations involving aqueous solutions (Yalcinkaya et al. 2020). The average pore size of these membranes is in increasing order with RO having pores in the order of angstrom units, NF in nanometers, and UF in tens of a nanometers to tenths of micrometers. Membrane processes work on the principle of size exclusion, adsorption, and electrostatic interaction.

The removal process in UF is purely based on size exclusion, while in RO and NF, it is combination of size and surface interactions normally referred to as physicochemical. On the other hand, removal of ECs in MF and UF is based on adsorption (Muhamad et al. 2016). The performance of a membrane is dependent on factors like type of membrane process, based on type of operation, issues related to membrane fouling, and type of membrane materials (Muhamad et al. 2016; Kumari et al. 2020). The merits of using membrane technology in wastewater treatments are higher efficiency, low energy consumption, less sludge production, minimum chemical requirements, and superior quality of treated water (Li and Visvanathan 2017).

UF exhibits poor removal of ECs due to higher pore size of these membranes in comparison with pollutants (Plakas and Karabelas 2012). Ibuprofen is a very small compound, where hydrophobic polyethersulfone membrane only retains 25% of pollutants (Kumari et al. 2020). Shah et al. in 2012 emphasized the transport mechanisms dominating NF removal of low-molecular-weight pollutants and the removal of sulfamethoxazole and carbadox, where rejection performance increased to 95% from 90% because of membrane charge repulsion at pH of 6.6. Wang et al. (2015a, b) highlighted that complete rejection of pollutants is based on steric effect of trace organic compounds on NF membrane.

UF is more versatile for the removal of microbial contaminants and widely used as membrane bioreactors in secondary treatment where biodegradable organic species are removed. Even when the sizes of chemical species are small, the sizes can be enhanced either by complexation as in the case of metal ions or adsorbed onto microparticles and processed through UF to remove the contaminants (Kavitha et al. 2020). RO and NF pressures are high. Further they cannot lead to near-complete decontamination as in UF because of the limitations of the osmotic pressure. Advancements in the membrane technology are necessary to enhance the performance of membrane technology and stability and to minimize issues related to fouling. The combination of membrane technology and AOPs is also considered as hybrid treatment.

4 Advanced Oxidation Processes (AOPs)

In the past decade, AOPs attained great research attention in the areas of energy and environmental remediation (Balakrishnan et al. 2020). AOPs are defined as a water treatment method conducted at normal temperature and pressure based on production of oxidizing agents like hydroxyl radicals to mineralize toxic compounds to CO_2 and H_2O (Oturan and Aaron 2014). AOPs involve reaction between strong radicals and chemical agents like ozone, hydrogen peroxide, energy sources like UV, ultrasonic, etc. Common AOP-based water technologies are ozonation, photocatalysis, sonocatalysis, and Fenton and photo-Fenton process (Dong et al. 2015; Patel et al. 2019). AOPs are also treated as an environment-friendly technology for the redemption of emerging contaminants (Oturan and Aaron 2014).

4.1 Ozonation

Ozone is a strongest oxidizing agent used for both disinfection and redemption of ECs from wastewater (Matilainen and Sillanpää 2010). The process of ozonation may take place either directly or indirectly. Direct ozonation is utilization of ozone in the absence of a catalyst or any irradiation, while indirect ozonation is an AOP which takes place under the presence of a catalyst (Patel et al. 2019). Ozone is electrophilic in nature and reacts with nucleophilic and electron-rich molecules. Reaction between ozone and hydroxide anions in water may generate hydroxyl radical formation (Patel et al. 2019). Lin et al. (2009) reported ozonation of sulfonamide to be faster than macrolides due to the existence of aromatic rings in sulfonamide. It's clear that ozonation shows very low mineralization despite of high removal efficiency because of formed by-products (Fares A. Almomani, et al. 2016). Limitations like high energy consumption, by-product formation, and influence of interfacial scavengers always hinder the efficiency of the ozonation process (Ahmed et al. 2017).

4.2 Fenton and Photo-Fenton

The Fenton process is based on the reaction between mixture of Fe salts with H_2O_2 with a pH less than 7 (Kanakaraju et al. 2018). The Fenton process can take place either in homogeneous or in heterogeneous conditions (using a suitable catalyst) (Patel et al. 2019). Here, hydroxyl radicals are the driving force for the oxidation reaction based on Fenton's reagent. The generalized reactions are shown in Eqs. 1, 2, 3, 4, and 5.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO. \tag{1}$$

$$Fe^{3+} + H_2O_2 \rightarrow H^+ + Fe\left(O_2H\right)^{2+} \tag{2}$$

$$Fe\left(O_2H\right)^{2+} \rightarrow Fe^{2+} + HO_2. \tag{3}$$

$$Fe\left(OH\right)^{2+} + H_2O_2 \rightarrow Fe\left(OH\right)\left(O_2H\right)^+ + H^+ \tag{4}$$

$$Fe\left(OH\right)\left(O_2H\right)^+ \rightarrow Fe^{2+} + HO_2^{\cdot} + HO^{?} \tag{5}$$

Literature studies report that both Fenton and photo-Fenton processes are adopted for the treatment of various emerging pollutants like antibiotics, anti-inflammatories, and analgesics, but are not applicable to wastewater containing high organic, chloride, nitrate, bicarbonate and carbonate concentrations (Patel et al. 2019).

4.3 Photolysis

Photolysis involves destruction of ECs under a suitable light source (artificial of natural solar light) through a sequence of photochemical reactions (Patel et al. 2019; Yap et al. 2019) . It's proved that photolysis is a potent remediation tool for pollution abatement specifically ECs like pesticides, herbicides, etc. (Kabra et al. 2004; Ahmed et al. 2017; Su et al. 2018). These experiments are conducted under four different light sources: (a) UV 254 nm, monochromatic light irradiated by low-pressure mercury lamp (LPML); (b) VUV 185 nm and 254 nm light, generated by LPML; (c) natural sunlight; and (d) medium-pressure UV, polychromatic light (Wang et al. 2020).

There are two different techniques: Direct photolysis and indirect photolysis (Patel et al., 2019; Santos et al., 2016). Direct photolysis exhibits direct absorption of light source by ECs before respective photochemical reactions (also called as photosensitized reaction). On irradiation of light sources, ground-state target ECs are shifted to excited state with higher-energy state through direct radiation and returned back to normal state with energy loss. This is also attributed due to formation of unstable intermediate compounds via sequence of photochemical reactions (Rubio-Clemente et al. 2014; Santos et al. 2016; Yap et al. 2019). In indirect photolysis, reactive species are formed by photosensitization using a catalyst followed by a set of chemical reactions (Santos et al. 2016; Patel et al. 2019). The photolytic performance is highly influenced by frequency and intensity of radiation, quantum yield of EC absorption spectra, and availability of ozone, H_2O_2, and singlet $O_{2.}$ Direct photolysis is a naturally occurring degradation process in our environment (Rubio-Clemente et al. 2014). Sometimes, these mechanisms produce toxic intermediates harmful to aquatic and marine life systems. Therefore, direct photolysis is ineffective than other remediation techniques. Therefore, a combination of catalysis and UV light is preferred to ensure effective water treatment (Rubio-Clemente et al. 2014).

4.4 Photocatalytic Degradation

Photocatalysis has garnered much research attention in the past decade for mineralization of ECs (Balakrishnan et al. 2020). The semiconductor-based materials are employed for the complete destruction of pollutants via photocatalysis (Paumo et al. 2020). The target pollutant molecules are attacked by utilizing the light energy and photocatalyst to generate radical groups. Materials like TiO_2, ZnS, ZnO, CdS, CeO_2, and Fe_2O_3 are employed for different applications (Mishra and Chun 2015; Lee et al. 2016; Cheng et al. 2018; Kanan et al. 2020). The semiconductor-based photocatalyst is used because of low toxicity, inexpensiveness, and photo and chemical stability (Kanan et al. 2020).

Heterogeneous photocatalysis follows the principle of green chemistry for the treatment of toxic emerging contaminants. The five major steps in heterogeneous photocatalysis on catalyst surface are (Dong et al. 2015):

1. Photo-excitation (absorption of light and generation of charge).
2. Diffusion.
3. Trapping of electrons.
4. Recombination of photo-generated holes and electrons.
5. Oxidation of organic pollutants.

The illumination of a light source like UV or visible light on the surface of photocatalyst resulting in the generation of an electron/hole pair is the first step in photocatalytic degradation (Eq. 6). In the presence of DO, trapped photo-generated electrons resulted in superoxide ion formation. Similarly, surface activated OH groups are formed through water ionization from the valence band forms OH radicals. Therefore, reactions limit the recombination and favor photodegradation; eventually ECs react with OH radicals to form CO_2 and minerals indicated in Eqs. 8 and 9 (Fig. 2). Therefore, hydroxyl radicals are completely responsible for mineralization of ECs (Balakrishnan et al. 2020).

$$\text{Photocatalyst} \rightarrow e^{-} + h^{+} \tag{6}$$

$$O_2 + e^{-} \rightarrow O_2^{\;-} \tag{7}$$

$$h^{+} + H_2O \rightarrow OH^{\cdot} + h^{+} \tag{8}$$

$$\text{Pollutant} + \text{photocatalyst} + OH^{\cdot} \rightarrow CO_2 + H_2O \tag{9}$$

The main limitations of nano-sized-based catalysts are (a) inefficient utilization of visible light, (b) poor adsorption of ECs, (c) and problems associated with recovery and aggregation of nano-sized particles (Dong et al. 2015; Balakrishnan et al. 2020). Different methods like doping, functionalization, grafting, and immobilization are adopted for enhancement of degradation efficiency (Vigneshwaran et al. 2019). Selli et al. (2008) reported that sonolysis is effective than photocatalytic degradation and photolysis for the removal of 1,4-DCB degradation. Moreover, drawbacks like catalyst fouling and restricted mass transfer in photocatalytic degradation are enhanced through sonolysis and sonocatalysis.

4.5 Sonolysis

Sonolysis is a type of AOP which utilizes ultrasonic irradiation in the absence of a catalyst to produce hydroxyl radicals in aqueous stream (Naddeo et al. 2013). The mutual interaction between sound energy and dissolved bubbles in aqueous stream

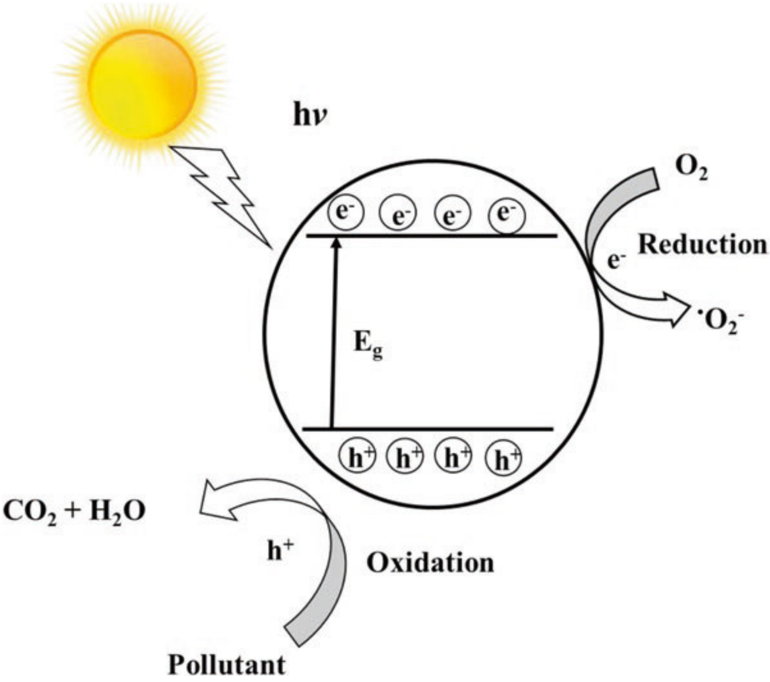


Fig. 2 Mechanistic preview for photocatalytic degradation of ECs

leads to bubble growth and eventually collapse, so this process is called as acoustic cavitation (Madhavan et al. 2019). The generated hydroxyl radicals through acoustic cavitation is responsible for the destruction of ECs (Madhavan et al. 2019). The degradation of ECs in sonolysis occurs in three different stages (Fig. 3):

(a) Inside the cavitation: the sonochemical degradation of ECs occurs by means of pyrolysis at high temperature and pressure (5000 K and 1000 atm). Under these conditions, H_2O and O_2 are thermally dissociated into perhydroxyl radicals and hydroxyl radical groups, respectively (Eren and Ince 2010; Yap et al. 2019).

(b) Interfacial region between cavitation bubble and bulk solution: the radical attack mechanism is predominant than pyrolysis at higher temperature (1000–2000 K). Moreover, recombination of hydroxyl radicals and. OOH leads to formation of hydrogen peroxide, reacts with perhydroxyl groups, diffuses from zone 1 to 2, and enhances the number of free radicals (Yap et al. 2011).

(c) Bulk solution: under normal temperatures, only radical mechanism is involved in the degradation of hydrophobic compounds in water. Majority of these ECs are degraded at bulk solution though a sonochemical reaction between $OH^{\cdot}$ and ECs (Yap et al. 2011; Madhavan et al. 2019).

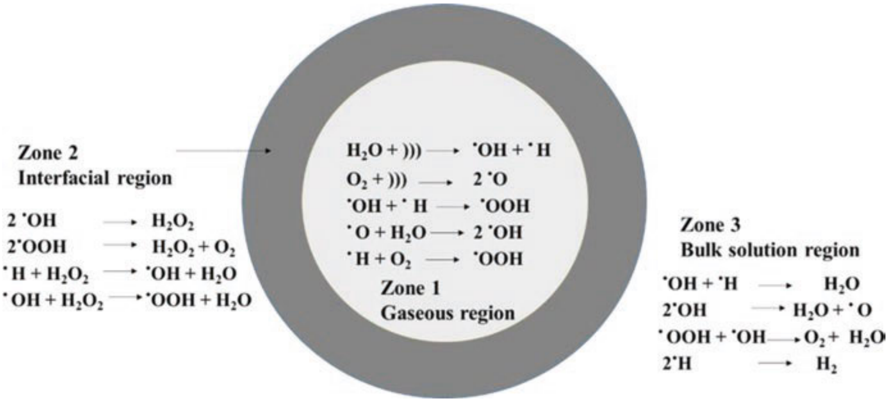


Fig. 3 Diagrammatic view of reaction zones in a ultrasonically reacted system

The generation of free radicals through implosion of cavitation bubbles benefitted in degradation of ECs as shown in Fig. 4. The sonodegradation mechanism is highly dependent on the nature, concentration, and other physical properties of the emerging contaminants (Yap et al. 2019). The destruction of organic compounds like volatile and hydrophobic compounds may decompose inside cavitation bubble through pyrolysis or by free radical mechanism, and nonvolatile and hydrophilic compounds can be treated in bulk solution through free radical mechanism (Madhavan et al. 2019).

Operational parameters like dissolved gases, ultrasonic frequency, acoustic power, temperature, and initial concentration of ECs have significant impact on sonodegradation of ECs (Torres-Palma and Serna-Galvis 2018). It's reported that ultrasonic frequency possesses significant impact on sonodegradation, as the frequency increases, collapse time gets shorter, resulting in reduction of bubble size (Torres-Palma and Serna-Galvis 2018; Pirsaheb and Moradi 2020). The optimum frequency for the radical production is between 200 and 350 KHz as reported by Kang et al. (1999). The enhancement in power input always increases the rate of removal due to increment in cavitation and generation of hydroxyl radicals. Brotchie et al. (2009) described that cavitation bubble size grows with ultrasonic power. So, this method is a prominent AOP because of its unique characteristics like simple operation, energy conservation, enhanced mass transfer, and high penetrability in aqueous streams (Gholami et al. 2019).

Yao et al. (2011) highlighted the sonolytic degradation of dimethoate using 619 Hz and 406 Hz for continuous and pulse sonolysis, respectively. The predominant oxidation and hydrolysis reaction of dimethoate and omethoate which takes place in water-bubble interface is the rate-determining step for sonolytic degradation, and degradation efficiency was found to be 90%.

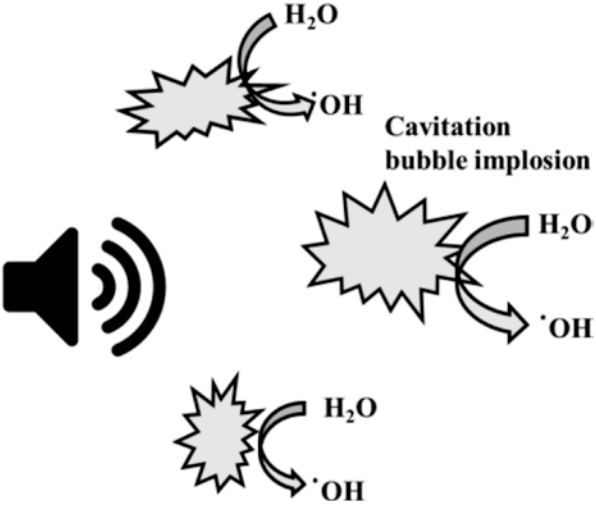


Fig. 4 Mechanistic preview of sonophotocatalytic degradation of ECs

4.6 Sonocatalysis

Sonocatalysis is the combination of sonochemistry and catalysis (Kuna et al. 2017). Under the presence of sonocatalysis, cavitation bubbles implode, and a turbulent flow is developed and later breaks sonocatalyst to smaller fragments with higher surface area with minimum fouling (Madhavan et al. 2019). An enhancement in mass transfer rate is largely due to increase in surface area of the sonocatalyst. The enhancement in production of free radicals also improves the degradation rate of ECs under the influence of a sonocatalyst. Higher concentration of free radicals makes the system more capable of treating hydrophilic and nonvolatile compounds in wastewater (Yap et al. 2011).

Different sonocatalysts employed for the degradation of ECs are TiO_2, ZnO, and CdS, where TiO_2 is the potential catalyst used due to better sonocatalytic activity (Khataee et al. 2015). This treatment method requires minimum chemical requirement and limited to laboratory-scale operations only. So, the modifications of such treatment process are necessary to improve the efficiency and to signify scope of commercialization with minimal operational cost.

4.7 Sonophotocatalysis

Sonophotocatalysis is a hybrid treatment technology which attained great attention toward the redemption of ECs. Sonolysis is a promising process in the field of water treatment specifically targeting ECs that are hydrophobic in nature due to its simplicity (Madhavan et al. 2019). Here hydrophobic contaminants are removed by adsorption to cavitation bubble interface which leads to the generation of OH· radicals (Madhavan et al. 2019). On the other hand, photocatalysis is a well-established green technology for the removal of hydrophilic components through preferential adsorption of ECs on the catalyst surface. The combination of both sonolysis and photocatalysis is referred to as sonophotocatalysis (Yap et al. 2019).

The different factors like mass transfer between ECs and catalyst, simultaneous generation of hydroxyl radicals, and additional nuclei formation for bubble under the influence of catalyst play a phenomenal role in the appraisal of degradation efficiency (Yap et al. 2019). The continuous adsorption of ECs on the catalyst surface leads to catalyst deactivation. The sintering effect of catalyst is attributed due to shielding effect and blockage of light activated surface which hinders the active sites for the degradation of ECs. This could be easily prevented through proper utilization of acoustic cavitation which cleans the catalytic surface and regenerate active sites (Madhavan et al. 2019).

Karim and Shriwastav (2020) investigated the removal studies of ciprofloxacin through photocatalytic, sonocatalytic, and sonophotocatalytic degradation using a novel multifrequency reactor with low frequencies and N-TiO_2. Studies reported 54.5%, 41.2%, and 44% for 210, 90, and 90 minutes, respectively, for photocatalysis, sonocatalysis, and sonophotocatalysis at optimum conditions due to enhanced visible light activity and extra nuclei cavitation, respectively. This remediation technology is a well-suited method as it overcomes all changes faced by photocatalysis and sonolysis. A summary on removal of ECs using different AOPs is reported in Table 4.

5 Catalytic Membrane Reactors

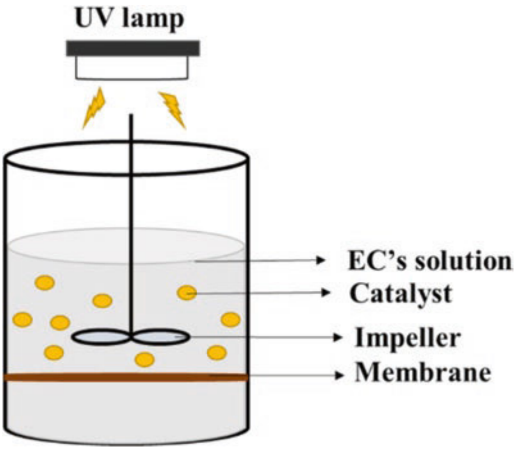
Catalytic membrane reactor (CMR) is a hybrid wastewater treatment technology, where process of separation by membranes and catalytic reactions takes place in parallel pathways. Catalytic membrane reactors specifically allow the transport of selected compounds from the feed solution based on principle of surface reactivity and activates a set of chemical reactions occurring at the catalyst surface of active membranes (Kumari et al. 2020). Development of a single hybrid system is an economical way of treating ECs by enhancing efficiency, stability of systems, and regeneration of systems (Daramola et al. 2012). Moreover, this advanced combination benefited in energy and time saving and helps intensify the catalytic process.

Photocatalytic membrane reactors are a combination of both membrane technology and photocatalytic reactors as shown in Fig. 5. It's a green technology as it completely mineralizes ECs to CO_2 and H_2O with minimum chemical requirements (Molinari et al. 2017). The TiO_2-based membrane technology is selected as a suitable photocatalyst due to its shorter band gap, high surface area, high photo- and chemical stability, and corrosion inertness. The TiO_2 is a UV-based catalyst with a band gap of 3.2 eV which restricts its utilization of TiO_2 under visible light (Balakrishnan et al. 2020). Different materials like PVDF, PSF, PES, PAN, alumina,

Table 4 Literature reports on removal of ECs using AOPs

Method	EC	Catalyst	Efficiency (%)	Reference
Ozonation	Ciprofloxacin		64.3	Lu et al. (2020)
	Real pharmaceutical wastewater		53	Huang et al. (2020)
Photo-Fenton process	Bisphenol-A	$Cu_{0.5}Mn_{0.5}Fe_2O_4$	95	Yang et al. (2020)
Solar photo-Fenton process	CEC's		60	Arzate et al. (2020)
Photocatalytic degradation	2,4-Dichlorophenoxyacetic acid	TiO_2/chitosan beads	92	Balakrishnan et al. (2020)
	Chlorpyrifos	g-C_3N_4 chitosan composites	85	Vigneshwaran et al. (2019)
	Cyanotoxins	Carbon nanotubes/TiO_2 nanotubes	95	Chae et al. (2019)
	Phenol	CNC/TiO_2 nanomotors	50	Li et al. (2019)
Sonolysis	Benzenesulfonic acid	–	50	Thomas et al. (2020)
	Ampicillin		100	Montoya-Rodríguez et al. (2020)
Sonocatalysis	Tylosin	WS_2@CeO_2	70	Yousef Tizhoosh et al. (2020)
	Carbamazepine Diclofenac	Graphene oxide	99 99	Al-Hamadani et al. (2018)
	Diclofenac	$FeCeO_x$	80	Chong et al. (2017)
	Cefazolin	Fe-cu layered double hydroxide biochar nanocomposites	97.6	Gholami et al. (2020a)
Sonophotocatalysis	Ofloxacin	TiO_2	98	Hapeshi et al. (2013)
	Tetracycline	WO_3/CNT	83.7	Isari et al. (2020)
	Sulfadiazine	Zn-cu-mg mixed metal hydroxide/g-C_3N_4 composite	93	Gholami et al. (2020b)

Fig. 5 Schematic representation of photocatalytic membrane reactor



titania, and metallic materials like stainless steels are used as substrate materials for the preparation of photocatalytically activated membrane (Bet-Moushoul et al. 2016). Selected substrates should possess high surface area, chemical and corrosion resistance, high abrasion, and photostability.

Photocatalytic membrane reactor is a hybrid remediation methodology used to minimize catalytic loss and improves reusability studies, making it economically fit. The PCMR possesses special features than other conventional water treatment technologies: (a) ensure proper catalyst contact in the reaction environment, (b) highly adoptable for commercial continuous water treatment processes, and (c) can easily separate and recover photocatalyst from the final product (Mozia et al. 2005; Zheng et al. 2017).Therefore, it proves the potential scope of commercialization to a greater extent. The summary on elimination of removal of ECs using CMR is highlighted in Table 5.

López et al. (2014) investigated the photocatalytic degradation of 33 contaminants including drugs, analgesics, and EDCs using Aeroxide® TiO_2-P25 treatment in a submerged photocatalytic reactor. Lopez reported that compounds except flame retardants like tris(2-chloroethyl) phosphate were removed using photocatalysis with compounds with amide groups slowly removed. The continuous removal of ECs was done in a photocatalytic reactor attached with a submerged ultrafiltration hollow fiber membrane and $TiO_{2.}$ Moreover, hydrophobic contaminants exhibited a greater tendency to absorb onto the membrane. Espíndola et al. (2019) studied the removal of oxytetracycline (OTC) using a photocatalytic membrane reactor with suspended and immobilized TiO_2-P25 photocatalyst. Espindola emphasized on integrated system coupled with microfiltration and UV-A photolysis or TiO_2/P25 photocatalyst for OTC elimination from synthetic and real wastewater with an OTC concentration of 5 mg/L. It's evident that OTC removal efficiency increased with increase in TiO_2 dosage, with a reduction in permeate flux because of denser TiO_2 cake layer formation. Meanwhile, the reduction in permeate flux is limited to some

Table 5 Different CMRs for the removal of ECs

Membrane/catalyst	Pollutant	Parameter	Removal %	Reference
Nitrogen and sulfur co-doped carbon quantum dots/TiO_2 on polysulfone membrane	Pharmaceuticals	Concentration 10 mg/L Reactor volume 2 L Light source visible	63%	Koe et al. (2020)
Visible/N-doped TiO_2/H_2O_2	Diclofenac	Concentration 50 mg/L Time 150 min Light source visible lamp of 50 W		Nguyen et al. (2020)
$ZnIn_2S_4$ deposited on PVDF	Fluvastatin	Concentration 10 mg/Laa Light source Xe lamp of 500 W Time 180 min	97% 53% TOC	Liu et al. (2020)
TiO_2 coated on thin film	17 β-estradiol 17 α-ethinylestradiol	Light source UV-c Reactor volume 5 L Oxidant dosing 2.7 mL/min	51/32% 48/30% (synthetic/real sample)	Castellanos et al. (2020)
Nano-TiO_2/carbon	Tetracycline	Concentration 50 mg/L pH (3.8-9.6) Temperature 25 °C	100% TC 87.8% COD	Liu et al. (2016)
TiO_2/carbon/Al_2O_3 membrane	Organic pollutants	Initial concentration 5 mg/L Light source 500 W Xe lamp	97%	Wang et al. (2015a)
N-doped-TiO_2 coated NaY zeolite membrane	Phenol	Light source Xe lamp 300 W Concentration 10 mg/L Time 180 min	89%	Cheng and Han (2016)

extent by using immobilized TiO_2 on membrane matrix thorough OTC oxidation on the surface or within pores of the matrix. This study also focused on elimination of OTC through continuous mode utilized for three continuous cycles with no loss in catalyst performance of TiO_2/P25 in the membrane matrix. Thus, it's concluded that PMR with immobilized catalyst showed good removal efficiency due to lower surface area for the adsorption of OTC on the catalyst surface.

6 Other Hybrid Treatment Methods

Holloway et al. (2014) explained elimination of trace organic chemicals using a novel hybrid UF-osmotic membrane bioreactor. This hybrid treatment technology uses UF and forward membrane arranged in parallel to obtain treated water from activated sludge for both potable and non-potable uses. The water is drawn by osmosis from activated sludge through a FO membrane. The diluted solution is again concentrated using a RO and produces water for different applications. The UF membrane prevents the accumulation of activated sludge in an osmostic membrane bioreactor. Results proved the capability of UFO-MBR in elimination of COD, total nitrogen, and total phosphorous with a removal efficiency of 99%, 82%, and 99%, respectively.

A novel electrocoagulation-electrocatalysis is a hybrid technology for the treatment of industrial effluents. Atomic layer desorption techniques were used for the deposition of TiO_2 nanofilm on the stainless steel cathode for the enhancement of degradation efficiency. Moreover, thin nanofilm was capable of inducing the two-step electro-Fenton process for the degradation of pollutants through the formation of oxygen species. Therefore, novel electrocoagulation-electrocatalysis cell with TiO_2 nanofim coated cathode was highly capable of handling textile treatment water, and it’s expected that this system is applied to different wastewater. The main advantages are as follows: enhanced removal of organic substrates seen in water, better usage of electrical energy, minimum chemical requirements, and makes the system more environment-friendly (Fan et al. 2020).

Naddeo et al. (2020) emphasized on a hybrid treatment process which combines ultrasound, adsorption, and UF membrane (UASMe) for the redemption of diclofenac, carbamazepine, and amoxicillin. UASMe technique was able to remove 99% of ECs compared to 90% removal for adsorption process. The improvement in efficiency was due to the combined effects of different methods. Ultrasonic irradiation degraded contaminants through sonolytic mechanism and also aided in adsorption of contaminants on powdered activated carbon. The phenomenon was facilitated by improved liquid phase mass transfer and intra-particle diffusion in the hybrid process. This technology possesses advantages like high efficiency and minimum sludge production with minimum fouling of membrane.

de Wilt et al. (2018) has proposed a three-step bio-ozone bio-treatment mechanism for the destruction of pharmaceutical compounds seen in wastewater. It’s clear that individual treatment processes are not highly capable for the treatment of ECs. In this treatment system, all the problems associated with individual units are overcome through a biological-ozone biological treatment mechanism. Studies report an extremely high removal efficiency of 95%, and no acute toxicity was determined on *D. magma* and *V. fischeri* even after direct exposure to the effluents in treatment system. This particular treatment system is adopted in the Netherlands and found to be a cost-effective treatment technology.

Guo et al. (2018) developed a ceramic-based catalytic membrane coated with $CuMn_2O_4$ for the detoxification of benzophenone-3 removal. It’s evident that this membrane enhanced ozonation and filtration through the surface coating of $CuMn_2O_4$ on the surface of tubular ceramic membrane using sol-gel method. The proper incorporation of $CuMn_2O_4$ on the surface of membrane was studied using characterization techniques like SEM, XRD etc. The improvement in removal efficiency was increased to 34% from 28% after the surface modification. Stability and detoxification were also enhanced to a certain level. The improvement in degradation efficiency was due to availability of large number of surface hydroxyl radicals on the ceramic membrane, which increased the number of potential catalytic active sites. The problems associated with fouling are resolved by adopting a combination of both ozonation and filtration, a novel tertiary wastewater treatment method for the destruction of emerging pollutants.

Al et al. (2019) depicted a hybrid electro-coagulation/forward osmosis for the treatment of produced water (in oil and gas exploration). Initially, pollutants undergo electro-coagulation (at three current densities) for 30 min followed by forward osmosis system using a polymeric membrane with orientation such as active layer facing draw solution and feed solution, respectively. Using this treatment technology, they achieved a total of 99% removal of total suspended solids. The yielded high-quality water signifies the potential applicability of hybrid system in water technology. Nippatla and Philip (2019) developed a hybrid treatment which comprises electrocoagulation-floatation-assisted pulsed power plasma technology for the detoxification of pollutants. This hybrid treatment technology reduced the treatment cost by 41% compared to power plasma technology, and consumption of electrode was reduced by 57%. The key advantages of this setup were minimum sludge production, high treatment efficiency, and minimum chemical requirements. Li et al. (2018) highlighted the development of integrated electro-coagulation carbon membrane coupling with electrochemical anodic oxidation system specifically targeting the removal of oil. Here, electrocoagulation is the primary wastewater treatment unit, followed by electrochemical anodic oxidation for further purification of wastewater in depth. Results emphasized the capability of hybrid system in removal of effluents with a TOC from 22 to 13 mg/L, respectively.

Kim et al. (2020) described on combined MOF with UF system for the complete mineralization of pharmaceutically active compounds like ibuprofen, 17 α-ethinyl estradiol and natural organics like humic acid, and tannic acid. The highly porous MOF system possesses wide attraction due to high efficiency and minimum fouling on adsorbent UF system. The MOF-UF system showed higher removal flux and low flux decline than powdered activated carbon/UF system. A hybrid treatment technology focused on combined moving bed bio-film reactor and activated sludge termed as Hybas. This treatment technology focused on removal of pharmaceuticals and municipal wastewater treatment. Hybas system comprises of six reactors arranged in series including pre-denitrification, denitirification, and post-denitrification in the biofilm reactor. This hybrid system exhibited a degradation efficiency of 90% of COD and 95% of NH_4N (Tang et al. 2020).

Table 6 compares different methods like electrocatalysis, photocatalysis, photoelectrocatalysis, sonocatalysis, adsorption, and membrane separation for the continuous elimination of ECs. Different studies claimed that advanced oxidation

Table 6 Comparison of different treatment methods for selective removal of organic pollutants

Pollutant	Removal method	Catalyst/material	Efficiency	Reference
Bisphenol-A	Electrocatalysis	Ti-based PbO_2-ionic liquid electrode	100	Ju et al. (2012)
	Photocatalysis	Immobilized TiO_2	97	Wang et al. (2009)
	Photoelectrocatalysis	Cu doped WO_3 electrode	80	
	Sonocatalysis	Magnetic biochar composite	94.25	Chu et al. (2021)
	Adsorption	Single-walled carbon nanotubes	>90%	Joseph et al. (2013)
	Ozonation		30	Kusvuran and Yildirim (2013)
	NF		95	Escalona et al. (2014)
	Bioremediation	Laccases from *P. ostreatus* and *P. pulmonarius*	85	de Freitas et al. (2017)
Ciprofloxacin	Electrocatalysis	Double-sided Ti-Pt/β-PbO2 anode	75	Wachter et al. (2019)
	Photocatalysis	Zn doped Cu_2O	94.6	Yu et al. (2019)
	Photoelectrocatalysis	Ni doped ZnO on F doped tin oxide glass	100	Hosseini et al. (2020)
	Membrane	CuO/TiO_2 ceramic UF membrane	99	Bhattacharya et al. (2019)
		Reverse osmosis	99	Alonso et al. (2018)
	Bioremediation	*Brassica parachinensis* L.	48.7	Huang et al. (2017)
	Sonocatalysis	TiO_2/montmorillonite	65	Hassani et al. (2017)
	Photo-electro-Fenton process	$MnO_x/g\text{-}C_3N_4$	96.23	Jia et al. (2021)
	Electro-Fenton degradation	Mesoporous $Mn_xCo_{3-x}O_4$	100	Mi et al. (2019)

(continued)

Table 6 (continued)

Pollutant	Removal method	Catalyst/material	Efficiency	Reference
Tetracycline	Electrocatalysis	TiO_2/RuO_2-IrO_2 Pt and BDD	98	Oturan et al. (2013)
	Photocatalysis	TiO_2/Fe_2O_3	93	Galedari et al. (2019)
	Photoelectrocatalysis	TiO_2 nanopore arrays electrode	80	Liu et al. (2009)
	Sonolysis		12.8	Soltani et al. (2019)
	Sonocatalysis	ZnO nanostructure incorporated nano-cellulose	87.6	
	Adsorption	Carbonaceous materials	96	Álvarez-Torrellas et al. (2016)
	Ozonation		40	Khan et al. (2010)
	Ozonation-biological activated sludge system		100	Gómez-Pacheco et al. (2011)
	Membrane	MgO/diatomite ceramic membrane	99.7	Meng et al. (2016)

process and membrane separation are found to be very prominent in the redemption of organic pollutants. Most of the studies showed that electrocatalysis exhibited degradation efficiency. Similarly, membrane separation attained great research attention due to its ease of operation, high efficiency, and reusability making them more suitable for large-scale applications. Overall, further research is necessary to overcome the limitations of the existing treatment methodology.

7 Conclusion

Presence of ECs is gradually increasing in the environment due to both natural and anthropogenic factors like industrialization, urbanization, population boom, etc. The elimination of ECs is a prerequisite for providing safe and adequate-quality drinking water and to support the sustainability of the environment. Different conventional treatments like adsorption, bioremediation, and membrane technology are described along with AOPs, catalytic membrane technology, and new hybrid treatment methods in elimination of pollutants. It is evident that different conventional treatment methods were incapable of complete mineralization of pollutants; however, AOPs exhibited better performance, but they require very high energy consumption. So, newly developed hybrid treatment technologies witnessed much research importance due to high efficiency, economic feasibility, and ease of maintenance, making them attractive. Over all, different treatment methods satisfy the criteria of efficient clean technologies but do not necessarily deem it as green technologies without additional developments.

References

Ahmed MB, Zhou JL, Ngo HH et al (2017) Progress in the biological and chemical treatment technologies for emerging contaminant removal from wastewater: a critical review. J Hazard Mater 323:274–298. https://doi.org/10.1016/j.jhazmat.2016.04.045

Al B, Benamor A, Hawari AA (2019) A hybrid electro-coagulation / forward osmosis system for treatment of produced water. Chem Eng J 143:107621. https://doi.org/10.1016/j.cep.2019.107621

Al-Hamadani YAJ, Lee G, Kim S et al (2018) Sonocatalytic degradation of carbamazepine and diclofenac in the presence of graphene oxides in aqueous solution. Elsevier Ltd

Almomani FA, Shawaqfan M, Rahul R, Bhosale AK (2016) Removal of emerging pharmaceuticals from wastewater by ozone-based advanced oxidation process. Environ Prog Sustain Energy 35:982–995. https://doi.org/10.1002/ep.12306

Alonso JJS, El Kori N, Melián-Martel N, Del Río-Gamero B (2018) Removal of ciprofloxacin from seawater by reverse osmosis. J Environ Manag 217:337–345. https://doi.org/10.1016/j.jenvman.2018.03.108

Álvarez-Torrellas S, Rodríguez A, Ovejero G, García J (2016) Comparative adsorption performance of ibuprofen and tetracycline from aqueous solution by carbonaceous materials. Chem Eng J 283:936–947. https://doi.org/10.1016/j.cej.2015.08.023

Arzate S, Campos-Mañas MC, Miralles-Cuevas S et al (2020) Removal of contaminants of emerging concern by continuous flow solar photo-Fenton process at neutral pH in open reactors. J Environ Manag 261. https://doi.org/10.1016/j.jenvman.2020.110265

Azubuike CC, Chikere CB, Okpokwasili GC (2016) Bioremediation techniques–classification based on site of application: principles, advantages, limitations and prospects. World J Microbiol Biotechnol 32. https://doi.org/10.1007/s11274-016-2137-x

Balakrishnan A, Appunni S, Gopalram K (2020) Immobilized TiO2/chitosan beads for photocatalytic degradation of 2,4-dichlorophenoxyacetic acid. Int J Biol Macromol 161:282–291. https://doi.org/10.1016/j.ijbiomac.2020.05.204

Barczak M, Dobrowolski R, Borowski P, Giannakoudakis DA (2020) Pyridine-, thiol- and amine-functionalized mesoporous silicas for adsorptive removal of pharmaceuticals. Microporous Mesoporous Mater 299:110132. https://doi.org/10.1016/j.micromeso.2020.110132

Bet-Moushoul E, Mansourpanah Y, Farhadi K, Tabatabaei M (2016) TiO2 nanocomposite based polymeric membranes: a review on performance improvement for various applications in chemical engineering processes. Chem Eng J 283:29–46. https://doi.org/10.1016/j.cej.2015.06.124

Bhattacharya P, Mukherjee D, Dey S et al (2019) Development and performance evaluation of a novel CuO/TiO 2 ceramic ultrafiltration membrane for ciprofloxacin removal. Mater Chem Phys 229:106–116. https://doi.org/10.1016/j.matchemphys.2019.02.094

Bolong N, Ismail AF, Salim MR, Matsuura T (2009) A review of the effects of emerging contaminants in wastewater and options for their removal. Desalination 239:229–246. https://doi.org/10.1016/j.desal.2008.03.020

Brotchie A, Grieser F, Ashokkumar M (2009) Effect of power and frequency on bubble-size distributions in acoustic cavitation. Phys Rev Lett 102:1–4. https://doi.org/10.1103/PhysRevLett.102.084302

Castellanos RM, Paulo Bassin J, Dezotti M et al (2020) Tube-in-tube membrane reactor for heterogeneous TiO2 photocatalysis with radial addition of H2O2. Chem Eng J 395:124998. https://doi.org/10.1016/j.cej.2020.124998

Chae S, Noeiaghaei T, Oh Y et al (2019) Effective removal of emerging dissolved cyanotoxins from water using hybrid photocatalytic composites. Water Res 149:421–431. https://doi.org/10.1016/j.watres.2018.11.016

Chakraborty R, Asthana A, Singh AK et al (2020) Adsorption of heavy metal ions by various low-cost adsorbents: a review. Int J Environ Anal Chem 00:1–38. https://doi.org/10.1080/03067319.2020.1722811

Chandrasekaran A, Patra C, Narayanasamy S, Subbiah S (2020) Adsorptive removal of ciprofloxacin and amoxicillin from single and binary aqueous systems using acid-activated carbon from Prosopis juliflora. Environ Res 109825. https://doi.org/10.1016/j.envres.2020.109825

Chao Y, Zhang J, Li H et al (2020) Synthesis of boron nitride nanosheets with N-defects for efficient tetracycline antibiotics adsorptive removal. Chem Eng J 387:124138. https://doi.org/10.1016/j.cej.2020.124138

Chauhan M, Saini VK, Suthar S (2020) Ti-pillared montmorillonite clay for adsorptive removal of amoxicillin, imipramine, diclofenac-sodium, and paracetamol from water. J Hazard Mater 399:122832. https://doi.org/10.1016/j.jhazmat.2020.122832

Cheng ZL, Han S (2016) Preparation of a novel composite electrode based on N-doped TiO2-coated NaY zeolite membrane and its photoelectrocatalytic performance. Chinese Chem Lett 27:467–470. https://doi.org/10.1016/j.cclet.2015.12.010

Cheng L, Xiang Q, Liao Y, Zhang H (2018) CdS-based photocatalysts. Energy. Environ Sci 11:1362–1391. https://doi.org/10.1039/c7ee03640j

Chong S, Zhang G, Wei Z et al (2017) Sonocatalytic degradation of diclofenac with FeCeOx particles in water. Ultrason Sonochem 34:418–425. https://doi.org/10.1016/j.ultsonch.2016.06.023

Chu JH, Kang JK, Park SJ, Lee CG (2021) Enhanced sonocatalytic degradation of bisphenol A with a magnetically recoverable biochar composite using rice husk and rice bran as substrate. J Environ Chem Eng 9:105284. https://doi.org/10.1016/j.jece.2021.105284

Crini G, Lichtfouse E (2019) Advantages and disadvantages of techniques used for wastewater treatment. Environ Chem Lett 17:145–155. https://doi.org/10.1007/s10311-018-0785-9

Daramola MO, Aransiola EF, Ojumu TV (2012) Potential applications of zeolite membranes in reaction coupling separation processes. Materials (Basel) 5:2101–2136. https://doi.org/10.3390/ma5112101

de Bezerra CO, Cusioli LF, Quesada HB et al (2020) Assessment of the use of Moringa oleifera seed husks for removal of pesticide diuron from contaminated water. Environ Technol (United Kingdom) 41:191–201. https://doi.org/10.1080/09593330.2018.1493148

de Freitas EN, Bubna GA, Brugnari T et al (2017) Removal of bisphenol A by laccases from Pleurotus ostreatus and Pleurotus pulmonarius and evaluation of ecotoxicity of degradation products. Chem Eng J 330:1361–1369. https://doi.org/10.1016/j.cej.2017.08.051

de Wilt A, van Gijn K, Verhoek T et al (2018) Enhanced pharmaceutical removal from water in a three step bio-ozone-bio process. Water Res. https://doi.org/10.1016/j.watres.2018.03.028

Dhaka S, Kumar R, Deep A et al (2019) Metal–organic frameworks (MOFs) for the removal of emerging contaminants from aquatic environments. Coord Chem Rev 380:330–352. https://doi.org/10.1016/j.ccr.2018.10.003

Dong H, Zeng G, Tang L et al (2015) An overview on limitations of TiO2-based particles for photocatalytic degradation of organic pollutants and the corresponding countermeasures. Water Res 79:128–146

Eren Z, Ince NH (2010) Sonolytic and sonocatalytic degradation of azo dyes by low and high frequency ultrasound. J Hazard Mater 177:1019–1024. https://doi.org/10.1016/j.jhazmat.2010.01.021

Escalona I, de Grooth J, Font J, Nijmeijer K (2014) Removal of BPA by enzyme polymerization using NF membranes. J Memb Sci 468:192–201. https://doi.org/10.1016/j.memsci.2014.06.011

Espíndola JC, Cristóvão RO, Mendes A et al (2019) Photocatalytic membrane reactor performance towards oxytetracycline removal from synthetic and real matrices: suspended vs immobilized TiO2-P25. Chem Eng J 378:122114. https://doi.org/10.1016/j.cej.2019.122114

Fan T, Deng W, Feng X et al (2020) Chemosphere an integrated electrocoagulation e Electrocatalysis water treatment process using stainless steel cathodes coated with ultrathin TiO 2 nano fi lms. Chemosphere 254:126776. https://doi.org/10.1016/j.chemosphere.2020.126776

Galedari M, Mehdipour Ghazi M, Rashid Mirmasoomi S (2019) Photocatalytic process for the tetracycline removal under visible light: presenting a degradation model and optimization using response surface methodology (RSM). Chem Eng Res Des 145:323–333. https://doi.org/10.1016/j.cherd.2019.03.031

García J, García-Galán MJ, Day JW et al (2020) A review of emerging organic contaminants (EOCs), antibiotic resistant bacteria (ARB), and antibiotic resistance genes (ARGs) in the environment: increasing removal with wetlands and reducing environmental impacts. Bioresour Technol 307:123228. https://doi.org/10.1016/j.biortech.2020.123228

Ghangrekar MM, Sathe SM, Chakraborty I (2020) In situ bioremediation techniques for the removal of emerging contaminants and heavy metals using hybrid microbial electrochemical technologies. INC

Gholami P, Khataee A, Soltani RDC, Bhatnagar A (2019) A review on carbon-based materials for heterogeneous sonocatalysis: fundamentals, properties and applications. Ultrason Sonochem 58:104681. https://doi.org/10.1016/j.ultsonch.2019.104681

Gholami P, Dinpazhoh L, Khataee A et al (2020a) Facile hydrothermal synthesis of novel Fe-Cu layered double hydroxide/biochar nanocomposite with enhanced sonocatalytic activity for degradation of cefazolin sodium. J Hazard Mater 381:120742. https://doi.org/10.1016/j.jhazmat.2019.120742

Gholami P, Khataee A, Vahid B et al (2020b) Sonophotocatalytic degradation of sulfadiazine by integration of microfibrillated carboxymethyl cellulose with Zn-Cu-Mg mixed metal hydroxide/g-C3N4 composite. Sep Purif Technol 245:116866. https://doi.org/10.1016/j.seppur.2020.116866

Gómez-Pacheco CV, Sánchez-Polo M, Rivera-Utrilla J, López-Peñalver J (2011) Tetracycline removal from waters by integrated technologies based on ozonation and biodegradation. Chem Eng J 178:115–121. https://doi.org/10.1016/j.cej.2011.10.023

Goyal N, Bulasara VK, Barman S (2018) Removal of emerging contaminants daidzein and coumestrol from water by nanozeolite beta modified with tetrasubstituted ammonium cation. J Hazard Mater 344:417–430. https://doi.org/10.1016/j.jhazmat.2017.10.051

Guo Y, Song Z, Xu B et al (2018) A novel catalytic ceramic membrane fabricated with CuMn2O4 particles for emerging UV absorbers degradation from aqueous and membrane fouling elimination. J Hazard Mater 344:1229–1239. https://doi.org/10.1016/j.jhazmat.2017.11.044

Gusain R, Kumar N, Ray SS (2020) Recent advances in carbon nanomaterial-based adsorbents for water purification. Coord Chem Rev 405:213111. https://doi.org/10.1016/j.ccr.2019.213111

Hapeshi E, Fotiou I, Fatta-Kassinos D (2013) Sonophotocatalytic treatment of ofloxacin in secondary treated effluent and elucidation of its transformation products. Chem Eng J 224:96–105. https://doi.org/10.1016/j.cej.2012.11.048

Harrison RM (2011) Pollution: causes, effects and control. Cambridge R Soc Chem. https://doi.org/10.1016/j.watres.2015.04.038

Hassani A, Khataee A, Karaca S et al (2017) Sonocatalytic degradation of ciprofloxacin using synthesized TiO2 nanoparticles on montmorillonite. Ultrason Sonochem 35:251–262. https://doi.org/10.1016/j.ultsonch.2016.09.027

Hernández-Abreu AB, Álvarez-Torrellas S, Águeda VI et al (2020) Enhanced removal of the endocrine disruptor compound bisphenol A by adsorption onto green-carbon materials. Effect of real effluents on the adsorption process. J Environ Manag 266. https://doi.org/10.1016/j.jenvman.2020.110604

Holloway RW, Regnery J, Nghiem LD, Cath TY (2014) Removal of trace organic chemicals and performance of a novel hybrid ultra filtration-osmotic membrane bioreactor

Hosseini M, Esrafili A, Farzadkia M et al (2020) Degradation of ciprofloxacin antibiotic using photo-electrocatalyst process of Ni-doped ZnO deposited by RF sputtering on FTO as an anode electrode from aquatic environments: synthesis, kinetics, and ecotoxicity study. Microchem J 154:104663. https://doi.org/10.1016/j.microc.2020.104663

Huang XP, Mo CH, Yu J et al (2017) Variations in microbial community and ciprofloxacin removal in rhizospheric soils between two cultivars of Brassica parachinensis L. Sci Total Environ 603–604:66–76. https://doi.org/10.1016/j.scitotenv.2017.06.040

Huang Y, Jiang J, Ma L et al (2020) Iron foam combined ozonation for enhanced treatment of pharmaceutical wastewater. Environ Res 183:109205. https://doi.org/10.1016/j.envres.2020.109205

Isari AA, Mehregan M, Mehregan S et al (2020) Sono-photocatalytic degradation of tetracycline and pharmaceutical wastewater using WO3/CNT heterojunction nanocomposite under US and visible light irradiations: a novel hybrid system. J Hazard Mater 390:122050. https://doi.org/10.1016/j.jhazmat.2020.122050

Jacob MM, Ponnuchamy M, Kapoor A, Sivaraman P (2020) Bagasse based biochar for the adsorptive removal of chlorpyrifos from contaminated water. J Environ Chem Eng 8:103904. https://doi.org/10.1016/j.jece.2020.103904

Jia X, Xie L, Li Z et al (2021) Photo-electro-Fenton-like process for rapid ciprofloxacin removal: the indispensable role of polyvalent manganese in Fe-free system. Sci Total Environ 768:144368. https://doi.org/10.1016/j.scitotenv.2020.144368

Joseph L, Boateng LK, Flora JRV et al (2013) Removal of bisphenol A and 17α-ethinylestradiol by combined coagulation and adsorption using carbon nanomaterials and powdered activated carbon. Sep Purif Technol 107:37–47. https://doi.org/10.1016/j.seppur.2013.01.012

Ju P, Fan H, Guo D et al (2012) Electrocatalytic degradation of bisphenol A in water on a Ti-based PbO 2-ionic liquids (ILs) electrode. Chem Eng J 179:99–106. https://doi.org/10.1016/j.cej.2011.10.065

Kabra K, Chaudhary R, Sawhney RL (2004) Treatment of hazardous organic and inorganic compounds through aqueous-phase photocatalysis: a review. Ind Eng Chem Res 43:7683–7696

Kanakaraju D, Glass BD, Oelgemöller M (2018) Advanced oxidation process-mediated removal of pharmaceuticals from water: a review. J Environ Manag 219:189–207

Kanan S, Moyet MA, Arthur RB, Patterson HH (2020) Recent advances on TiO2-based photocatalysts toward the degradation of pesticides and major organic pollutants from water bodies. Catal Rev - Sci Eng 62:1–65. https://doi.org/10.1080/01614940.2019.1613323

Kang J-W, Hung H-M, Lin A, Hoffmann MR (1999) Sonolytic destruction of methyl tert -butyl ether by ultrasonic. Environ Sci Technol 33:3199–3205

Karim AV, Shriwastav A (2020) Degradation of ciprofloxacin using photo, sono, and sonophotocatalytic oxidation with visible light and low-frequency ultrasound: degradation kinetics and pathways. Chem Eng J 392:124853. https://doi.org/10.1016/j.cej.2020.124853

Kavitha E, Kedia R, Babaria N et al (2020) Optimization of process using carboxymethyl chitosan for the removal of mixed heavy metals from aqueous streams. Int J Biol Macromol. https://doi.org/10.1016/j.ijbiomac.2020.01.066

Khan MH, Bae H, Jung JY (2010) Tetracycline degradation by ozonation in the aqueous phase: proposed degradation intermediates and pathway. J Hazard Mater 181:659–665. https://doi.org/10.1016/j.jhazmat.2010.05.063

Khataee A, Sheydaei M, Hassani A et al (2015) Sonocatalytic removal of an organic dye using TiO2/ montmorillonite nanocomposite. Ultrason Sonochem 22:404–411. https://doi.org/10.1016/j.ultsonch.2014.07.002

Kim S, Muñoz-Senmache JC, Jun BM et al (2020) A metal organic framework-ultrafiltration hybrid system for removing selected pharmaceuticals and natural organic matter. Chem Eng J. https://doi.org/10.1016/j.cej.2019.122920

Koe WS, Chong WC, Pang YL et al (2020) Novel nitrogen and Sulphur co-doped carbon quantum dots/titanium oxide photocatalytic membrane for in-situ degradation and removal of pharmaceutical compound. J Water Process Eng 33:101068. https://doi.org/10.1016/j.jwpe.2019.101068

Kumari P, Bahadur N, Dumée LF (2020) Photo-catalytic membrane reactors for the remediation of persistent organic pollutants – a review. Sep Purif Technol 230. https://doi.org/10.1016/j.seppur.2019.115878

Kuna E, Behling R, Valange S et al (2017) Sonocatalysis: a potential sustainable pathway for the valorization of lignocellulosic biomass and derivatives. Top Curr Chem 375. https://doi.org/10.1007/s41061-017-0122-y

Kusvuran E, Yildirim D (2013) Degradation of bisphenol A by ozonation and determination of degradation intermediates by gas chromatography-mass spectrometry and liquid chromatography-mass spectrometry. Chem Eng J 220:6–14. https://doi.org/10.1016/j.cej.2013.01.064

Lee KM, Lai CW, Ngai KS, Juan JC (2016) Recent developments of zinc oxide based photocatalyst in water treatment technology: a review. Water Res 88:428–448

Li L, Visvanathan C (2017) Membrane technology for surface water treatment: advancement from microfiltration to membrane bioreactor. Rev Environ Sci Biotechnol 16:737–760. https://doi.org/10.1007/s11157-017-9442-1

Li C, Feng G, Song C et al (2018) PT SC. Colloids Surf A Physicochem Eng Asp. https://doi.org/10.1016/j.colsurfa.2018.09.043

Li X, Sun YM, Zhang ZY et al (2019) Visible light-driven multi-motion modes CNC/TiO2 nanomotors for highly efficient degradation of emerging contaminants. Carbon N Y 155:195–203. https://doi.org/10.1016/j.carbon.2019.08.039

Lin AYC, Lin CF, Chiou JM, Hong PKA (2009) O3 and O3/H2O2 treatment of sulfonamide and macrolide antibiotics in wastewater. J Hazard Mater 171:452–458. https://doi.org/10.1016/j.jhazmat.2009.06.031

Liu Y, Gan X, Zhou B et al (2009) Photoelectrocatalytic degradation of tetracycline by highly effective TiO2 nanopore arrays electrode. J Hazard Mater 171:678–683. https://doi.org/10.1016/j.jhazmat.2009.06.054

Liu Z, Zhu M, Wang Z, et al (2016) Effective degradation of aqueous tetracycline using. 1–14. https://doi.org/10.3390/ma9050364

Liu T, Wang L, Liu X et al (2020) Dynamic photocatalytic membrane coated with ZnIn2S4 for enhanced photocatalytic performance and antifouling property. Chem Eng J 379:122379. https://doi.org/10.1016/j.cej.2019.122379

López R, Mcdonald JA, Khan SJ, Le-clech P (2014) Removal of pharmaceuticals and endocrine disrupting chemicals by a submerged membrane photocatalysis reactor (MPR). Separation Purification Technol 127:131–139. https://doi.org/10.1016/j.seppur.2014.02.031

Lu P, Lin K, Gan J (2020) Enhanced ozonation of ciprofloxacin in the presence of bromide: kinetics, products, pathways, and toxicity. Water Res 116105. https://doi.org/10.1016/j.watres.2020.116105

Madhavan J, Theerthagiri J, Balaji D, Sunitha S et al (2019) Hybrid advanced oxidation processes involving ultrasound: an overview. Molecules 24:3341. https://doi.org/10.3390/molecules24183341

Mansour HB, Mosrati R, Barillier D et al (2012) Bioremediation of industrial pharmaceutical drugs. Drug Chem Toxicol 35:235–240. https://doi.org/10.3109/01480545.2011.591799

Mansour F, Al-Hindi M, Yahfoufi R et al (2018) The use of activated carbon for the removal of pharmaceuticals from aqueous solutions: a review. Rev Environ Sci Biotechnol 17:109–145. https://doi.org/10.1007/s11157-017-9456-8

Matilainen A, Sillanpää M (2010) Removal of natural organic matter from drinking water by advanced oxidation processes. Chemosphere 80:351–365. https://doi.org/10.1016/j.chemosphere.2010.04.067

Meng X, Liu Z, Deng C et al (2016) Microporous nano-MgO/diatomite ceramic membrane with high positive surface charge for tetracycline removal. J Hazard Mater 320:495–503. https://doi.org/10.1016/j.jhazmat.2016.08.068

Mi X, Li Y, Ning X et al (2019) Electro-Fenton degradation of ciprofloxacin with highly ordered mesoporous MnCo2O4-CF cathode: enhanced redox capacity and accelerated electron transfer. Chem Eng J 358:299–309. https://doi.org/10.1016/j.cej.2018.10.047

Mishra M, Chun DM (2015) α-Fe2O3 as a photocatalytic material: a review. Appl Catal A Gen 498:126–141

Molinari R, Lavorato C, Argurio P (2017) Recent progress of photocatalytic membrane reactors in water treatment and in synthesis of organic compounds. A review. Catal Today 281:144–164. https://doi.org/10.1016/j.cattod.2016.06.047

Montoya-Rodríguez DM, Serna-Galvis EA, Ferraro F, Torres-Palma RA (2020) Degradation of the emerging concern pollutant ampicillin in aqueous media by sonochemical advanced oxidation processes - parameters effect, removal of antimicrobial activity and pollutant treatment in hydrolyzed urine. J Environ Manag 261:110224. https://doi.org/10.1016/j.jenvman.2020.110224

Mozia S, Tomaszewska M, Morawski AW (2005) A new photocatalytic membrane reactor (PMR) for removal of azo-dye acid red 18 from water. Appl Catal B Environ 59:131–137. https://doi.org/10.1016/j.apcatb.2005.01.011

Muhamad MS, Salim MR, Lau WJ, Yusop Z (2016) A review on bisphenol A occurrences, health effects and treatment process via membrane technology for drinking water. Environ Sci Pollut Res 23:11549–11567. https://doi.org/10.1007/s11356-016-6357-2

Naddeo V, Landi M, Scannapieco D, Belgiorno V (2013) Sonochemical degradation of twenty-three emerging contaminants in urban wastewater. Desalin Water Treat 51:6601–6608. https://doi.org/10.1080/19443994.2013.769696

Naddeo V, Freda M, Secondes N et al (2020) Ultrasonics - Sonochemistry Removal of contaminants of emerging concern from real wastewater by an innovative hybrid membrane process – UltraSound, Adsorption, and Membrane ultra-filtration (USAMe®). Ultrason - Sonochem 68:105237. https://doi.org/10.1016/j.ultsonch.2020.105237

Nguyen TP, Tran QB, Ly QV et al (2020) Enhanced visible photocatalytic degradation of diclofen over N-doped TiO2 assisted with H2O2: a kinetic and pathway study. Arab J Chem. https://doi.org/10.1016/j.arabjc.2020.05.023

Nippatla N, Philip L (2019) Electrocoagulation-floatation assisted pulsed power plasma technology for the complete mineralization of potentially toxic dyes and real textile wastewater. Process Saf Environ Prot 125:143–156. https://doi.org/10.1016/j.psep.2019.03.012

Niti C, Sunita S, Kamlesh K, Rakesh K (2014) Bioremediation: an emerging technology for remediation of pesticides

Oturan MA, Aaron JJ (2014) Advanced oxidation processes in water/wastewater treatment: principles and applications. A review. Crit Rev Environ Sci Technol 44:2577–2641. https://doi.org/10.1080/10643389.2013.829765

Oturan N, Wu J, Zhang H et al (2013) Electrocatalytic destruction of the antibiotic tetracycline in aqueous medium by electrochemical advanced oxidation processes: effect of electrode materials. Appl Catal B Environ 140–141:92–97. https://doi.org/10.1016/j.apcatb.2013.03.035

Patel M, Kumar R, Kishor K et al (2019) Pharmaceuticals of emerging concern in aquatic systems: chemistry, occurrence, effects, and removal methods. Chem Rev 119:3510–3673. https://doi.org/10.1021/acs.chemrev.8b00299

Paumo HK, Das R, Bhaumik M, Maity A (2020) Visible-light-responsive nanostructured materials for photocatalytic degradation of persistent organic pollutants in water. 1–29. https://doi.org/10.1007/978-3-030-16427-0_1

Philip JM, Aravind UK, Aravindakumar CT (2018) Emerging contaminants in Indian environmental matrices – a review. Chemosphere 190:307–326. https://doi.org/10.1016/j.chemosphere.2017.09.120

Pirsaheb M, Moradi N (2020) Sonochemical degradation of pesticides in aqueous solution: investigation on the influence of operating parameters and degradation pathway-a systematic review. RSC Adv 10:7396–7423. https://doi.org/10.1039/c9ra11025a

Plakas KV, Karabelas AJ (2012) Removal of pesticides from water by NF and RO membranes - a review. Desalination 287:255–265. https://doi.org/10.1016/j.desal.2011.08.003

Ramanayaka S, Tsang DCW, Hou D et al (2020) Green synthesis of graphitic nanobiochar for the removal of emerging contaminants in aqueous media. Sci Total Environ 706:135725. https://doi.org/10.1016/j.scitotenv.2019.135725

Rodriguez-Narvaez OM, Peralta-Hernandez JM, Goonetilleke A, Bandala ER (2017) Treatment technologies for emerging contaminants in water: a review. Chem Eng J 323:361–380. https://doi.org/10.1016/j.cej.2017.04.106

Román S, Nabais JMV, Ledesma B et al (2020) Surface interactions during the removal of emerging contaminants by hydrochar-based adsorbents. Molecules 25:1–12. https://doi.org/10.3390/molecules25092264

Rubio-Clemente A, Torres-Palma RA, Peñuela GA (2014) Removal of polycyclic aromatic hydrocarbons in aqueous environment by chemical treatments: a review. Sci Total Environ 478:201–225. https://doi.org/10.1016/j.scitotenv.2013.12.126

Salimi M, Esrafili A, Gholami M et al (2017) Contaminants of emerging concern: a review of new approach in AOP technologies. Environ Monit Assess 189. https://doi.org/10.1007/s10661-017-6097-x

Sanchez W, Egea E (2018) Health and environmental risks associated with emerging pollutants and novel green processes. Environ Sci Pollut Res

Santos MSF, Alves A, Madeira LM (2016) Chemical and photochemical degradation of polybrominated diphenyl ethers in liquid systems - a review. Elsevier Ltd

Selli E, Bianchi CL, Pirola C et al (2008) Efficiency of 1,4-dichlorobenzene degradation in water under photolysis, photocatalysis on TiO2 and sonolysis. J Hazard Mater 153:1136–1141. https://doi.org/10.1016/j.jhazmat.2007.09.071

Shah AD, Huang CH, Kim JH (2012) Mechanisms of antibiotic removal by nanofiltration membranes: model development and application. J Memb Sci 389:234–244. https://doi.org/10.1016/j.memsci.2011.10.034

Singh J, Yadav P, Mishra V (2020) Low-cost bio-adsorbent for emerging inorganic pollutants. INC

Soltani RDC, Mashayekhi M, Naderi M et al (2019) Sonocatalytic degradation of tetracycline antibiotic using zinc oxide nanostructures loaded on nano-cellulose from waste straw as nanosonocatalyst. Ultrason Sonochem 55:117–124. https://doi.org/10.1016/j.ultsonch.2019.03.009

Sophia AC, Lima EC (2018) Removal of emerging contaminants from the environment by adsorption. Ecotoxicol Environ Saf 150:1–17. https://doi.org/10.1016/j.ecoenv.2017.12.026

Sowmya A, Meenakshi S (2014) Zr(IV) loaded cross-linked chitosan beads with enhanced surface area for the removal of nitrate and phosphate. Int J Biol Macromol 69:336–343. https://doi.org/10.1016/j.ijbiomac.2014.05.043

Su L, Sivey JD, Dai N (2018) Emerging investigator series: sunlight photolysis of 2,4-D herbicides in systems simulating leaf surfaces. Environ Sci Process Impacts 20:1123–1135. https://doi.org/10.1039/c8em00186c

Sutherland DL, Ralph PJ (2019) Microalgal bioremediation of emerging contaminants - opportunities and challenges. Water Res 164:114921. https://doi.org/10.1016/j.watres.2019.114921

Tang K, Ooi GTH, Torresi E et al (2020) Municipal wastewater treatment targeting pharmaceuticals by a pilot-scale hybrid attached biofilm and activated sludge system (Hybas™). Chemosphere. https://doi.org/10.1016/j.chemosphere.2020.127397

Tara N, Siddiqui SI, Rathi G et al (2019) Nano-engineered adsorbent for the removal of dyes from water: a review. Curr Anal Chem 16:14–40. https://doi.org/10.2174/1573411015666190117124344

Thomas S, Rayaroth MP, Menacherry SPM et al (2020) Sonochemical degradation of benzenesulfonic acid in aqueous medium. Chemosphere 252:126485. https://doi.org/10.1016/j.chemosphere.2020.126485

Thue PS, Lima DR, Naushad M et al (2020) High removal of emerging contaminants from wastewater by activated carbons derived from the shell of cashew of Para. Carbon Lett. https://doi.org/10.1007/s42823-020-00145-x

Torres-Palma RA, Serna-Galvis EA (2018) Sonolysis. Elsevier Inc.

Trivedi NS, Mandavgane SA (2018) Fundamentals of 2, 4 Dichlorophenoxyacetic acid removal from aqueous solutions. Sep Purif Rev 47:337–354. https://doi.org/10.1080/15422119.2018.1450765

USEPA (2017) Ground water and drinking water regulation. https://www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-regulations

USGS (2017) Contaminants of emerging concern in the environment. Environment Health-Toxic substances Hydrology program. U.S. Geological Survey. 1–2

Vigneshwaran S, Preethi J, Meenakshi S (2019) Removal of chlorpyrifos, an insecticide using metal free heterogeneous graphitic carbon nitride (g-C 3 N 4) incorporated chitosan as catalyst: Photocatalytic and adsorption studies. Elsevier B.V

Wachter N, Aquino JM, Denadai M et al (2019) Optimization of the electrochemical degradation process of the antibiotic ciprofloxacin using a double-sided β-PbO2 anode in a flow reactor:

kinetics, identification of oxidation intermediates and toxicity evaluation. Environ Sci Pollut Res 26:4438–4449. https://doi.org/10.1007/s11356-018-2349-8

Wang R, Ren D, Xia S et al (2009) Photocatalytic degradation of Bisphenol A (BPA) using immobilized TiO2 and UV illumination in a horizontal circulating bed photocatalytic reactor (HCBPR). J Hazard Mater 169:926–932. https://doi.org/10.1016/j.jhazmat.2009.04.036

Wang G, Chen S, Yu H, Quan X (2015a) Integration of membrane filtration and photoelectrocatalysis using a TiO2/carbon/Al2O3 membrane for enhanced water treatment. Elsevier BV. https://doi.org/10.1016/j.jhazmat.2015.06.005

Wang XM, Li B, Zhang T, Li XY (2015b) Performance of nanofiltration membrane in rejecting trace organic compounds: experiment and model prediction. Desalination. https://doi.org/10.1016/j.desal.2015.05.010

Wang L, Zhang Q, Chen B et al (2020) Photolysis and photocatalysis of haloacetic acids in water: a review of kinetics, influencing factors, products, pathways, and mechanisms. J Hazard Mater 391:122143. https://doi.org/10.1016/j.jhazmat.2020.122143

Xiang W, Zhang X, Chen J et al (2020) Biochar technology in wastewater treatment: a critical review. Chemosphere 252:126539. https://doi.org/10.1016/j.chemosphere.2020.126539

Yalcinkaya F, Boyraz E, Maryska J, Kucerova K (2020) A review on membrane technology and chemical surface modification for the oily wastewater treatment. Materials (Basel)

Yang J, Zhang Y, Zeng D et al (2020) Enhanced catalytic activation of photo-Fenton process by Cu0·5Mn0·5Fe2O4 for effective removal of organic contaminants. Chemosphere 247:125780. https://doi.org/10.1016/j.chemosphere.2019.125780

Yao JJ, Hoffmann MR, Gao NY et al (2011) Sonolytic degradation of dimethoate: kinetics, mechanisms and toxic intermediates controlling. Water Res 45:5886–5894. https://doi.org/10.1016/j.watres.2011.08.042

Yap WF, Yunus WMM, Talib ZA, Yusof NA (2011) X-ray photoelectron spectroscopy and atomic force microscopy studies on crosslinked chitosan thin film. Int J Phys Sci 6:2744–2749. https://doi.org/10.5897/IJPS11.121

Yap HC, Pang YL, Lim S et al (2019) A comprehensive review on state-of-the-art photo-, sono-, and sonophotocatalytic treatments to degrade emerging contaminants. Int J Environ Sci Technol 16:601–628. https://doi.org/10.1007/s13762-018-1961-y

Yousef Tizhoosh N, Khataee A, Hassandoost R et al (2020) Ultrasound-engineered synthesis of WS2@CeO2 heterostructure for sonocatalytic degradation of tylosin. Ultrason Sonochem 67:105114. https://doi.org/10.1016/j.ultsonch.2020.105114

Yu X, Zhang J, Zhang J et al (2019) Photocatalytic degradation of ciprofloxacin using Zn-doped Cu2O particles: analysis of degradation pathways and intermediates. Chem Eng J 374:316–327. https://doi.org/10.1016/j.cej.2019.05.177

Zheng X, Shen Z, Shi L, Cheng R (2017) Photocatalytic membrane reactors (PMRs) in water treatment : configurations and influencing factors. https://doi.org/10.3390/catal7080224

Zhuang S, Chen R, Liu Y, Wang J (2020) Magnetic COFs for the adsorptive removal of diclofenac and sulfamethazine from aqueous solution: adsorption kinetics, isotherms study and DFT calculation. J Hazard Mater 385:121596. https://doi.org/10.1016/j.jhazmat.2019.121596

Emerging Contaminant Removal from Domestic Wastewater by Advanced Treatment Technologies

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Abstract Water reuse/wastewater treatment and desalination are two major options to reduce water scarcity. However, recycling wastewater is hampered by the presence of emerging contaminants (ECs) such as pharmaceuticals, personal care products, etc. Pharmaceuticals are of major concern because of their potential toxicity to aquatic organisms and human health. The classical wastewater treatment techniques are inadequate for the elimination of these trace ECs; thus, these compounds are predominantly found in various environmental matrices. Various advanced oxidation process (AOPs) have been utilized for the removal of trace organics. Coupled treatment techniques such as AOPs and membrane process are attractive technologies for complete removal of ECs because each technique complements the advantage and overcomes the downside of the other. The technological flexibility of the membrane process has allowed it to be coupled with various AOPs as a pre-treatment or post-treatment method or as a hybrid process for concurrent membrane filtration and degradation of trace organics. On the other hand, various desalination techniques, both thermal and membrane-based, are discussed in detail for seawater and brackish saltwater treatment. This chapter also reviews the membrane modification techniques using nanotechnology for enhancement in desalination performance.

Keywords Water reuse · Emerging contaminants · Pharmaceuticals · Advanced oxidation process · Degradation · Membrane technology · Photocatalytic membrane reactor · Desalination

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1 Introduction

Freshwater is considered as the most necessary and basic need of humanity. Although the planet is rich with water resources, there are very limited freshwater sources available for human consumption and beneficial uses. Water reuse and wastewater treatment are major options to reduce water scarcity. However, recycling wastewater is hampered by the presence of emerging contaminants (ECs) such as pharmaceuticals, personal care products, endocrine-disrupting compounds, pesticides, etc. Pharmaceuticals are of major concern because of its potential toxicity to aquatic organisms and human health, and their continuous accumulation in environmental matrix led to the development of antibiotic-resistant genes. Pharmaceuticals are the medicines/drugs used in human and veterinary applications for diagnosis, treatment, or prevention of diseases. Pharmaceutically active compounds (PhACs) include analgesics, antibiotics, antihyperlipidemics, antiepileptics, and stimulants. Pharmaceutically active compounds entering into the environment through various pathways undergo different processes. These compounds can reach surface and groundwater through wastewater treatment plant (WWTP) effluents (Kolpin et al. 2002; Heberer et al. 2004), hospital effluent (Kümmerer 2001), landfill (Holm et al. 1995), septic tank leakage (Verstraeten et al. 2005; Swartz et al. 2006), and agricultural runoff (Pedersen et al. 2005). The main sources and pathways of PhACs are represented in Fig. 1 (Lapworth et al. 2012). The WWTP effluents are identified as one of the major sources (Santos et al. 2010), and most of the compounds are not completely removed during wastewater treatment. The fate of the pharmaceutical compounds in the environmental depends on the properties of the specific drug and nature of the environment. A compound having low volatility and high polarity will

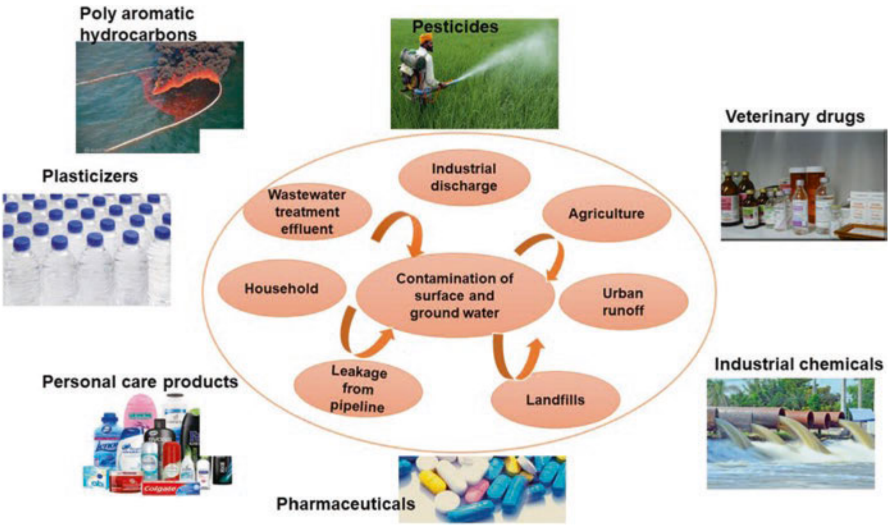

Fig. 1 Sources and occurrence of emerging contaminants in the aquatic environment

remain in aqueous phase (Daughton and Ternes 1999). In WWTP, it can be converted to less toxic or more toxic metabolites, persistent and complex intermediates, or simple mineralized end products. Sometimes these compounds get attached to the suspended particles and escape from the treatment units. Therefore, chances of removal of emerging contaminants in WWTP are highly uncertain (Tiwari et al. 2017). Deblonde and Cossu-Leguille (2011) consolidated the removal rates of different classes of ECs based on the data obtained from various studies. They reported that except some of the psychostimulants and antidepressants, all other compounds are removed by less than 90%. On the other hand, some of the antiepileptics are not at all removed to a significant extent in the WWTP treatment units.

The classical wastewater treatment techniques are inadequate for the elimination of these trace ECs; thus, these compounds are predominantly found in various environmental matrices. Various advanced oxidation process (AOPs) have been utilized for removal of trace organics such as ozonation, Fenton's process, electrochemical process, photocatalysis, etc. Coupled treatment techniques such as AOPs and membrane process are exciting technologies for complete removal of ECs. The hybrid technique complements the advantage and overcomes the downside of each other. The technical flexibility of membrane process has allowed being coupled with various AOPs as a pre-treatment or post-treatment method or as a hybrid process for concurrent membrane filtration and degradation of trace organics. The possibility of coupling the advanced process with membrane technology has also been discussed in this chapter.

2 Toxicology of Emerging Contaminants

Emerging contaminants (ECs) in water bodies are well-known to cause irreversible harmful effects to living beings and are being recognized as a worldwide threat (Santos et al. 2010; Prieto-Rodriguez et al. 2012; Stuart et al. 2012). These ECs are toxic and tend to remain persistent in water bodies even at a lower concentration (μg/L to ng/L). In order to assess the potential risk of these ECs, the European Union (EU) has issued the guidelines on risk assessment in aquatic system (Commission, EC directive 93/97/EEC, 2003). Mainly three approaches are applicable for risk assessment: persistence, bioaccumulation, and toxicity assessment. It is impossible to evaluate the chronic toxic effect of ECs on human health. However, the toxicity effect of these ECs is being measured on other aquatic species that possess a human-like or animal-like metabolic pathway, receptors, or bio-molecules (Santos et al., 2010). The studies conducted using aquatic organisms (algae, fishes, bacteria, crustaceans, etc.) revealed the nature of EC toxicity with respect to their growth rate, bioaccumulation, reproduction, and genotoxicity along with their morphological and physiological abnormalities (Santos et al., 2010).

Pharmaceuticals are extremely important as an emerging contaminant because continuous consumption through drinking water even at very low concentrations is anticipated to cause irreversible effect on human health. Antibiotics are widely studied because of their utmost importance. Continuous exposure to antibiotics may lead the bacteria to become resistant against these medicines (Sanderson et al. 2004). However, there is not much data available on their toxicity to humans due to consumption of water containing single and multiple ECs (Daughton and Ternes 1999; Stackelberg et al. 2004). Pharmaceuticals can cause a particular physiological action in the body. It has the capability to resist any kind of inactivation before executing its intended effect (Santos et al. 2010). In the same manner, these compounds, when they enter into a living organism, will be able to cause changes inside the body of the organism. In this way, the presence of pharmaceuticals in water primarily affects the aquatic organisms. Even if these compounds are present at very low concentrations, the toxic level increases due to continuous exposure during the lifecycle of the organism that will become visible in future generations (Daughton and Ternes 1999).

Carbamazepine (CBZ) is one of the commonly used neuroactive pharmaceutical compounds. Its effective concentration (EC_{50}) values were found to be 52.5 mg/L (5 min exposure) and 76.3 mg/L (96 h exposure) in *V. fischeri* and *D. magna* species, respectively (Kim et al. 2007). However, chronic toxicity of this compound is reported even at lower concentration (μg/L) on different aquatic species (Ferrari et al. 2003). The 3-(4,5-dimethyl-2thiazholyl)-2,5-diphenyl-2H tetrazolium bromide (MTT) test was applied to cell populations isolated from the zebra mussel, and it was observed that CBZ has affected the digestive gland cell and mitochondrial function of the gill (Parolini et al. 2011).

Metronidazole (MNZ) is an antibiotic used against a wide spectrum of anaerobic bacteria and protozoans such as *Trichomonas vaginitis* and *Giardia lamblia (Lau et al.* 1992*).* Its 72 h EC_{10} and EC_{50} values were 2.08 and 12.5 mg/L and 19.9 and 40.4 mg/L for *Chlorella* and *Selenastrum capricornutum*, respectively (Lanzky and Halling-Sørensen 1997). Soybean plants (cv. A4045) were adversely affected when exposed to MNZ concentration of 0.5 mg/g of soil. This could be due to the hydrophilic nature of MNZ, which tends to remain in the aqueous phase enabling higher uptake by plants (Jjemba 2002).

Triclosan (TCS) is a well-known anti-bacterial compound used in a wide variety of medicines, soaps, tooth pastes, hand sanitizers, mouthwash, etc. (Weatherly and Gosse 2017). Previous studies revealed that TCS is an endocrine-disrupting compound (EDC) for both human (Koeppe et al. 2013) and various species (Ishibashi et al. 2004; Raut and Angus 2010; Axelstad et al. 2013; Wang and Tian 2015; Louis et al. 2017). The epidemiological studies conducted in a human mother shows that exposure to TCS had been associated with a decrease in T4 hormone level and cognitive impairment in the child (Haddow et al. 1999; Ghassabian et al. 2011). A decrease in sperm count was observed in fishes, and changes in hormone levels were noticed in rat after exposure to TCS. Further, the test conducted with invertebrates showed reduced juvenile count, increased heat shock protein 70 gene expression, and generated DNA strand breaks.

3 Advanced Oxidation Process for Removal of Emerging Contaminants

Advanced oxidation processes (AOPs) are the process that require the application of external energy such as electrical, chemical, or radiative to produce highly reactive species (hydroxyl radicals, hydrogen peroxide, and superoxide) in the reaction zone. The main oxidation species of AOPs is hydroxyl radical ($OH^{\bullet}$). AOPs involve two stages of oxidation: (i) the formation of strong oxidants and (ii) the reaction of these oxidants with contaminants in water. The $OH^{\bullet}$ is nonselective and highly reactive against the electron-rich organic compounds. The oxidation potential (E_0) of $OH^{\bullet}$ is + 2.8 V versus normal hydrogen electrode (NHE) in acidic medium and 1.55 V versus NHE in basic medium. Many organic contaminants in water exhibit second-order degradation rate constants in the order of magnitude 10^8 to 10^9 L mole^{-1}s^{-1} (which correlates to the magnitude of diffusion-limited acid-base reactions, ~10^9). Therefore, the reaction of $OH^{\bullet}$ radicals with trace organics is considered to be the quickest aqueous phase chemical reactions apart from acid-base reactions. AOPs include photochemical and non-photochemical process like Fenton, photo-Fenton, H_2O_2/UV, O_3, O_3/H_2O_2, O_3/UV, O_3/H_2O_2/UV, and photocatalysis.

Advanced wastewater treatment technologies are required primarily to meet the strict discharge specifications of wastewater treatment plant effluent to comply within the limits set by the central pollution control board. In the water and wastewater treatment sectors, the implementation of AOPs to reduce the harmful effects of ECs has gained popularity considering the limitations of conventional treatment systems. Numerous studies in this area are ongoing and some of the AOPs are elaborated in the following subsections.

3.1 *Ozonation*

Ozonation is a chemical oxidation process, it can be a stand-alone process (O_3) or can be combined with UV (O_3/UV) and H_2O_2 (O_3/H_2O_2), and it has been widely applied for disinfection and the elimination of trace organics (Andreozzi et al. 2005; Ikehata et al. 2006; Almomani et al. 2016; Kıdak and Doğan 2018). The oxidation potential (E_0) of O_3 is +2.07 V versus NHE in acidic medium and 1.25 V versus NHE in basic medium. In acidic medium, ozone exhibits direct electrophilic attack, whereas in a basic medium, the attack is indirect through the formation of $OH^{\bullet}$ radicals. The mineralization of pharmaceuticals using ozonation has been influenced by ozone dose, pH, and temperature. Moreover, the pH is the governing factor in ozonation because it can alter the reaction kinetics and PhACs degradation mechanism. Real-time application of ozonation is of a great challenge due to the short lifetime of generated ozone and high energy demand (Ikehata et al. 2006).

Previous studies have reported the high removal efficiency of PhACs but incomplete mineralization due to the formation of persistent by-products during the process (Almomani et al. 2016). The low ozone doses were reported to achieve complete degradation of target PhACs but had low mineralization. The results highlighted the need to determine the influent and effluent toxicity. Ikehata et al. (2006) have shown the degradation of some selected pharmaceutical wastes and pesticides using ozonation. It was found that some compounds are extremely reactive toward ozone and hydroxyl radicals, such as some antibiotics, carbamazepine, 17-estradiol, diclofenac, and pentachlorophenol. On the other hand, it was found that halogenated pesticides, X-ray contrast agents, and surfactants were resistant to oxidative degradation. The research by Zhao et al. (2017) stated that complete degradation of anti-inflammatory drug indomethacin was achieved within 7 min with four varying ozone doses (2–35 mg/L). However, at maximum dose of ozone (35 mg/L), only 50% of total organic carbon (TOC) was eliminated within 30 min. Higher degradation efficiency was obtained for tetracycline and propranolol, while TOC reduction was only 65% (90 min), thus indicating the formation of stable intermediates (Wang et al. 2011; Dantas et al. 2011). Furthermore, the combination of UV irradiation and H_2O_2 addition can improve the mineralization of PhACs (Wallace et al. 1987; Liu et al. 2019).

Kıdak and Doğan (2018) reported that the degradation of amoxicillin was pH-dependent. The degradation process was conducted at different pH (3, 7, and 10). The efficiency of degradation at alkaline pH 10 was more compared to acidic or neutral due to the increased generation of $OH^•$ radicals by ozone decomposition. Contrarily, the degradation of salicylic acid was more in acidic pH 4 (40–50%) compared to alkaline or basic medium (10–20%). The degradation process of salicylic acid was driven by direct ozone oxidation rather than $OH^•$ (Hu et al. 2016). Almomani et al. (2016) evaluated the performance of ozonation for the degradation of PhACs at various water matrices (synthetic water, surface, and WWTP effluent). It was reported that the degradation of PhACs required a higher O_3 dose (222.3 mg/h) for surface water and WWTP effluent compared to synthetic water. This can be ascribed to the presence of organic matter in both surface water and WWTP effluent.

The conventional ozonation, photolytic ozonation, TiO_2 catalytic ozonation, TiO_2 photocatalytic oxidation, and TiO_2 photocatalytic ozonation were employed for the degradation of PhACs (atenolol, hydrochlorothiazide, ofloxacin, and trimethoprim) (Márquez et al. 2014). Compared to other techniques, solar photocatalytic ozonation was a promising oxidation method as it supported higher mineralization (85%) and toxicity removal (90%). In a full-scale WWTP located in Beijing, 13 PhACs and PPCPs were removed via sequential UV and ozonation process. Many of the target PPCPs were effectively removed, and the mean removal efficiency for individual PPCPs ranged from 13% to 89% (Sui et al. 2014). The principal drawbacks of ozonation are its high energy demand and generation of toxic by-products.

3.2 Fenton and Photo-Fenton

Fenton's process is the catalytic formation of $OH^{\bullet}$ in which Fe^{2+}/Fe^{3+} acts like a catalyst to decompose H_2O_2 under mild acidic conditions (Eq. 1).

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + H_2O + HO^{\bullet}. \tag{1}$$

However, the Fe^{2+} catalyst can be regenerated from Fe^{3+} represented in Eq. (2).

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^+. \tag{2}$$

Fenton and photo-Fenton process are efficient for PhACs degradation. When the Fenton process gets activated by UV-Vis radiation (i.e., photo-Fenton process), the efficiency was found to increase. Ay and Kargi (2010) investigated the effect of Fe (II) and H_2O_2 concentrations on the degradation of amoxicillin at pH 3 and determined that amoxicillin could be completely degraded, with 37% of its initial amount mineralized at the optimum H_2O_2/Fe/amoxicillin weight concentrations of 255/25/105 mg/L. Li et al. (2012) studied the removal of 20 emerging contaminants from wastewater. They reported that all tested compounds, except atrazine and iopromide, were completely removed by Fenton oxidation process carried out using a 20 mg/L Fe (II) concentration and a 2.5 H_2O_2/Fe (II) molar ratio.

The Fenton's process is not much energy-intensive such as ozonation and UV irradiation process. But it requires a lower pH for activating Fenton's process. At higher pH values (more than 3), Fe^{3+} precipitates as Fe $(OH)_3$, whereas the generation of Fe (II) complexes leads to a decrease in Fe^{2+} concentration. To deal with real-time samples, the Fenton and photo-Fenton process has been modified to work under neutral or near-neutral pH. Klamerth et al. (2010) studied the degradation of 15 emerging contaminants (100 μg/L) at low concentrations in simulated and real effluent of municipal wastewater treatment plant with photo-Fenton at unchanged pH. The iron dose of 5 mg/L was used, and the target compounds were degraded to negligible concentrations. They reported that carbonate and bicarbonate ions act as radical scavengers and decrease the efficiency of the system. Toxicity tests with *Aliivibrio fischeri* showed that degradation of the compounds in real effluent wastewater led to toxicity increase. The complete removal of 203 μmol/L oxacillin was achieved at pH ~6 after 50 min with 30 W (365 nm) light source under the optimum concentration of Fe^{2+} (90 μmol/L) and H_2O_2 (10 mmol/L) (Giraldo-Aguirre et al. 2018). One of the problems of this process is the requirement of the supply of H_2O_2 as a reactant and Fe^{2+} ions. Also, the treatment of sludge containing Fe ions from the wastewater treatment systems is expensive and needs a large amount of chemicals and human resources.

Electro-Fenton process (E-Fenton) is an emerging process, which provides a solution to the negative aspect of Fenton and photo-Fenton process. Electrochemical reduction of O_2 at cathode facilitates the in situ production of H_2O_2 and regeneration of Fe^{2+} continuously with the aid of external power supply. Continuous in situ $HO^{\bullet}$

generation enhances the oxidation rate of contaminants. The oxidative degradation efficiency of levofloxacin in E-Fenton was about 91% at the end of 6 h (Yahya et al. 2016). The E-Fenton experiments were carried out in an electrochemical cell with carbon felt as a cathode at an optimum Fe^{2+} concentration (0.1 mM) and the current value of 400 mA. At the end of 6 h of electrolysis time, mineralization of > 91 % was achieved. The same researcher investigated E-Fenton removal of moxifloxacin in acidic medium (pH 3.0) and observed complete moxifloxacin removal in 8 min. For nearly complete removal of trace organics in E-Fenton process, the low pH was found to be the governing factor. The major drawback of this process is the requirement for a continuous supply of oxygen to the reactor.

3.3 Sonolysis

Sonolysis is the process of **in situ** generation of hydroxyl radicals by passing ultrasound radiation through an aqueous medium. The technique uses high-strength acoustic cavity bubbles from water pyrolysis to generate $HO^{\bullet}$ (Güyer and Ince 2011) Eqs. (3–5).

$$H_2O + \text{Ultrasound radiation} \rightarrow HO^{\bullet} + H^{\bullet} \tag{3}$$

$$2HO^{\bullet} \rightarrow H_2O_2 \tag{4}$$

$$2HO^{\bullet} \rightarrow H_2O + O \tag{5}$$

The efficiency of degradation of PhACs using sonolysis process depends upon the frequency and power of applied ultrasound radiation (Méndez-Arriaga et al. 2008; Ince 2018; Kıdak and Doğan 2018). A study by De Bel et al. (2011) reported on the degradation efficiency of ciprofloxacin at three different frequencies (544, 801, and 1081 kHz). The results indicated that the lowest frequency (544 kHz) showed the highest degradation rate (0.007 min^{-1}) for 15 mg/L ciprofloxacin concentration. Naddeo et al. (2013) demonstrated sonochemical degradation for urban wastewater containing 23 ECs. They reported that increasing power densities (100–400 W/L) indicated higher degradation efficiency of PhACs. Similarly, the enhanced degradation was observed for piroxicam when power densities increased from 20 to 60 W/L. It can be attributed to the increased generation of hydroxyl radicals and intense mixing rate (Lianou et al. 2018). The sonochemical treatment efficacy also depends upon cavitational activity. The increase in power intensity enhances the degradation efficiency due to the formation of cavitation bubbles and results in more $HO^{\bullet}$ formation in the system. The sonolysis process was enhanced with the addition of additives such as mannitol, calcium carbonate, and Fe-containing additives (Güyer and Ince 2011; Rayaroth et al. 2016). The degradation of diclofenac by sonochemical treatment was performed with three different additives such as Fenton reagent, zerovalent iron, and superparamagnetic iron-oxide NPs. At a frequency of 861 kHz, the efficacies of elimination of diclofenac by superparamagnetic iron-oxide NPs, zerovalent iron, and Fenton reagent were 41.54, 1.65, and 0.016 μM/mg, respectively. The superparamagnetic iron-oxide NPs showed better efficacy than other additives containing sonochemical treatment systems. It can be explained that superparamagnetic iron-oxide NPs have a large surface area and more amount of cavitation nuclei. The major downside of sonochemical process is the heat generation in the system. Huge heat is produced in sonochemical process, and thus, temperature control is important for these systems. Besides, sonochemical process need intense energy to produce cavitation within the water.

3.4 Electrochemical Oxidation

Electrochemical oxidation process generates reactive species in situ via electricity at ambient temperature without the addition of chemicals, thus making this technique attractive in recent times (Garcia-Segura et al. 2018). The electrochemical technology is classified as electrochemical degradation (i.e., anodic oxidation) and electrochemical separation (i.e., electrochemical coagulation and dialysis) (Sirés and Brillas 2012). The electrochemical oxidation can be achieved by two mechanisms: (a) specific anodic oxidation in which the pollutants are adsorbed on the anode surface and eliminated by the anodic electron transfer reaction and (b) direct oxidation in bulk, facilitated by electrochemically formed oxidants such as $HO^{\bullet}$, O_3, and H_2O_2 (Feng et al. 2013).

The boron-doped anodes are widely applied in electrochemical oxidation systems for the degradation of trace organics than conventional electrodes (IrO_2, Pt, or PbO) due to their stability and ability to generate more reactive species. Previous studies have proved the efficacy of boron-doped anodes for the degradation of PhACs. The electrochemical oxidation with boron-doped anodes was employed for treating synthetic and hospital effluent containing 17-α-ethinylestradiol, sulfamethoxazole, diclofenac, and iopromide. The experiments were conducted at influent different flow rates (125, 250, and 500 L/h). At the highest flow rate of 500 L/h with an applied current of 0.9 A, the first-order degradation rate constant for diclofenac and 17-α-ethinylestradiol increased for synthetic wastewater, while for sulfamethoxazole and iopromide the rate constants were unaffected (Loos et al. 2018). In an electrochemical study, the used *niobium (Nb)*/boron-doped anode and Ti/IrO_2 anode was used for the degradation of carbamazepine and the electrochemical oxidation process was mediated by Cl^- ions. The Nb/boron-doped anode performed better than Ti/IrO_2 anode, and the process was dependent on treatment time and current applied. The increase in residual chlorine was observed with an increase in treatment time, which was clearly evident in acute toxicity test conducted with *Aliivibrio fischeri*. At a treatment time of 20 min, the toxicity of effluent was 11.35 TU, whereas after 90 min of treatment, the toxicity increased to 30.44 TU. The electrochemical oxidation efficacy solely depends on the electrodes and their application in real time is limited.

3.5 High-Voltage Pulse Power Technology

High-voltage electrical discharge in water or air creates plasma that is a mixture of heavy molecules, atoms, free radicals, ions, electrons, and photons. The plasma generated can be projected directly onto the target contaminants present in the aqueous medium. The in situ reactive species such as $HO^{\bullet}$, H_2O_2, O_3, hydroperoxyl, and molecular oxygen are formed and react with the pollutants (Joshi et al. 1995; Sun et al. 1999). Gerrity et al. (2010) investigated a pilot-scale unit with a needle to plane geometry corona discharge reactor for the treatment of different trace organics (atenolol, carbamazepine, primidone, dilantin, trimethoprim, meprobamate, and atrazine). For a voltage of 8 kV and 500Hz frequency, the average degradation efficiency was above 90% in 19 min with energy consumption varying from 16.93 to 61.11 kWh/mg/L. A study by Magureanu et al. (2011) reported a nearly complete removal of three antibiotics (ampicillin, amoxicillin, and oxacillin). The experiment was conducted separately for each antibiotic with an initial concentration of 100 mg/L, and the influent was made to spray as a film over the surface of the plasma reactor's inner electrode, thereby producing the discharge at the gas-liquid interface. The treatment time and energy consumption for the degradation of oxacillin, ampicillin, and amoxicillin were 30, 20, and 10 min, respectively, and 0.00018, 0.00017, and 0.00005 kWh/mg/L, respectively. The degradation of endocrine-disrupting compounds (carbamazepine, clofibric acid, and iopromide) in aqueous and landfill leachate solution using corona discharge over a liquid surface is also investigated (Krause et al. 2009). There were no signs of estrogen activity after 15 min of treatment of iopromide (for both parent compound and intermediates) when tested with E-screen assay. Though the pulse power plasma process shows higher efficiency against trace organic mineralization, the safety and higher installation/maintenance costs are the main drawbacks in its field-scale application.

3.6 Radiation

Radiation-based techniques are classified based on the source and energy of radiation. Gamma radiation, electron beam radiation, and UV irradiation (presence of oxidants/photocatalysts) are the three primary sources of radiation used for the production of hydroxyl radicals in AOPs. Water radiolysis occurs in the presence of radioactive sources such as gamma radiation or electron beam radiation. Gamma radiation is generated from radioactive elements such as caesium-137 or cobalt-60, while electron beam (E-beam) is produced utilizing electron accelerator. Reactive species like $HO^{\bullet}$, a hydrogen atom, hydrated electron (e_{aq}^{-}), H_2, H_2O_2, H_{aq}^{+}, and OH_{aq}^{-} are formed in water due to these radiations.

The efficiency of ionizing radiation-based AOPs for degrading ECs depends on radiation dose, solution pH, and water matrices (Wang and Chu 2016). The gamma radiation is efficient than UV due to its high penetrating ability and subsequently enhanced generation of $HO^{\bullet}$ and e_{aq}^{-}. The carbamazepine degradation was investigated using single gamma radiation for activation of peroxymonosulfate. The activation of peroxymonosulfate leads to nearly complete degradation of carbamazepine. Also, with the increase in single gamma radiation dose, the carbamazepine degradation efficiency has increased (Wang and Wang 2018). Another study by Liu et al. (2016) studied the degradation efficacy of carbamazepine in a combined E-beam/H_2O_2 process. A carbamazepine degradation efficiency of 95% was achieved by applying 1 kGy of E-beam/10 mM H_2O_2. The results indicated that an increase in H_2O_2 concentration from 50 to 200 mM had decreased the rate constant, suggesting that the use of an appropriate concentration of H_2O_2 is essential for higher degradation rate.

The performance of gamma radiation and E-beam was employed to compare the degradation efficiency of multi-pollutants present in WWTP influent. It was found that E-beam was more efficient to eliminate the pharmaceuticals, and the treatment time was also reduced by 35 times when compared to gamma radiation process (Reinholds et al. 2017). The radiation-based AOPs are reported to be a cleaner process with no requirement of chemical addition; also, it is considered as an energy-effective process. However, there is limited information related to radiation-induced transformation products, toxicity, and its applicability in the field.

3.6.1 UV and UV/H_2O_2 Process

The UV process is widely used for disinfection. The UV and H_2O_2 process can be used individually to degrade trace contaminants. However, the spectrum of contaminants that can individually degrade UV and H_2O_2 is limited. The time taken for degradation can be quite long. Besides, the crucial factors governing the degradation kinetics of UV direct photolysis include the rate constant (k), molar extinction coefficient (Ɛ), and quantum yield (ϕ) (Luo et al. 2018). The combination of H_2O_2 and UV allows a fast and effective method to remove the contaminants. H_2O_2 and UV combined process leads to the generation of hydroxyl radicals as shown below (Eq. 6).

$$H_2O_2 + UV \rightarrow 2HO^{\bullet} \tag{6}$$

The degradation of sulfasalazine by direct UV (UV-C, 254 nm) photolysis was reported to be photostable, whereas its metabolites sulfapyridine and 5-aminosalicylic were degraded to a certain extent. The ϕ values for sulfapyridine and 5-aminosalicylic were 8.6×10^{-3} and 2.4×10^{-2} mol Einstein^{-1}, respectively. The combination of UV process with H_2O_2 and peroxydisulfate increased the degradation efficiency of sulfasalazine to 93.1 and 96.2%, respectively. However, it can be attributed to the formation of $HO^{\bullet}$ and $SO_4^{\bullet}$ (Ji et al. 2018). Amoxicillin was effectively degraded when UV photolysis was combined with 10 mM of H_2O_2 (Jung et al. 2012). The nonsteroidal anti-inflammatory drugs (carprofen, ketoprofen, and diclofenac) were degraded using the UV/H_2O_2 process. The authors reported higher degradation rate kinetics for carprofen ($1.54 \times 10^{-4}\ s^{-1}$) followed by ketoprofen ($5.9 \times 10^{-5}\ s^{-1}$), and diclofenac ($7.8 \times 10^{-6}\ s^{-1}$) (Li et al. 2017). The process efficiency of UV-C/H_2O_2 and UV/$S_2O_8^{2-}$ was compared in terms of the degradation of PhACs (carbamazepine, 17b-estradiol, 7a-ethinylestradiol, azithromycin, oxytetracycline, erythromycin, and dexamethasone) (Markic et al. 2018). The rate of degradation of PhACs was higher for UV/$S_2O_8^{2-}$ than for UV-C/H_2O_2. In contrast, a study by Perisic et al. (2016) compared the removal efficiency of two process UV/H_2O_2 and UV/TiO_2 for degradation of 29.62 mg/L of diclofenac. In the UV/H_2O_2 process, nearly complete degradation of diclofenac was observed in 2 min at an optimal concentration of H_2O_2 (16.8 mM). Besides, with 1.306 g/L concentration of TiO_2, the UV/TiO_2 took more than 2.5 h for complete degradation of the same concentration of diclofenac. The ε and ϕ values for sulfamethoxazole and ibuprofen were quantified by experimental and modeling approaches at two different pH (3 and 7.5) values (Luo et al. 2018). The ϕ values for sulfamethoxazole at pH 3 and 7.5 were 0.09 and 0.02 mol Einsten^{-1}, respectively, while for ibuprofen the values were 0.02 and 0.1 mol Einsten^{-1}, respectively. However, there were discrepancies in ε and ϕ values when compared with other literatures for the same compounds. It can be ascribed to the difference in experimental conditions such as geometry and volume of reactor, light source, etc. The key drawback of UV/H_2O_2 process is that the chemical oxidation of pollutants is controlled by the rate of hydroxyl radical formation, and with the wavelength above 250 nm, the process efficiency dramatically decreases (Legrini et al. 1993). In addition, it is important to maintain alkaline condition for better performance.

3.6.2 Photocatalysis

Photocatalysis is the method of producing reactive species by photochemical reaction, by irradiating the catalyst with a light source. If the photocatalyst and chemical reactant are not in the same phase, it is called heterogeneous photocatalysis. Among the various semiconducting photocatalysts, TiO_2 and ZnO are the more effective and extensively studied photocatalysts for the degradation of organic compounds (Topkaya et al., 2014). The band gap energies of TiO_2 (anatase) and ZnO are 3.2 eV and 3.4 eV, respectively; therefore, it needs UV radiation for excitation (Daghrir et al., 2013). When catalysts absorb light, the transition of electrons from the valence to the conduction band takes place and leaving holes behind the valence band. Both of these photogenerated electrons in the conduction band (e_{cb}^-) and holes in the valence band (h_{vb}^+) can undergo oxidation and reduction in aqueous solution and produce $HO^\bullet$ radicals. $HO^\bullet$ is produced due to the reaction between the holes left behind the valence band and water molecules adsorbed on the surface of the catalyst. Similarly, it reacts with molecular oxygen to produce superoxide radicals ($O_2^{\bullet -}$), which undergoes further reaction and forms $HO^\bullet$ radical (Nakata and Fujishima, 2012). Reactions occurring on the surface of TiO_2 can be written as follows (Eqs. 7–9):

$$\mathrm{TiO_2} + hv(< 380\,\mathrm{nm}) \rightarrow \mathrm{e_{cb}}^- + \mathrm{h_{vb}}^+) \tag{7}$$

$$\mathrm{h_{vb}}^+ + \mathrm{H_2O} \rightarrow \mathrm{HO}^\bullet + \mathrm{H}^+ \,(\mathrm{Oxidation}) \tag{8}$$

$$\mathrm{e_{cb}}^- + \mathrm{O_2} \rightarrow \mathrm{O_2}^\bullet \,(\mathrm{Reduction}). \tag{9}$$

Generation of reactive species in the presence of UV light on the surface of the photocatalyst is given in Fig. 2.

Many studies have investigated heterogeneous photocatalysis for degradation of PhACs, PPCPs, and EDCs (Carabin et al. 2015; Gmurek et al. 2017; Hama Aziz et al. 2017; Neghi and Kumar 2017). The photocatalysis based-AOPs hold a bright future in the field of water/wastewater treatment due to their enhanced degradation efficiency and cost-effective photocatalyst synthesis (Kanakaraju et al. 2014). Generally, the use of $\mathrm{TiO_2}$ as a catalyst is common for the degradation of ECs because of its cost-effective, abundant, nontoxic, photoreactive, and chemically and biologically inert nature (Friedmann et al. 2010). The photocatalytic degradation studies are majorly conducted with anti-inflammatory drugs and antiepileptic, antibiotic, analgesic, and lipid regulators because of their higher consumption rates and relevance to the environment (Zhu et al. 2013; Kanakaraju et al. 2015) (summarized in Table 1).

Studies related to photocatalysis often investigate the effect of operating conditions such as catalyst dose, light intensity, feed concentration, solution pH, water matrix, pharmaceutical degradation rate constant, and transformation products (Carbajo et al. 2016). Apart from these common parameters, sparging rate of gas, the effect of temperature, and a stirring speed of the feed solution were also studied.

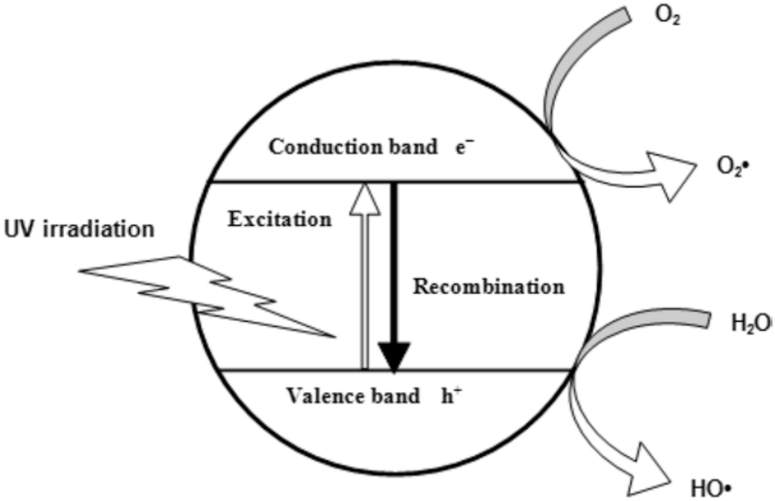

Fig. 2 Reaction mechanism of photocatalysis

Table 1 TiO_2 photocatalytic oxidation of PhACs

PhACs compounds	Water matrix	Irradiation source	Reactor	Inference	References
Carbamazepine	Distilled water	UVA lamps (wavelength, maximum of 365 nm; energy, 24W)	Batch reactor with stirring (volume: 200 mL)	The effect of operating parameters such as TiO_2 dose, TiO_2 types (P25, P90, PC500, UV100, and ST01), pH, light intensity, and treatment time. The optimum P90 TiO_2 dose for maximum degradation of carbamazepine (99%) was 1.5 g/L	Carabin et al. (2015)
Chlorhexidine	Ultrapure water	UVA lamp (10 W)	Batch slurry reactor (volume: 100 mL)	The maximum degradation of chlorhexidine (62.8%) occurred with TiO_2 dose of 200 mg/L within 60 min at alkaline pH (10.5). P25 performed better than TiO_2 pure anatase for mineralization of chlorhexidine	Das et al. (2014)
Acetaminophen	Deionized and tap water	UVA lamp (wavelength: 315–400 nm) UV irradiance: 75 W/m^2	Batch reactor (volume: 500 mL)	Deionized water Nearly complete acetaminophen degradation after 6 h >98% acetaminophen degradation by micro-sized K1077 TiO_2 catalyst The presence of inference ions impacted the mineralization of acetaminophen	Bianchi et al. (2017)
Ibuprofen and diclofenac	Aqueous solution	UVA lamps (wavelength, maximum of 350 nm; energy, 105 W)	Planar falling film (volume: 9.86L)	The combined photocatalytic ozonation AOPs enhanced ibuprofen degradation. The generation of more hydroxyl radicals promoted ibuprofen degradation	Hama Aziz et al. (2017)

(continued)

Table 1 (continued)

PhACs compounds	Water matrix	Irradiation source	Reactor	Inference	References
Metronidazole	Deionized water	UVC lamp (wavelength, 254 nm; power, 32 W)	Stirred batch reactor (volume: 1.9 L)	The removal rate of metronidazole was modeled using a first-order rate equation. The acute toxicity test of the samples from *Aliivibrio fischeri* was solely due to the suspended TiO_2 nanoparticles	Neghi and Kumar (2017)

It is generally accepted that the degradation rate of PhACs differs with the geometry and design of the photoreactor (Malato et al. 2009; Friedmann et al. 2010; Carbajo et al. 2016). A study by Van Doorslaer et al. (2012) investigated the effect of operating parameters such as TiO_2 dose, stirring speed, and varying gas sparging rates (oxygen, air, and nitrogen) on the degradation of moxifloxacin. The authors concluded that the degradation of moxifloxacin effectively occurred at ambient temperature, but the other operating parameters influenced degradation rates. The degradation rate constant of dicloxacillin (50 mg/L) was largely affected by the change in light power (30 and 150W). The rate of degradation of dicloxacillin was found to be more at natural pH, and the acidic (pH 3) or basic pH (7 or 9) inhibited the degradation.

The effect of operating parameters such as TiO_2 dose, type of TiO_2, initial feed concentration, solution pH, and water matrix was systematically examined for diclofenac mineralization. The authors concluded that the presence of ions and organic matter significantly affected the degradation rate of diclofenac. The variation in photocatalytic performance depends upon the catalyst properties such as morphology, structure, phase, porosity, surface area, electronics (i.e., band gap), charge, particle size distribution, and hydroxyl density on the surface (Carp et al. 2004; Carbajo et al. 2016).

The effect of water matrices on photocatalyst efficiency needs to be established for application in real-time wastewater treatment. The environmental matrices are loaded with organic matter and interference ions such as Cl^-, SO_4^-, NO_3^-, CO_3^-, and HCO_3^- which can be a potential radical scavenger. It has been previously reported that these interference ions can either inhibit or enhance the rate of PhACs degradation. The rate of degradation of methotrexate was found to increase with increasing concentration of HCO_3^- (20–400 mg/L) in the system owing to self-recombination and a large lifetime of CO_3^- compared to $OH^•$. It has been reported earlier that the presence of organic matter (i.e., humic or fluvic acid) in the system affects the TiO_2 photocatalytic process in two ways: (a) it can act as scavengers of reactive species generated by adsorbing to the catalyst surface or (b) it acts as a photosensitizer to enhance the photocatalytic activity. The degradation of CBZ increased in the presence of lower organic matter concentration (Drosos et al. 2015).

Another study reported that CBZ and the removal efficiency of its derivatives (carbamazepine epoxide, acridone, and acridine) enhanced when the system had a higher organic matter concentration (Haroune et al. 2014).

Improving TiO_2 efficiency from near-visible to visible region is essential as only 5% of solar irradiation falls within the UV (near-visible) range. This would have a significant impact on the application of this technology in the field of environmental protection (Khin et al. 2012). This can be achieved by doping of TiO_2 with metallic species (Ag, Fe, Co, Cu) or non-metallic elements (N, C, and S), photosensitizer, and composite semiconductor (ZnO) (Diwald et al. 2004; Ni et al. 2007). A study by Nasr et al. (2019) has shown that doping of TiO_2 with Au, Ag, and Pt enhances the photocatalytic activity of TiO_2 in the visible range. It can be due to electron trapping and increased interface charge transfer, which prevents recombination of electron-hole pairs (You et al. 2005; Pelaez et al. 2012). Moreover, doping of TiO_2 with non-metallic elements results in a shift of valence band gap edge. Therefore, the energy band gap of TiO_2 will be narrowed, which occurs due to the exchange of p states of elements with 2p states of O atoms PhACs (Ni et al. 2007; Gupta and Tripathi 2011). Recently several studies have come up with TiO_2 doped catalyst for photocatalytic degradation of PhACs (summarized in Table 2). The present data suggest that TiO_2 photocatalytic oxidation is a good choice of technology in the field of water/wastewater treatment. However, the data on multi-pollutant degradation system is limited as it may lead to additive, synergistic, or antagonistic effects. Also, the hybrid AOPs is a good option to improve the degradation efficiency of PhACs and reduce the toxicity of the system.

3.7 Coupling Membrane Process with Advanced Oxidation Process (AOPs)

The membrane filtration process are combined with various AOPs such as ozonation (Javier Benitez et al. 2009; Saquib et al. 2010; Real et al. 2012), Fenton oxidation, photo-assisted Fenton process (Westerhoff et al. 2009; Miralles-Cuevas et al. 2013), and photocatalysis (Mozia 2010; Chakraborty et al. 2017; Neghi et al. 2018; Molinari et al. 2019) as pre-treatment or post-treatment options. The combination of photocatalysis and membrane filtration is more scintillating, and it has gained immense attention due to many advantages such as catalyst recovery, concurrent photocatalytic degradation of contaminants, and membrane filtration, self-cleaning, anti-fouling resistance of membrane due to foulant degradation, and high applicability for commercial use (Ma et al. 2010; Ramasundaram et al. 2013).

The coupling of photocatalysis and membrane technology can be used as a pre-treatment or post-treatment option or hybrid/one-pot process. The post-treatment is considered in a slurry photocatalytic reactor wherein the photocatalyst is kept under suspension. The photocatalytic membrane reactors (PMRs) consist of either a hybrid photocatalytic reactor and a membrane unit or one-pot/single unit in a

Table 2 Photocatalytic degradation of PhACs using TiO_2-based nanocomposite catalyst

PhACs	Irradiation source	Nanocomposites	Inference	References
Acetaminophen	Solar stimulator (Xe lamp, 1 kW) UV lamp	A/TiO_2 Au/TiO_2 Pt/TiO_2	The maximum degradation efficiency of acetaminophen was observed with Pt/TiO_2. Enhanced mineralization of acetaminophen under solar light	Nasr et al. (2019)
Tetracycline	UV lamps (wavelength, maximum of 254 nm; intensity, 2500W/cm^2)	FeNi3/SiO2/ TiO_2	Nearly complete removal of tetracycline was achieved at an optimum initial concentration (10 mg/L), catalyst dose (5 mg/L), pH 9, and UV irradiation time of 200 min. -Possibility of recovery and reuse of the catalyst	Khodadadi et al. (2018)
Amoxicillin	Xe lamp with UV-C filter	Co-doped TiO_2	Maximum amoxicillin degradation (90%) was attained with 0.4% wt/v Co-doped TiO_2 nanocomposite. The photocatalytic degradation of amoxicillin was achieved within 240 min and 300 min under UV light and visible light, respectively	Çağlar Yılmaz et al. (2020)
Bisphenol A	UV source: mercury lamp (power: 400 W) Visible light source: halogen (power: 500 W)	PANI supported-Ag/ TiO_2	Under both UV and visible light, bisphenol A showed a maximum degradation of 99.8 % within 110 min irradiation. The efficiency of PANI-supported Ag/TiO_2 catalyst lasted for four repetitive cycles	Sambaza et al. (2019)
Diclofenac	UV lamp	TiO_2-SnO_2	The maximum degradation efficiency was attained at an optimum initial concentration (20 mg/L), catalyst dose (800 mg/L), and pH 5. The efficiency of the catalyst reduced to 17% after three repetitive cycles	Mugunthan et al. (2019)

(continued)

Table 2 (continued)

PhACs	Irradiation source	Nanocomposites	Inference	References
Ketoprofen	Medium-pressure Hg vapor lamp (wavelength: 254–546 nm)	Bi_2S_3/TiO_2 Montmorillonite	Nearly complete degradation of ketoprofen was achieved after 120 min irradiation and at pH 11. The degradation of ketoprofen followed pseudo-first-order kinetics	Djouadi et al. (2018)

chamber with or without photocatalytic membranes (PMs). The PMs can be either a free-standing photocatalyst or the photocatalyst supported on any substrate (Shan et al. 2010). Furthermore, the parameters considered for the selection of appropriate substrate for the synthesis of PMs include strong catalyst adherence, high abrasion and chemical resistance, and high stability for catalysts. The substrates employed for PMs preparation are polymer (Tahiri Alaoui et al. 2009), alumina (Ma et al. 2010), glass fiber (Liu et al. 2012), and stainless steel (Ramasundaram et al. 2013).

For a photocatalytic slurry system, the membrane process will serve as a single-step process for the recovery of catalysts from treated water. The main drawback of this configuration is the deterioration of membrane water permeability and fouling of the membrane. The solution to this problem might be the application of PMs. The oxidation by hydroxyl radicals ($^{\bullet}OH$) occurs in this configuration on the outer surface and inside the membrane pores, while reactants permeate in a one-pass flow (Georgi and Kopinke 2005; Ramasundaram et al. 2013). Moreover, studies have reported that the properties of catalyst such as self-cleansing and the performance of PMs are comparatively lower than that of suspended photocatalyst in the slurry system. It can be due to the lesser exposed surface area and short lifetime and diffusion length of $^{\bullet}OH$ (Mozia 2010; Shi et al. 2019). Besides, proper membrane selection, UV irradiation resistance, and hydroxyl radicals are needed (Chin et al. 2006; Chakraborty et al. 2017). The membrane may serve as a barrier for the transformation products formed after decomposition in both configurations, i.e., for photocatalyst in suspension or immobilized in or within the membrane (Molinari et al. 2002). This process strongly depends upon the membrane process used and its separating characteristics. During photocatalytic degradation of trace organics, typically smaller molecular weight compounds are formed. Therefore, ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) may only be considered as process capable of separating these substances in the case of pressure-driven membrane processes (Van der Bruggen et al. 2003).

The most common configurations of PMRs are depicted in Figure 3. Three reactors as shown in Fig. 3 (a–c) represent the photocatalytic slurry systems; the difference in the design is due to the position of irradiation source and can be classified as follows: (a) irradiation on top of the membrane module, (b) irradiation of the feed tank, (c) irradiation source situated in the separate additional reservoir, and (d) irradiation source positioned above the membrane with catalyst immobilized in or within the membrane (Mozia 2010) (Fig. 3d).

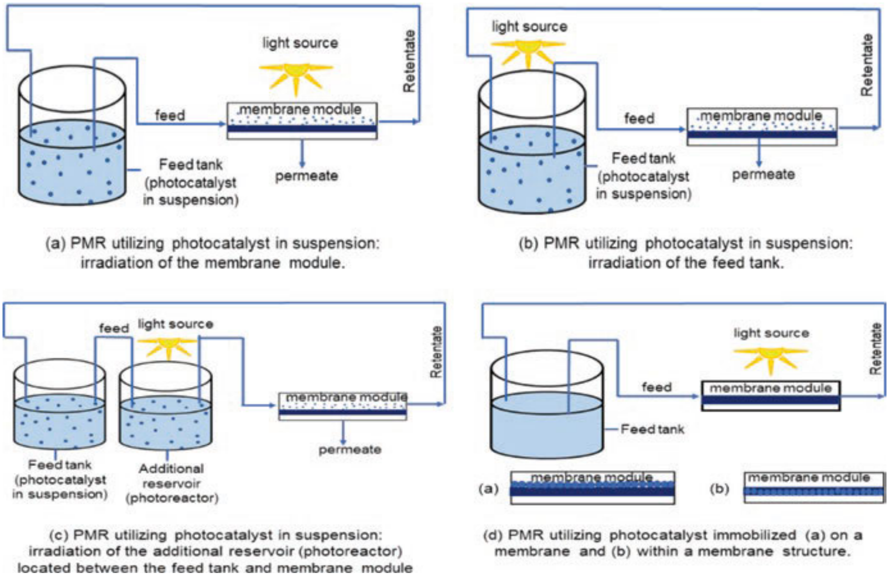

Fig. 3 The most common PMR configurations

The PMR design depends upon the mode of operation (dead-end filtration or cross-flow, batch or continuous), membrane process used (UF or NF), type of membrane modules employed (flat sheet, spiral, or hollow), or the nature of light source used.

3.7.1 Application of PMR for Concurrent Photodegradation and Membrane Filtration

A study was conducted by Chakraborty et al. (2017) on the development and testing of photocatalytic hollow fiber UF membranes to assess them for the degradation of organic compounds commonly found in pharmaceutical wastewater. Methylene blue (MB) and chlorhexidine digluconate (CHD) were used as model compounds in this study. The photocatalytic PES membranes (2% TiO_2) developed through sol-gel achieved a degradation of more than 30% and 40% of MB and CHD, respectively, showcasing the potential of coated UF membranes for the treatment of pharmaceutical wastewater. Bai et al. (2015) developed CNT/ZnO/TiO_2 nanocomposite CA UF membranes for concurrent photocatalytic degradation and filtration of acid orange 7 (AO7) dye. The modified nanocomposite membrane showed enhanced permeability, mechanical strength, anti-fouling propensity, and high photocatalytic activity. The photocatalytic oxidation tests for AO7 verified that the CNT/ZnO/TiO_2 nanocomposite membrane has a greater adsorption potential and achieved a faster rate of photodegradation than commercial P25.

The TiO_2/Al_2O_3 ceramic membranes were developed for simultaneous separation and photocatalytic degradation of dyes. The TiO_2 incorporation improved the membrane hydrophilicity, and a high and stable water flux was obtained for composite membranes under UV irradiation. The highest photocatalytic degradation efficiency of AO7 was noticed under acidic pH due to good adsorption properties (Mendret et al. 2013). A study by Liu et al. (2012) synthesized Ag/TiO_2 polyvinylpyrrolidone (PVP) nanofiber using an electrospinning technique for concurrent filtration and photocatalytic disinfection/degradation. The modified membrane showed high membrane water permeability. The solar photocatalytic disinfection against *Escherichia coli* (*E. coli*) K12 ER2925 and methylene blue (MB) dye degradation using Ag/TiO_2 nanofiber were 99.9% and 80%, respectively, with 30 min of irradiation.

Though proof of concept of concurrent filtration and photocatalytic degradation was demonstrated, this needs further development. It is important to optimize the catalyst coating protocol further to minimize the impact on membrane permeability (e.g., by controlling the pore size distribution of TiO_2 nanoparticles). However, it is also important to test the long-term stability of the coating and UV exposure. The factors affecting the efficiency of PMR, such as hydraulic retention time (HRT), light intensity, photocatalyst type and loading, pH, the presence of ions, etc. needs to be investigated. The maximum degradation of pollutants and their separation also need to be ensured.

4 Conclusions and Future Research Directions

With increasing water scarcity and water pollution, the demand for drinking water has tremendously increased all around the world, involving many developed countries and developing countries like India. Water and wastewater treatment can deal with the problems of water scarcity. Moreover, the water treated using conventional water treatment technologies hardly meet and satisfy potable water quality standards. Especially the complete removal of ECs (PhACs, PCPs, etc.) from the aqueous systems has never been achieved with conventional treatment processes. As a result, these ECs are present at higher median concentrations in the receiving environmental waters globally. However, with certain advanced treatment technologies like AOPs (ozonation, UV/H_2O_2, Fenton, electro-Fenton, electrochemical process, sonolysis, pulse power plasma, etc.), the removal of ECs from water and wastewater has been made possible with many kinds of research worldwide. One of the major concerns about the degradation of ECs by AOPs is the final oxidation products as remnants, as certain intermediate products may be more harmful than the original parent compound. Additionally, AOPs are energy-intensive, are expensive, and occasionally involve the addition of harsh chemicals (e.g., H_2O_2).

In recent times, photocatalysis has been gaining importance as it holds a great future due to its nonselective approach and high potential to mineralize ECs. However, the use of catalytic water treatment methods generates several toxic intermediates, and inorganic contaminants often escape along with the effluent. Thus, the pollutants tend to remain in the treated water, reducing the efficacy of the treatment process. Besides, the separation of catalyst from the treated water also possesses a major problem with its repeated use. On the other hand, advances in membrane technology could greatly help to handle the demand for clean water supplies. At present, UF, NF, and RO membranes have been in use extensively for the treatment of water and wastewater. The distinctive feature of membrane technology is its high technological flexibility, which provides space for combining it with photocatalytic treatment forming a good basis for the development of new/advanced water treatment processes. In this respect, an integrated process combining membrane technology and AOP may overcome all the issues mentioned above. The application of PMRs is a very promising approach for solving problems about the separation of the photocatalyst as well as photodecomposition by-products from the reaction mixture. The PMR process also minimizes membrane fouling as it involves the incorporation of the nanoparticles on the membrane surface, making it more hydrophilic and complementing the process by enhanced degradation of organic foulants. In this approach, it is important to redesign the membrane as a photocatalytic membrane, which serves dual purposes of support for the catalyst as well as the filtration process, thus providing unique multifunctional concurrent separation and photocatalytic degradation. However, the method of coating the photocatalyst on the membrane surface needs to be tested. Also, understanding of the factors affecting the efficiency of the PMR, such as HRT, light intensity, photocatalyst types and loading, pH, and the presence of ions and membrane stability to UV exposure, is limited. Moreover, the intermediates produced during the process of degradation are several times more toxic than the parent compounds. To confirm the mineralization of the compound, it is essential to carry out the ecotoxicity test on microorganisms. The toxicity of the parent compound and the by-products obtained during the treatment processes could be measured with the ecotoxicity assays, thereby suggesting the reliability of the treated water to be used for different beneficiary uses.

The performance of integrated PMR/RO to treat the secondary effluent needs to be investigated in terms of water quality, the toxicity of the treated water, and energy consumption for its application in real time.

References

Almomani FA, Shawaqfah M, Bhosale RR, Kumar A (2016) Removal of emerging pharmaceuticals from wastewater by ozone-based advanced oxidation processes. Environ Prog Sustain Energy 35:982–995. https://doi.org/10.1002/ep.12306

Andreozzi R, Canterino M, Marotta R, Paxeus N (2005) Antibiotic removal from wastewaters: The ozonation of amoxicillin. J Hazard Mater 122:243–250. https://doi.org/10.1016/j.jhazmat.2005.03.004

Axelstad M, Boberg J, Vinggaard AM et al (2013) Triclosan exposure reduces thyroxine levels in pregnant and lactating rat dams and in directly exposed offspring. Food Chem Toxicol 59:534–540. https://doi.org/10.1016/j.fct.2013.06.050

Ay F, Kargi F (2010) Advanced oxidation of amoxicillin by Fenton's reagent treatment. J Hazard Mater 179:622–627. https://doi.org/10.1016/j.jhazmat.2010.03.048

Bai H, Zan X, Zhang L, Sun DD (2015) Multi-functional CNT/ZnO/TiO2 nanocomposite membrane for concurrent filtration and photocatalytic degradation. Sep Purif Technol 156:922–930. https://doi.org/10.1016/J.SEPPUR.2015.10.016

Bianchi CL, Sacchi B, Pirola C et al (2017) Aspirin and paracetamol removal using a commercial micro-sized TiO2 catalyst in deionized and tap water. Environ Sci Pollut Res 24:12646–12654. https://doi.org/10.1007/s11356-016-7781-z

Çağlar Yılmaz H, Akgeyik E, Bougarrani S et al (2020) Photocatalytic degradation of amoxicillin using Co-doped TiO_2 synthesized by reflux method and monitoring of degradation products by LC–MS/MS. J Dispers Sci Technol 41:414–425. https://doi.org/10.1080/01932691.2019.1583576

Carabin A, Drogui P, Robert D (2015) Photo-degradation of carbamazepine using TiO2 suspended photocatalysts. J Taiwan Inst Chem Eng 54:109–117. https://doi.org/10.1016/j.jtice.2015.03.006

Carbajo J, Jiménez M, Miralles S et al (2016) Study of application of titania catalysts on solar photocatalysis: Influence of type of pollutants and water matrices. Chem Eng J 291:64–73. https://doi.org/10.1016/j.cej.2016.01.092

Carp O, Huisman CL, Reller A (2004) Photoinduced reactivity of titanium dioxide. Prog Solid State Chem 32:33–177

Chakraborty S, Loutatidou S, Palmisano G et al (2017) Photocatalytic hollow fiber membranes for the degradation of pharmaceutical compounds in wastewater. J Environ Chem Eng 5:5014–5024. https://doi.org/10.1016/j.jece.2017.09.038

Chin SS, Chiang K, Fane AG (2006) The stability of polymeric membranes in a TiO2 photocatalysis process. J Membr Sci 275:202–211. https://doi.org/10.1016/J.MEMSCI.2005.09.033

Daghrir R, Drogui P, Delegan N, El Khakani MA (2013) Electrochemical degradation of chlortetracycline using N-doped Ti/TiO2 photoanode under sunlight irradiations. Water Research, Elsevier Ltd, 47(17): 6801–6810

Dantas RF, Sans C, Esplugas S (2011) Ozonation of Propranolol: Transformation, Biodegradability, and Toxicity Assessment. J Environ Eng 137:754–759. https://doi.org/10.1061/(ASCE)EE.1943-7870.0000377

Das R, Sarkar S, Chakraborty S et al (2014) Remediation of antiseptic components in wastewater by photocatalysis using TiO2 nanoparticles. Ind Eng Chem Res 53:3012–3020. https://doi.org/10.1021/ie403817z

Daughton CG, Ternes TA (1999) Pharmaceuticals and personal care products in the environment: Agents of subtle change? Environ Health Perspect 107:907–938

De Bel E, Janssen C, De Smet S et al (2011) Sonolysis of ciprofloxacin in aqueous solution: Influence of operational parameters. Ultrason Sonochem 18:184–189. https://doi.org/10.1016/j.ultsonch.2010.05.003

Deblonde T, Cossu-Leguille C (2011) Emerging pollutants in wastewater: A review of the literature. Int J Hyg Environ Health 214:442–448. https://doi.org/10.1016/J.IJHEH.2011.08.002

Diwald O, Thompson TL, Zubkov T et al (2004) Photochemical activity of nitrogen-doped rutile TiO 2(110) in visible light. J Phys Chem B 108:6004–6008. https://doi.org/10.1021/jp031267y

Djouadi L, Khalaf H, Boukhatem H et al (2018) Degradation of aqueous ketoprofen by heterogeneous photocatalysis using Bi2S3/TiO2–Montmorillonite nanocomposites under simulated solar irradiation. Appl Clay Sci 166:27–37. https://doi.org/10.1016/j.clay.2018.09.008

Drosos M, Ren M, Frimmel FH (2015) The effect of NOM to TiO2: Interactions and photocatalytic behavior. Appl Catal Environ 165:328–334. https://doi.org/10.1016/j.apcatb.2014.10.017

Feng L, van Hullebusch ED, Rodrigo MA et al (2013) Removal of residual anti-inflammatory and analgesic pharmaceuticals from aqueous systems by electrochemical advanced oxidation processes. A review Chem Eng J 228:944–964

Ferrari B, Paxéus N, Giudice R. Lo, Pollio A, Garric J (2003) Ecotoxicological impact of pharmaceuticals found in treated wastewaters: study of carbamazepine, clofibric acid, and diclofenac. Ecotoxicol Environ Saf Elsevier, 55(3):359–370

Friedmann D, Mendive C, Bahnemann D (2010) TiO2 for water treatment: Parameters affecting the kinetics and mechanisms of photocatalysis. Appl Catal Environ 99:398–406. https://doi.org/10.1016/j.apcatb.2010.05.014

Garcia-Segura S, Ocon JD, Chong MN (2018) Electrochemical oxidation remediation of real wastewater effluents — A review. Process Saf Environ Prot 113:48–67

Georgi A, Kopinke FD (2005) Interaction of adsorption and catalytic reactions in water decontamination processes: Part I. Oxidation of organic contaminants with hydrogen peroxide catalyzed by activated carbon. Appl Catal Environ 58:9–18. https://doi.org/10.1016/j.apcatb.2004.11.014

Gerrity D, Stanford BD, Trenholm RA, Snyder SA (2010) An evaluation of a pilot-scale nonthermal plasma advanced oxidation process for trace organic compound degradation. Water Res 44:493–504. https://doi.org/10.1016/j.watres.2009.09.029

Ghassabian A, Bongers-Schokking JJ, Henrichs J et al (2011) Maternal thyroid function during pregnancy and behavioral problems in the offspring: The generation R study. Pediatr Res 69:454–459. https://doi.org/10.1203/PDR.0b013e3182125b0c

Giraldo-Aguirre AL, Serna-Galvis EA, Erazo-Erazo ED et al (2018) Removal of β-lactam antibiotics from pharmaceutical wastewaters using photo-Fenton process at near-neutral pH. Environ Sci Pollut Res 25:20293–20303. https://doi.org/10.1007/s11356-017-8420-z

Gmurek M, Olak-Kucharczyk M, Ledakowicz S (2017) Photochemical decomposition of endocrine disrupting compounds – A review. Chem Eng J 310:437–456

Gupta SM, Tripathi M (2011) A review of TiO2 nanoparticles. Chin Sci Bull 56:1639–1657

Güyer GT, Ince NH (2011) Degradation of diclofenac in water by homogeneous and heterogeneous sonolysis. Ultrason Sonochem 18:114–119. https://doi.org/10.1016/j.ultsonch.2010.03.008

Haddow JE, Palomaki GE, Allan WC et al (1999) Maternal thyroid deficiency during pregnancy and subsequent neuropsychological development of the child. N Engl J Med 341:549–555. https://doi.org/10.1056/NEJM199908193410801

Hama Aziz KH, Miessner H, Mueller S et al (2017) Degradation of pharmaceutical diclofenac and ibuprofen in aqueous solution, a direct comparison of ozonation, photocatalysis, and non-thermal plasma. Chem Eng J 313:1033–1041. https://doi.org/10.1016/j.cej.2016.10.137

Haroune L, Salaun M, Ménard A et al (2014) Photocatalytic degradation of carbamazepine and three derivatives using TiO2 and ZnO: Effect of pH, ionic strength, and natural organic matter. Sci Total Environ 475:16–22. https://doi.org/10.1016/j.scitotenv.2013.12.104

Heberer T, Mechlinski A, Fanck B et al (2004) Field Studies on the Fate and Transport of Pharmaceutical Residues in Bank Filtration. Groundw Monit Remediat 24:70–77. https://doi.org/10.1111/j.1745-6592.2004.tb00714.x

Holm JV, Rugge K, Bjerg PL, Christensen TH (1995) Occurrence and Distribution of Pharmaceutical Organic Compounds in the Groundwater Downgradient of a Landfill (Grindsted, Denmark). Environ Sci Technol 29:1415–1420. https://doi.org/10.1021/es00005a039

Hu R, Zhang L, Hu J (2016) Study on the kinetics and transformation products of salicylic acid in water via ozonation. Chemosphere 153:394–404. https://doi.org/10.1016/j.chemosphere.2016.03.074

Ikehata K, Jodeiri Naghashkar N, Gamal El-Din M (2006) Degradation of Aqueous Pharmaceuticals by Ozonation and Advanced Oxidation Processes: A Review. Ozone Sci Eng 28:353–414. https://doi.org/10.1080/01919510600985937

Ince NH (2018) Ultrasound-assisted advanced oxidation processes for water decontamination. Ultrason Sonochem 40:97–103. https://doi.org/10.1016/j.ultsonch.2017.04.009

Ishibashi H, Matsumura N, Hirano M et al (2004) Effects of triclosan on the early life stages and reproduction of medaka Oryzias latipes and induction of hepatic vitellogenin. Aquat Toxicol 67:167–179. https://doi.org/10.1016/j.aquatox.2003.12.005

Javier Benitez F, Acero JL, Real FJ, Garcia C (2009) Combination of chemical oxidation-membrane filtration processes for the elimination of phenyl-ureas in water matrices. J Chem Technol Biotechnol 84:1883–1893. https://doi.org/10.1002/jctb.2260

Ji Y, Yang Y, Zhou L et al (2018) Photodegradation of sulfasalazine and its human metabolites in water by UV and UV/peroxydisulfate processes. Water Res 133:299–309. https://doi.org/10.1016/j.watres.2018.01.047

Jjemba PK (2002) The effect of chloroquine, quinacrine, and metronidazole on both soybean plants and soil microbiota. Chemosphere 46:1019–1025. https://doi.org/10.1016/S0045-6535(01)00139-4

Joshi AA, Locke BR, Arce P, Finney WC (1995) Formation of hydroxyl radicals, hydrogen peroxide and aqueous electrons by pulsed streamer corona discharge in aqueous solution. J Hazard Mater 41:3–30. https://doi.org/10.1016/0304-3894(94)00099-3

Jung YJ, Kim WG, Yoon Y et al (2012) Removal of amoxicillin by UV and UV/H2O2 processes. Sci Total Environ 420:160–167. https://doi.org/10.1016/j.scitotenv.2011.12.011

Kanakaraju D, Glass BD, Oelgemöller M (2014) Titanium dioxide photocatalysis for pharmaceutical wastewater treatment. Environ Chem Lett 12:27–47

Kanakaraju D, Motti CA, Glass BD, Oelgemöller M (2015) TiO2 photocatalysis of naproxen: Effect of the water matrix, anions and diclofenac on degradation rates. Chemosphere 139:579–588. https://doi.org/10.1016/j.chemosphere.2015.07.070

Khin MM, Nair AS, Babu VJ et al (2012) A review on nanomaterials for environmental remediation. Energ Environ Sci 5:8075–8109

Khodadadi M, Ehrampoush MH, Ghaneian MT et al (2018) Synthesis and characterizations of FeNi3@SiO2@TiO2 nanocomposite and its application in photo- catalytic degradation of tetracycline in simulated wastewater. J Mol Liq 255:224–232. https://doi.org/10.1016/j.molliq.2017.11.137

Kıdak R, Doğan Ş (2018) Medium-high frequency ultrasound and ozone based advanced oxidation for amoxicillin removal in water. Ultrason Sonochem 40:131–139. https://doi.org/10.1016/j.ultsonch.2017.01.033

Kim Y, Choi K, Jung J, Park S, Kim PG, Park J (2007) Aquatic toxicity of acetaminophen, carbamazepine, cimetidine, diltiazem and six major sulfonamides, and their potential ecological risks in Korea. Environment International, Elsevier Ltd, 33(3):370–375

Klamerth N, Rizzo L, Malato S et al (2010) Degradation of fifteen emerging contaminants at μg L-1 initial concentrations by mild solar photo-Fenton in MWTP effluents. Water Res 44:545–554. https://doi.org/10.1016/j.watres.2009.09.059

Koeppe ES, Ferguson KK, Colacino JA, Meeker JD (2013) Relationship between urinary triclosan and paraben concentrations and serum thyroid measures in NHANES 2007-2008. Sci Total Environ 445–446:299–305. https://doi.org/10.1016/j.scitotenv.2012.12.052

Kolpin DW, Furlong ET, Meyer MT et al (2002) Pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999-2000: A national reconnaissance. Environ Sci Technol 36:1202–1211. https://doi.org/10.1021/es011055j

Krause H, Schweiger B, Schuhmacher J et al (2009) Degradation of the endocrine disrupting chemicals (EDCs) carbamazepine, clofibric acid, and iopromide by corona discharge over water. Chemosphere 75:163–168. https://doi.org/10.1016/j.chemosphere.2008.12.020

Kümmerer K (2001) Drugs in the environment: Emission of drugs, diagnostic aids and disinfectants into wastewater by hospitals in relation to other sources - A review. Chemosphere 45:957–969. https://doi.org/10.1016/S0045-6535(01)00144-8

Lanzky PF, Halling-Sørensen B (1997) The toxic effect of the antibiotic metronidazole on aquatic organisms. Chemosphere 35:2553–2561. https://doi.org/10.1016/S0045-6535(97)00324-X

Lapworth DJ, Baran N, Stuart ME, Ward RS (2012) Emerging organic contaminants in groundwater: A review of sources, fate and occurrence. Environ Pollut 163:287–303

Lau AH, Lam NP, Piscitelli SC et al (1992) Clinical Pharmacokinetics of Metronidazole and Other Nitroimidazole Anti-Infectives. Clin Pharmacokinet 23:328–364

Legrini O, Oliveros E, Braun AM (1993) Photochemical Processes for Water Treatment. Chem Rev 93:671–698. https://doi.org/10.1021/cr00018a003

Li W, Nanaboina V, Zhou Q, Korshin GV (2012) Effects of Fenton treatment on the properties of effluent organic matter and their relationships with the degradation of pharmaceuticals and personal care products. Water Res 46:403–412. https://doi.org/10.1016/j.watres.2011.11.002

Li J, Ma LY, Li LS, Xu L (2017) Photodegradation kinetics, transformation, and toxicity prediction of ketoprofen, carprofen, and diclofenac acid in aqueous solutions. Environ Toxicol Chem 36:3232–3239. https://doi.org/10.1002/etc.3915

Lianou A, Frontistis Z, Chatzisymeon E et al (2018) Sonochemical oxidation of piroxicam drug: effect of key operating parameters and degradation pathways. J Chem Technol Biotechnol 93:28–34. https://doi.org/10.1002/jctb.5346

Liu L, Liu Z, Bai H, Sun DD (2012) Concurrent filtration and solar photocatalytic disinfection/degradation using high-performance Ag/TiO2 nanofiber membrane. Water Res 46:1101–1112. https://doi.org/10.1016/j.watres.2011.12.009

Liu N, Lei ZD, Wang T et al (2016) Radiolysis of carbamazepine aqueous solution using electron beam irradiation combining with hydrogen peroxide: Efficiency and mechanism. Chem Eng J 295:484–493. https://doi.org/10.1016/j.cej.2016.03.040

Liu Z, Hosseinzadeh S, Wardenier N et al (2019) Combining ozone with UV and H2O2 for the degradation of micropollutants from different origins: lab-scale analysis and optimization. Environ Technol (United Kingdom) 40:3773–3782. https://doi.org/10.1080/09593330.2018.1491630

Loos G, Scheers T, Van Eyck K et al (2018) Electrochemical oxidation of key pharmaceuticals using a boron doped diamond electrode. Sep Purif Technol 195:184–191. https://doi.org/10.1016/j.seppur.2017.12.009

Louis GW, Hallinger DR, Braxton MJ et al (2017) Effects of chronic exposure to triclosan on reproductive and thyroid endpoints in the adult Wistar female rat. J Toxicol Environ Heal - Part A Curr Issues 80:236–249. https://doi.org/10.1080/15287394.2017.1287029

Luo S, Wei Z, Spinney R et al (2018) UV direct photolysis of sulfamethoxazole and ibuprofen: An experimental and modelling study. J Hazard Mater 343:132–139. https://doi.org/10.1016/j.jhazmat.2017.09.019

Ma N, Zhang Y, Quan X et al (2010) Performing a microfiltration integrated with photocatalysis using an Ag-TiO2/HAP/Al2O3 composite membrane for water treatment: Evaluating effectiveness for humic acid removal and anti-fouling properties. Water Res 44:6104–6114. https://doi.org/10.1016/j.watres.2010.06.068

Magureanu M, Piroi D, Mandache NB et al (2011) Degradation of antibiotics in water by non-thermal plasma treatment. Water Res 45:3407–3416. https://doi.org/10.1016/j.watres.2011.03.057

Malato S, Fernández-Ibáñez P, Maldonado MI et al (2009) Decontamination and disinfection of water by solar photocatalysis: Recent overview and trends. Catal Today 147:1–59

Markic M, Cvetnic M, Ukic S et al (2018) Influence of process parameters on the effectiveness of photooxidative treatment of pharmaceuticals. J Environ Sci Heal Part A 53:338–351. https://doi.org/10.1080/10934529.2017.1401394

Márquez G, Rodríguez EM, Beltrán FJ, Álvarez PM (2014) Solar photocatalytic ozonation of a mixture of pharmaceutical compounds in water. Chemosphere 113:71–78. https://doi.org/10.1016/j.chemosphere.2014.03.093

Méndez-Arriaga F, Torres-Palma RA, Pétrier C et al (2008) Ultrasonic treatment of water contaminated with ibuprofen. Water Res 42:4243–4248. https://doi.org/10.1016/j.watres.2008.05.033

Mendret J, Hatat-Fraile M, Rivallin M, Brosillon S (2013) Hydrophilic composite membranes for simultaneous separation and photocatalytic degradation of organic pollutants. Sep Purif Technol 111:9–19. https://doi.org/10.1016/j.seppur.2013.03.030

Miralles-Cuevas S, Arqués A, Maldonado MI et al (2013) Combined nanofiltration and photo-Fenton treatment of water containing micropollutants. Chem Eng J 224:89–95. https://doi.org/10.1016/j.cej.2012.09.068

Molinari R, Borgese M, Drioli E et al (2002) Hybrid processes coupling photocatalysis and membranes for degradation of organic pollutants in water. Catalysis Today. Elsevier, In, pp 77–85

Molinari R, Lavorato C, Argurio P et al (2019) Overview of Photocatalytic Membrane Reactors in Organic Synthesis, Energy Storage and Environmental Applications. Catalysts 9:239. https://doi.org/10.3390/catal9030239

Mozia S (2010) Photocatalytic membrane reactors (PMRs) in water and wastewater treatment. A review Sep Purif Technol 73:71–91. https://doi.org/10.1016/J.SEPPUR.2010.03.021

Mugunthan E, Saidutta MB, Jagadeeshbabu PE (2019) Photocatalytic degradation of diclofenac using TiO_2–SnO_2 mixed oxide catalysts. Environ Technol 40:929–941. https://doi.org/10.1080/09593330.2017.1411398

Naddeo V, Landi M, Scannapieco D, Belgiorno V (2013) Sonochemical degradation of twenty-three emerging contaminants in urban wastewater. Desalin Water Treat 51:6601–6608. https://doi.org/10.1080/19443994.2013.769696

Nakata K, Fujishima A (2012) TiO2 photocatalysis: Design and applications. Journal of Photochemistry and Photobiology C: Photochemistry Reviews, Elsevier, 13(3):169–189

Nasr O, Mohamed O, Al-Shirbini AS, Abdel-Wahab AM (2019) Photocatalytic degradation of acetaminophen over Ag, Au and Pt loaded TiO 2 using solar light. J Photochem Photobiol A Chem 374:185–193. https://doi.org/10.1016/j.jphotochem.2019.01.032

Neghi N, Kumar M (2017) Performance Analysis of Photolytic, Photocatalytic, and Adsorption Systems in the Degradation of Metronidazole on the Perspective of Removal Rate and Energy Consumption. Water Air Soil Pollut 228:339. https://doi.org/10.1007/s11270-017-3532-0

Neghi N, Krishnan NR, Kumar M (2018) Analysis of metronidazole removal and micro-toxicity in photolytic systems: Effects of persulfate dosage, anions and reactor operation-mode. J Environ Chem Eng 6:754–761. https://doi.org/10.1016/j.jece.2017.12.072

Ni M, Leung MKH, Leung DYC, Sumathy K (2007) A review and recent developments in photocatalytic water-splitting using TiO2 for hydrogen production. Renew Sustain Energy Rev 11:401–425

Parolini M, Quinn B, Binelli A, Provini A (2011) Cytotoxicity assessment of four pharmaceutical compounds on the zebra mussel (Dreissena polymorpha) haemocytes, gill and digestive gland primary cell cultures. Chemosphere 84:91–100. https://doi.org/10.1016/j.chemosphere.2011.02.049

Pedersen JA, Soliman M, Suffet IH (2005) Human pharmaceuticals, hormones, and personal care product ingredients in runoff from agricultural fields irrigated with treated wastewater. J Agric Food Chem 53:1625–1632. https://doi.org/10.1021/jf049228m

Pelaez M, Nolan NT, Pillai SC et al (2012) A review on the visible light active titanium dioxide photocatalysts for environmental applications. Appl Catal Environ 125:331–349

Perisic DJ, Kovacic M, Kusic H et al (2016) Comparative analysis of UV-C/H2O2 and UV-A/TiO2 processes for the degradation of diclofenac in water. React Kinet Mech Catal 118:451–462. https://doi.org/10.1007/s11144-016-1027-4

Prieto-Rodriguez L, Miralles-Cuevas S, Oller I et al (2012) Treatment of emerging contaminants in wastewater treatment plants (WWTP) effluents by solar photocatalysis using low TiO2 concentrations. J Hazard Mater 211:131–137

Ramasundaram S, Yoo HN, Song KG et al (2013) Titanium dioxide nanofibers integrated stainless steel filter for photocatalytic degradation of pharmaceutical compounds. J Hazard Mater 258–259:124–132. https://doi.org/10.1016/j.jhazmat.2013.04.047

Raut SA, Angus RA (2010) Triclosan has endocrine-disrupting effects in male western mosquitofish, Gambusia affinis. Environ Toxicol Chem 29:n/a. https://doi.org/10.1002/etc.150

Rayaroth MP, Aravind UK, Aravindakumar CT (2016) Degradation of pharmaceuticals by ultrasound-based advanced oxidation process. Environ Chem Lett 14:259–290

Real FJ, Benitez FJ, Acero JL, Roldan G (2012) Combined chemical oxidation and membrane filtration techniques applied to the removal of some selected pharmaceuticals from water systems. J Environ Sci Heal - Part A Toxic/Hazardous Subst Environ Eng 47:522–533. https://doi.org/10.1080/10934529.2012.650549

Reinholds I, Pugajeva I, Perkons I et al (2017) Decomposition of multi-class pharmaceutical residues in wastewater by exposure to ionising radiation. Int J Environ Sci Technol 14:1969–1980. https://doi.org/10.1007/s13762-017-1290-6

Sambaza S, Maity A, Pillay K (2019) Enhanced degradation of BPA in water by PANI supported Ag/TiO 2 nanocomposite under UV and visible light. J Environ Chem Eng 7:102880. https://doi.org/10.1016/j.jece.2019.102880

Sanderson H, Brain RA, Johnson DJ et al (2004) Toxicity classification and evaluation of four pharmaceuticals classes: antibiotics, antineoplastics, cardiovascular, and sex hormones. Toxicology 203:27–40. https://doi.org/10.1016/j.tox.2004.05.015

Santos LHMLM, Araújo AN, Fachini A et al (2010) Ecotoxicological aspects related to the presence of pharmaceuticals in the aquatic environment. J Hazard Mater 175:45–95. https://doi.org/10.1016/j.jhazmat.2009.10.100

Saquib M, Vinckier C, van der Bruggen B (2010) The effect of UF on the efficiency of O3/H2O2 for the removal of organics from surface water. Desalination 260:39–42. https://doi.org/10.1016/j.desal.2010.05.003

Shan AY, Ghazi TIM, Rashid SA (2010) Immobilisation of titanium dioxide onto supporting materials in heterogeneous photocatalysis: A review. Appl Catal Gen 389:1–8

Shi Y, Huang J, Zeng G et al (2019) Photocatalytic membrane in water purification: is it stepping closer to be driven by visible light? J Membr Sci 584:364–392

Sirés I, Brillas E (2012) Remediation of water pollution caused by pharmaceutical residues based on electrochemical separation and degradation technologies: A review. Environ Int 40:212–229. https://doi.org/10.1016/J.ENVINT.2011.07.012

Stackelberg PE, Furlong ET, Meyer MT et al (2004) Persistence of pharmaceutical compounds and other organic wastewater contaminants in a conventional drinking-water-treatment plant. Sci Total Environ 329:99–113. https://doi.org/10.1016/j.scitotenv.2004.03.015

Stuart M, Lapworth D, Crane E, Hart A (2012) Review of risk from potential emerging contaminants in UK groundwater. Sci Total Environ 416:1–21

Sui Q, Huang J, Lu S et al (2014) Removal of pharmaceutical and personal care products by sequential ultraviolet and ozonation process in a full-scale wastewater treatment plant. Front Environ Sci Eng 8:62–68. https://doi.org/10.1007/s11783-013-0518-z

Sun B, Sato M, Clements JS (1999) Use of a pulsed high-voltage discharge for removal of organic compounds in aqueous solution

Swartz HC, Reddy S, Benotti JM et al (2006) Steroid Estrogens, Nonylphenol Ethoxylate Metabolites, and Other Wastewater Contaminants in Groundwater Affected by a Residential Septic System on Cape Cod, MA. Environ Sci Technol. https://doi.org/10.1021/ES052595+

Tahiri Alaoui O, Nguyen QT, Mbareck C, Rhlalou T (2009) Elaboration and study of poly(vinylidene fluoride)-anatase TiO2 composite membranes in photocatalytic degradation of dyes. Appl Catal Gen 358:13–20. https://doi.org/10.1016/j.apcata.2009.01.032

Tiwari B, Sellamuthu B, Ouarda Y et al (2017) Review on fate and mechanism of removal of pharmaceutical pollutants from wastewater using biological approach. Bioresour Technol 224:1–12

Topkaya E, Konyar M, Yatmaz HC, Öztürk K (2014) Pure ZnO and composite ZnO/TiO2 catalyst plates: A comparative study for the degradation of azo dye, pesticide and antibiotic in aqueous solutions. J Colloid Interface Sci, Elsevier, 430:6–11

Van der Bruggen B, Vandecasteele C, Van Gestel T et al (2003) A review of pressure-driven membrane processes in wastewater treatment and drinking water production. Environ Prog 22:46–56. https://doi.org/10.1002/ep.670220116

Van Doorslaer X, Heynderickx PM, Demeestere K et al (2012) TiO 2 mediated heterogeneous photocatalytic degradation of moxifloxacin: Operational variables and scavenger study. Appl Catal Environ 111–112:150–156. https://doi.org/10.1016/j.apcatb.2011.09.029

Verstraeten IM, Fetterman GS, Meyer MT et al (2005) Use of tracers and isotopes to evaluate vulnerability of water in domestic wells to septic waste. Groundw Monit Remediat 25:107–117. https://doi.org/10.1111/j.1745-6592.2005.0015.x

Wallace JL, Vahadi B, Fernandes JB, Boyden BH (1987) The Combination of Ozone/Hydrogen Peroxide and Ozone/UV Radiation for Reduction of Trihalomethane Formation Potential in Surface Water. Ozone Sci Eng 10:103–112. https://doi.org/10.1080/01919518808552509

Wang J, Chu L (2016) Irradiation treatment of pharmaceutical and personal care products (PPCPs) in water and wastewater: An overview. Radiat Phys Chem 125:56–64

Wang CF, Tian Y (2015) Reproductive endocrine-disrupting effects of triclosan: Population exposure, present evidence and potential mechanisms. Environ Pollut 206:195–201

Wang S, Wang J (2018) Degradation of carbamazepine by radiation-induced activation of peroxymonosulfate. Chem Eng J 336:595–601. https://doi.org/10.1016/j.cej.2017.12.068

Wang Y, Zhang H, Zhang J et al (2011) Degradation of tetracycline in aqueous media by ozonation in an internal loop-lift reactor. J Hazard Mater 192:35–43. https://doi.org/10.1016/j.jhazmat.2011.04.086

Weatherly LM, Gosse JA (2017) Triclosan exposure, transformation, and human health effects. J. Toxicol. Environ Heal - Part B Crit Rev 20:447–469

Westerhoff P, Moon H, Minakata D, Crittenden J (2009) Oxidation of organics in retentates from reverse osmosis wastewater reuse facilities. Water Res 43:3992–3998. https://doi.org/10.1016/j.watres.2009.04.010

Yahya MS, El Karbane M, Oturan N et al (2016) Mineralization of the antibiotic levofloxacin in aqueous medium by electro-Fenton process: kinetics and intermediate products analysis. Environ Technol 37:1276–1287. https://doi.org/10.1080/09593330.2015.1111427

You X, Chen F, Zhang J, Anpo M (2005) A novel deposition precipitation method for preparation of Ag-loaded titanium dioxide. Catal Lett 102:247–250. https://doi.org/10.1007/s10562-005-5863-5

Zhao Y, Kuang J, Zhang S et al (2017) Ozonation of indomethacin: Kinetics, mechanisms and toxicity. J Hazard Mater 323:460–470. https://doi.org/10.1016/j.jhazmat.2016.05.023

Zhu XD, Wang YJ, Sun RJ, Zhou DM (2013) Photocatalytic degradation of tetracycline in aqueous solution by nanosized TiO2. Chemosphere 92:925–932. https://doi.org/10.1016/j.chemosphere.2013.02.066

Advanced Treatment Technologies to Combat Antibiotic-Resistant Bacteria and Antibiotic Resistance Genes from Urban Wastewater

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Abstract According to the World Health Organization, antibiotic resistance is one of the major global threats to human health and the environment. Urban wastewater treatment plants are identified as a hotspot for the occurrence and dissemination of antibiotic-resistant bacteria (ARB) and antibiotic resistance genes (ARGs) to the environment. Advanced wastewater treatment processes are considered to be the vital step to control the spread of ARB and ARGs for the reclaimed water reuse applications or their release into the environment. This chapter reviews the various advanced treatment strategies that can be adapted to combat the ARB and ARGs in urban wastewater. Advanced oxidation processes (AOPs) are considered to be promising processes to treat a wide range of contaminants through the production of highly active reactive oxygen species. The ability of various AOPs such as Fenton, photocatalysis, UV-driven oxidation along with H_2O_2 and ozonation on the removal of ARB and ARGs in urban wastewater is discussed. The influence of operational

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parameters and the mechanism of inactivation of ARB and ARGs are discussed. The removal efficacy of ARB and ARGs through membrane bioreactor and constructed wetland is also presented. Furthermore, the application of nanomaterials in controlling the dissemination of antibiotic resistance in the environment is elaborated.

Keywords Antibiotic-resistant bacteria · Antibiotic resistance genes · Removal mechanism · Advanced oxidation process · Constructed wetland · Nanomaterials

1 Introduction

Overuse of antibiotics in humans and livestocks end up contaminating the environment continuously. The development of antimicrobial resistance (AMR) in the environment is a severe public health crisis since it potentially diminishes the therapeutic usage of antimicrobial drugs against preventing the diseases (Pruden et al. 2006; Pruden 2014; Sivagami et al. 2018). Antibiotics act as a selective pressure to develop resistance in bacteria in connection with a specific category of antibiotics. Long-term exposure increases the threat of developing multiple drug resistance (MDR) in bacteria (Amador et al. 2015). Antibiotic resistance is acquired through spontaneous mutations, horizontal gene transfer of ARGs from donor bacteria, virus or free ARGs from the environment to host bacteria and could also be intrinsic in nature (Pruden et al. 2006; Barancheshme and Munir 2018). Urban wastewater and wastewater treatment plants (WWTPs) are considered as the major hot spot for the propagation since they accumulate the microbes of various origins such as environment, human and animals (Aali et al. 2014; Manaia et al. 2018). The release of partially treated and untreated wastewater to the environment containing antibiotics, ARGs and ARB is considered a potential threat to humans and other lives for disseminating antibiotic resistance (Aali et al. 2014; Pazda et al. 2019). Antibiotics are grouped into various categories such as sulfonamides, fluoroquinolones, macrolides, β-lactams, aminoglycosides, penicillins and arsenicals, and the resistances in bacteria are developed towards single or multiple antibiotics (Xu et al. 2015). The WHO announced antibiotic resistance as the greatest threat to human lives and listed it as ‘priority pathogens’. About 250,000 people are being killed by drug-resistant tuberculosis yearly (WHO 2017). Death due to antimicrobial resistance in Europe and the USA is about 25,000 and 23,000 per year (WHO 2014). The cost of hospitalization of people infected with MRD bacteria in the USA alone is $ 2.2 billion annually based on 2014 data, whereas it is EUR 1.5 billion in Europe (Thorpe et al. 2018; Pazda et al. 2019). Apart from that, a huge quantity of antibiotics is used in livestock industries to prevent diseases and enhance growth. China alone uses 46% of produced antibiotics, representing 210,000 tons for animal farming (Founou et al. 2016).

Various ARGs and ARB are being reported in urban wastewater worldwide. ARGs identified in various water and wastewater include sulfonamide (*sul*), tetracycline (*tet*), fluoroquinolone (*qnr*), colistin (*mcr*), β-lactam (*bla*), methicillin (*mec*), macrolide (*erm*) and chloramphenicol (*cml*, *flo*) (Pruden 2014; Amarasiri et al.

2019; Cacace et al. 2019). The mean concentrations of ARB in raw municipal and hospital wastewater samples were reported up to 1.24×10^7 CFU/100 ml for gentamicin, 3.29×10^7 CFU/100 ml for chloramphenicol and 5.54×10^7 for CFU/100 ml ceftazidime (Aali et al. 2014). The presence of ARG copies per cell in untreated sewage was reported to be 1.93, whereas it is estimated to be 5.94 for faecal samples, 0.2 for activated sludge and 0.44 for WWTP effluents (Li et al. 2015; Hendriksen et al. 2019; Yin et al. 2019). The genetic biomarker element for tracking antibiotic resistance is reported to be the class 1 integron (*int1*) gene (Cacace et al. 2019). Dominant ARGs in the water and wastewater samples are bla_{TEM}, *tetA* and *sul1* (Aali et al. 2014). The presence of antibiotic resistance genetic elements such as *ermB*, *sul1*, *sul2*, *tetW* and *int1* was reported in river water and sediment samples that receive the treated effluents of WWTP treating mixture of domestic (78%) and industrial (22%) wastewaters (Sabri et al. 2020). Sulfonamide resistance genes (*sul1*) were identified in the concentration range of 3.16×10^3 to 3.16×10^6 copies/g in the sediment samples, whereas the genes in the river water samples were identified in the range from 1.00×10^3 up to 1.00×10^6 copies/L. The presence of ARGs was found to be up to 20 km downstream of receiving waterbodies (Sabri et al. 2020). Further, the concentration of ARGs and ARB in hospital wastewater is found to be 3–4 folds higher than domestic wastewater (WHO 2014). Hence, treatment of wastewaters plays an important role in mitigating the dissemination of antibiotic resistance to the environment. This chapter reviews various treatment strategies, their removal efficiencies and the influence of operating parameters on removing ARGs and ARB. Treatment processes that are considered in this chapter include chlorination, ozonation, advanced oxidation processes (Fenton-related processes, UV-related processes, photocatalysis, electrochemical oxidation), biological and natural processes (membrane bioreactor/sequential bioreactors, constructed wetlands) and application of nanomaterials.

2 Development of Antibiotic Resistance in Wastewater

Wastewater from households, hospital and pharmaceutical industries are reservoirs of antibiotics, ARB and ARG. Antibiotic concentrations, ARB and ARGs vary depending on the source of wastewater (Sasikaladevi et al. 2020). Antibiotics at concentrations above the minimum inhibitory concentration levels are known to select ARB (Drlica 2003). However, antibiotics at sub-lethal concentration induce resistance in non-resistant bacteria (Gullberg et al. 2011). Also, repeated exposure to antibiotics at sub-lethal concentrations could force non-resistant bacteria to acquire resistance in wastewater (Sandegren 2014). Antibiotics at sub-lethal concentrations promote genetic recombination and horizontal resistance gene transfer (HGT) and supposedly activate integrating elements enabling resistance dissemination (Gullberg et al. 2011). Bacteria acquiring resistance due to selection pressure at low antibiotic concentration are highly stable (Andersson and Hughes 2012). On the other hand, excessive use and disposal of antibiotics could induce mutation in ARG

(Kurasam et al. 2018). The mutation rates in ARGs vary depending on the concentration of antibiotics (Köhler et al. 1997). Mutation in ARG is often referred to as vertical evolution and this trait can be passed on to subsequent generations (Martinez and Baquero 2000).

ARB could acquire and transfer resistance both vertically and horizontally. Vertical gene transfer is a resistance gene transfer to progeny. Conjugation, transduction, gene transfer agents and transformation mechanisms enable HGT (Barancheshme and Munir 2018). HGT mechanism is mediated by mobile genetic elements (MGEs), namely, conjugative plasmids, transposons, conjugative transposons and integrons (Hegstad et al. 2010). MGEs carry accessory genes such as ARG (Frost et al. 2005). Resistance gene acquisition through MGE could result in MDR (Li et al. 2019a). The ability of bacteria to confer resistance is encoded in the resistance-determining regions (RDR). Antibiotic selection pressure could induce mutation in RDR, which could result in cross-resistance to other antibiotics (Kurasam et al. 2018). Depending on the types of mutations (synonymous, non-synonymous and non-sense mutation), drug resistance response is altered (Minarini and Darini 2012). A strong correlation was demonstrated between RDR and ARG expression in environmental bacteria (Lamba et al. 2018).

Metals are widely reported to induce and disseminate antibiotic resistance by means of co-selection (Baker-Austin et al. 2006). ARGs and metal resistance genes often co-occur and are genetically linked (Baker-Austin et al. 2006; Li et al. 2017a). MGEs also play an important role in co-selection (Barancheshme and Munir 2018). Co-selection of antibiotics and metal-resistant bacteria involves three major mechanisms, namely, co-resistance, co-regulation and cross-resistance (Baker-Austin et al. 2006). The mechanisms can be explained as follows: (i) Co-resistance is possible by gene coupling where two or more genes confer resistance to both metal and antibiotics. These genes are located on MGEs that enable easy dissemination. (ii) Co-regulation mechanism regulates expression of the genes conferring antibiotics and metal resistance. (iii) Cross-resistance trait confers resistance to more than two antibiotics and metal. Di Cesare et al. (2016) observed co-resistance, co-regulation, co-regulation and co-occurrence of integrase 1 (MGE), antibiotics and heavy metal resistance genes in wastewater. This suggests the influence of unrelated factors on antibiotic resistance development and dissemination in wastewater environment.

3 Advanced Treatment Strategies

Various treatment strategies including chemical, photochemical and electrochemical processes, membrane filtration, biological reactors, constructed wetlands and applications of nanomaterials and their removal efficiencies and the influence of operating parameters on the removal of ARGs and ARB are discussed in the following sections.

3.1 Chemical, Photochemical and Electrochemical Processes

Treatment processes for the removal of ARB and ARGs include chlorination, coagulation, ozonation and advanced oxidation processes (Fenton-related processes, UV-related processes, photocatalysis, electrochemical oxidation and others).

3.1.1 Chlorination

Chlorine available in the form of HOCl, OCl^- and Cl_2 in aqueous medium is a non-selective oxidant (Shang and Blatchley 1999). Non-selective interactions with cell wall and cell components impart metabolic activities (Nybo et al. 2019). This interaction results in oxidative cell wall damage and release of cellular components such as proteins, DNA and RNA, thus inactivating the bacteria (Venkobachar et al. 1977). Similar interaction mechanism can be assumed for ARB disinfection with chlorine. However, a high dose of chlorine is required for leakage of DNA (Venkobachar et al. 1977). HOCl interacts with amino group of pyrimidine and purine bases of the nucleotides in the DNA (Hoyano et al. 1973). The interaction is a slow process but effective denaturation of native DNA is possible (Prütz 1996). In the case of a double-stranded DNA, rather less reactivity of HOCl is reported (Prütz 1996). Yoon et al. (Yoon et al. 2017) suggested bactericidal activity of chlorine resulting in cell wall damage followed by plasmid ARG damage and non-specific DNA damage in ARB. Inactivation of ARB and ARG removal with chlorine is widely studied. Yuan et al. observed a significant reduction of nine heterotrophic ARBs after chlorination (Yuan et al. 2015). However, ARBs resistant to sulfadiazine and erythromycin showed tolerance to low Cl_2 concentration and were not removed even at chlorine concentrations 60 and 150 mg Cl_2 min/L, respectively (Yuan et al. 2015). Huang et al. (Huang et al. 2011) observed the regrowth of ARB after chlorination. Chlorination has also been reported to select ARB and induce resistance (Huang et al. 2013; Pang et al. 2016). Yuan et al. and Zhang et al. (Yuan et al. 2015; Zhang et al. 2015) observed low ARG removal with low chlorine dosages. Moreover, the transforming ability of DNA remained intact even after complete cell inactivation (Dodd 2012). Certain ARGs were not removed by chlorination (Yuan et al. 2015). However, high ARG removal has been observed at chlorine dosage 30–45 mg Cl_2 min/L (Zhang et al. 2015; Yoon et al. 2017). Sometimes, dosage as high as 160 mg Cl_2/L with 120 min contact time and > 80 mg Cl min/L was required to inactivate certain ARGs and to suppress ARG transfer (Guo et al. 2015; Zhuang et al. 2015).

Low cost, readily available, ease of application and effectiveness in inactivating a wide range of microorganisms make chlorination the most preferred choice of disinfection method. Chlorination could result in cell wall damage, cell component leakage and DNA damage. However, reversal and regrowth are potential problems at low chlorine concentration (Virto et al. 2005). Intracellular ARG (iARG) and extracellular ARG (eARG) were reported to increase during treatment at low chlorine concentration (Liu et al. 2018). Moreover, at low chlorine concentration the transformation ability of the DNA remains unaffected (Öncü et al. 2011). Hence, a high dosage of chlorine is required for cell death and DNA damage. At high chlorine concentrations, DNA damage was caused by chlorination of amino- and heterocyclic NH groups of the DNA bases and not oxidative fragmentation (Prütz 1996). Hence, the DNA damage is reversible. High chlorine concentrations potentially produce more toxic by-products (Richardson et al. 1998) and are impractical (Oh et al. 2014; Sharma et al. 2016). Chlorination does not significantly remove ARB and ARG at low chlorine dosages (Munir et al. 2011; Garrido-Cardenas et al. 2020). Other advanced and combined treatment technologies can be considered for effective ARB and ARG removal. For instance, ozonation effectively removed ARB and ARGs compared to chlorination (Oh et al. 2014). H_2O_2/sunlight process was reported to be effective in controlling ARB regrowth (Fiorentino et al. 2015), while UV could be a better option to control ARG transfer (Guo et al. 2015). Sequential UV/chlorination showed better ARG removal efficiency (Zhang et al. 2015). Advanced oxidation process such as electrochemical oxidation, photocatalysis, Fenton, etc., could also be used in place of chlorination.

3.1.2 Coagulation

Coagulation process is frequently used to remove suspended colloidal particles through charge neutralization and aggregation mechanism from water and wastewater. It is also often used as one of the tertiary treatment options to conventional wastewater treatment (Henderson et al. 2006; Sillanpää et al. 2018). Coagulants reduce the repulsive potential of the electrical double layer at the solid-liquid interface that promotes the aggregation of suspended particles such as bacteria (generally having negative surface charge) through adsorption and complexation mechanism gets settled (Henderson et al. 2006; Sillanpää et al. 2018). Commonly used coagulants are alum, ferric/ferrous salts and poly-aluminium chloride. Li et al. (Li et al. 2017b) studied the removal of sulfonamide (*sul1* and *sul2*) and tetracycline (*tetO*, *tetW* and *tetQ*) resistance genes and class 1 integron gene (*intI1*) through ferric and polyferric chloride coagulants. About 0.5 to 3.1 log reduction of ARGs was observed. Grehs et al. (Grehs et al. 2019) compared the removal of ARGs/ARB using aluminium sulphate and tannin coagulants. Both the coagulants removed ARB and ARGs; however, reactivation of ARB was observed when tannin was used as a coagulant. Up to 0.76 log reduction of 16S RNA gene was reported by Zhang et al. (Zhang et al. 2016b) in a full-scale advanced water treatment facility in China.

3.1.3 Ozonation

Ozonation is being widely used across several water treatment plants (Wert et al. 2009; Quero-Pastero et al. 2014) and is an economically feasible tertiary treatment (Czekalski et al. 2016). Ozone is a strong oxidant ($E^0 = 2.07$ V) and an effective disinfectant, which helps to degrade a host of organic contaminants in water and wastewater treatment applications (Oneby et al. 2010). It primarily targets unsaturated bonds (Srinivasan and Nambi 2020) and breaks down complex organic contaminants into simpler and lower molecular weight molecules, resulting in more biodegradability of residual contaminants. With respect to disinfection and the removal of ARBs and ARGs, ozone typically targets cellular nucleic acids, resulting in a range of damages such as base lesions, single- and double-strand breaks and cellular envelope (Czekalski et al. 2016). At low ozone concentrations and exposures, heavy membrane damage and inactivation of *E. coli* were observed. However, ozone concentrations more than a threshold value (0.2 mg/L) were required for disruption or leakage of intracellular DNA and iARG (Czekalski et al. 2016). This is in line with the suggestion that damage of iARG happens post-viability loss (Dodd 2012).

Pak et al. (2016) have studied the effects of various factors such as solution pH, suspended solids and humic acids (model dissolved and solid organic matter), on the removal of antibiotic resistance and inactivation of ARB. These tests are based on small sample numbers. With an increase in hydroxide ion concentration (increase in pH), ozone decomposition rate increases. This decomposition is represented by Eq. (1). It further leads to the formation of hydroxyl radical (•OH) according to Eq. (2). Hence, the influence of pH on ARB inactivation is a trade-off between ozone ($E^0 = 2.07$ V) and •OH (E^0 value = 2.8 V) concentrations. Zuma et al. (2009) found that ensuring a significant ozone concentration (by maintaining a lower pH) helps in bacterial inactivation more than that by •OH formed out of decomposition of ozone. Greater humic acid concentrations result in higher antibiotic resistance removal (Pak et al., 2016). Ozone and humic acid react to form easily biodegradable low-molecular-weight oxygenated by-products that are polar and hydrophilic than their precursors (Gracia et al. 1996). The suspended solids consume ozone and radicals formed during ozonation, negatively influencing the efficiency of ozonation in the removal of antibiotic resistance. The suspended solids initially decompose to form high-molecular-weight compounds followed by further decomposition to form lower-molecular-weight compounds (Kawara 1977).

$$\left[O_3\right]+\left[OH^-\right]\rightarrow\left[HO_2^-\right]+\left[O_2\right] \tag{1}$$

$$\left[O_3\right]+\left[HO_2^-\right]\rightarrow HO^\bullet+\left[O_2^{\bullet-}\right]+\left[O_2\right] \tag{2}$$

Michael-Kordatou et al. (Michael-Kordatou et al. 2017) observed the elimination of erythromycin and ethyl paraben-resistant *E. coli* when subjected to ozonation for 15 min. It was found that the former is more resilient to ozonation than the latter ARB. The removal of antibiotics increased with increase in ozone concentration. The optimal pH for the removal of antibiotics was found to be 8. In some research studies, there were additional treatment technologies used independently or along with ozonation. Ozone dosage required to remove 90% of ARGs and ARBs was 10 times lesser than chlorine doses, proving that ozonation is a practical method of eliminating antibiotic resistance (Oh et al. 2014). Moreira et al. (Moreira et al.

2016) investigated the treatment of wastewater effluents and surface water effluents by photocatalytic ozonation and observed a significant reduction in *blaTEM*, *qnrS* and *sul1* ARGs in treated wastewaters. However, the removal of 16S rRNA (common to all bacteria) and *intI*1 (common in gram-negative bacteria) genes was just transient. In the case of surface water, photocatalytic ozonation resulted in reduction of *blaTEM* from 10^4 gene copy number per 100 mL to close to its limit of quantification and a 3 log reduction of the 16S rRNA and *intI*1 genes. A study on the removal of ARGs and microorganisms from urban wastewater using ozonation and UV treatment showed ~2 log reduction in 16S rRNA and *intI*1 genes and 3–4 log reduction in total heterotrophs, enterobacteria and enterococci and close to limit of quantification for ARGs within 30 min of both ozonation and UV (Sousa et al. 2017). However, the removal of 16S rRNA, *intI1* and ARGs was transient (similar to the study by Moreira et al. (2016)). They bounced back to pre-treatment concentrations after a 3-day wait. Zhuang et al. (Zhuang et al. 2015) investigated the inactivation of *intI1* and ARGs – *sul1* and *tetG* – in municipal wastewater by chlorination, UV and ozonation. Similarly, regrowth phenomenon was corroborated by Iakovides et al. (2019) as well (Iakovides et al. 2019). Even after prolonged ozonation, a small number of living cells may persist leading to regrowth. This must be carefully addressed while employing ozonation for the removal of ARB and ARGs. Zhuang et al. (Zhuang et al. 2015) investigated the inactivation of ARGs – *sul1*, *tetG* and *intI1* – using ozonation and found a significant reduction in 16S rDNA; however, ozonation failed to inactivate the ARGs. Zheng et al. (Zheng et al. 2018b) investigated the treatment of a hospital wastewater and the removal of ARGs by (i) an initial pre-treatment process using electro-peroxone (a combination of electrolysis and ozonation, where the in situ electro-generated H_2O_2 combines with ozone to form •OH (Yuan et al. 2015; Srinivasan and Nambi 2020)) followed by (ii) a sequencing batch reactor (SBR). Electro-peroxone pre-treatment process significantly reduced the ARG production and resulted in the efficient treatment of hospital wastewater. A representative schematic of the electro-peroxone-SBR setup is given in Fig. 1.

Considering that ozonation is already widely used as a tertiary treatment process in many wastewater treatment plants, employing ozonation for the removal of ARB and ARGs makes it pragmatic. Moreover, ozone generation (using ozone generators) at the treatment site reduces storage and transportation hazards, as is the case with other oxidants. Furthermore, the efficiency of ozonation may be enhanced by the addition of peroxide or persulfate (Sharma et al. 2016). This would result in the generation of •OH and sulphate radicals (•SO_4^-), respectively, causing effective removal of such contaminants. While ozonation has been investigated as an independent treatment method or in combination with other technologies for the removal of ARGs and ARB, it has many limitations. Consumption of ozone by other organic contaminants such as humic acid is another problem that is often encountered (Zhuang et al. 2015). Moreover, ozone being a selective oxidant efficiently oxidizes only certain organics and inorganics (Peña et al. 2003; Van Geluwe et al. 2011). It primarily targets unsaturated bonds and seldom results in complete mineralization, leaving behind low-molecular-weight partial oxidation products that are less reactive (Rosal et al. 2008). Other limitations of ozone are its low aqueous solubility and

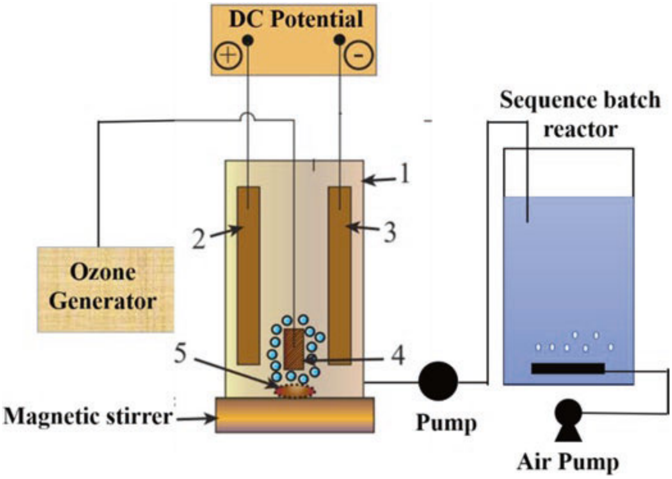

Fig. 1 A representative schematic of an electro-peroxone-SBR setup (1, electro-peroxone reactor; 2 and 3, electrodes; 4, diffuser; and 5, magnetic pellet)

the slow kinetic rate in degrading certain organic contaminants (Quero-Pastero et al. 2014). With special attention to disinfection using ozonation, its efficacy is variable and depends on multiple factors as listed here: (i) type of bacterial strain, (ii) stage of cell growth, (iii) cell envelope, (iv) efficacy of repair mechanisms, (v) matrix effects and several others as highlighted by Czekalski et al. (Czekalski et al. 2016).

3.1.4 UV-Related Processes

UV technology is a widely employed disinfection process. The mechanism of cell inactivation by UV radiation can be both intracellular and extracellular (Dodd 2012). UV irradiation of cells initiates photochemical reaction within the cell resulting in cell inactivation and DNA damage. UV can also penetrate the cells resulting in photocatalytic degradation and intracellular genetic material inactivation (Destiani et al. 2017). Damage to DNA can happen in any of the three following ways: (i) pyrimidine dimerization, (ii) pyrimidine coupling and (iii) DNA-protein cross-linking, thereby preventing DNA and cell replication (Dodd 2012). UV can degrade both intracellular and extracellular ARGs (Yoon et al. 2017). UV treatment is often coupled with chlorination, H_2O_2 and photocatalysis to improve efficiency. Oxidants such as •OH and chlorine ensure better ARB and ARG removal. Interaction of these oxidants with cell and DNA is explained in Sects. 3.1.1 and 3.1.2. Other UV hybrid technologies will be discussed in the other advanced treatment technology Sect. 3.1.7. No apparent reduction of ARGs, namely, *tetM*, *tetO*, *tetQ*, *tetW*, *sul1*, *sul2* and *intI1*, was observed during UV treatment of wastewater (Chen and Zhang 2013). In a similar study, Destiani et al. (Destiani et al. 2019) observed only 1.7 log reduction of *tetA*, *bla*-$_{TEM1}$, *sul1* and *mphA* genes in drinking water after UV treatment. Yoon et al. (Yoon et al. 2017) investigated inactivation kinetics of ARB, iARG and eARG by UV and UV/H_2O_2 at pH 7 and 8. At pH 7, 4 log reduction of e*amp*^{R}, i*amp*^{R}, i*kan*^{R} and e*kan*^{R} required UV fluence of 37, 67, 50 and 72 mJcm^{-2}, respectively, while at pH 8, the energy required for UV inactivation was 152, 92, 376 and 81 mJcm^{-2}, respectively. In the case of UV/H_2O_2 process, at pH 7 the energy required was 44,146, 44 and 130, and at pH 8, the energy required was 71, 132, 46 and 105 for 4 log reduction of e*amp*^{R}, i*amp*^{R}, i*kan*^{R} and e*kan*^{R}, respectively. Ferro et al. (Ferro et al. 2016) also observed the removal of antibiotic-resistant *E. coli* and ARGs *bla*$_{TEM}$, *qnr*S and *tet*W by UV/H_2O_2 process.

McKinney and Pruden (McKinney and Pruden 2012) observed limited removal of intracellular and extracellular *mecA*, *vanA*, *tetA* and *ampC* in wastewater. The major limitation being impracticality in achieving higher ARG log reduction at practical disinfectant exposures (McKinney and Pruden 2012). At practical UV exposure, about 90% of eARGs and iARGs are inactivated (He et al. 2019). However, photo-reactivation under field conditions is a threat (McKinney and Pruden 2012). ARG inactivation is faster than membrane damage during UV and UV/H_2O_2 treatment (Yoon et al. 2017). Hence, regrowth of ARB is also a potential problem after UV disinfection (Destiani et al. 2019). Slow iARG inactivation rate is compared to eARG inactivation rate as iARGs are protected by cellular components during UV and UV/H_2O_2 treatment, as observed by Yoon et al. (Yoon et al. 2017). However, the transforming ability of the extracellular plasmids (eARG) was not eliminated after UV and UV/H_2O_2 treatment even though eARG inactivation was faster than iARG inactivation (Chang et al. 2017;Yoon et al. 2018). Similar observations were reported by Ferro et al. for ARG removal by UV/H_2O_2 (Ferro et al. 2016). Interestingly, constructed wetland showed better *tetM*, *tetO*, *tetQ*, *tetW*, *sul1*, *sul2* and *intI1* removal than UV treatment (Chen and Zhang 2013). Sequential UV/chlorination is also reportedly effective in inactivating *sul1*, *tetX*, *tetG* and *intI1* genes and ARB (Zhang et al. 2015; Zhang et al. 2019).

3.1.5 Photocatalysis and Photoelectrocatalysis

Photocatalysis is the irradiation of a catalyst to photochemically generate reactive species as indicated in Eq. (3) and is in turn used for the degradation of contaminants in water. When light irradiates the photocatalyst, electrons in the valence band are excited to the conduction band, and holes are left behind. Holes (h_{vb}^+) come in contact with water to form •OH, which mineralizes the pollutants. Similarly, oxygen undergoes one-electron reduction when it encounters the electrons in valence band (e_{cb}^-) to form superoxide anion radicals which help oxidize the organic contaminants (Eqs. 4–5) (Zhang and Nosaka 2014). However, photocatalysis suffers from the issue of rapid recombination of charge carriers (e_{cb}^- and h_{vb}^+), which results in lower efficiency (Yang et al. 2014). The recombination rate can be reduced to a great extent by employing photoelectrocatalysis (PEC).

$$TiO_2 + h\upsilon \rightarrow e^-_{cb} + h^+ \tag{3}$$

$$h^+ + H_2O \rightarrow \bullet OH + H^+ \tag{4}$$

$$e^- + O_2 \rightarrow O_2^{\bullet -} + H^+ \tag{5}$$

A research investigation by Biancullo et al. (Biancullo et al. 2019) shows that the inactivation of ARBs reached up to 2 log units by TiO_2 heterogeneous photocatalysis using UVA-LEDs. However, the treatment was not successful in inhibiting the regrowth of bacteria. The antibiotic resistance post-regrowth was similar to that of before treatment. Such a regrowth after treatment closely resembles a few ozonation studies. Guo et al. (Guo et al. 2018) investigated the removal of ARGs *ampC* and *mecA* from the host ARB *Pseudomonas aeruginosa* and methicillin-resistant *Staphylococcus aureus* (MRSA), respectively. A TiO_2-based photocatalytic process (along with UV/H_2O_2) was employed and it was observed that the system could remove iARGs and eARGs. Photocatalysis with TiO_2 under 6 and 12 mJ/cm^2 UV$_{254}$ fluence dose achieved around 4.5–5 and 5–5.8 log reduction in ARB, respectively. In the case of ARGs, a 4.7 log *amp*C and 5.8 log *mec*A reduction were observed at 120 mJ/cm^2 UV$_{254}$ fluence dose and TiO_2. The addition of H_2O_2 positively influenced the removal of ARB and ARGs. A research study by Karaolia et al. (Karaolia et al. 2014) investigated graphene-based TiO_2 composite photocatalysts for the removal of antibiotics, ARB, total genomic DNA and ARGs (predominantly *sul1*, *ampC*, *ermB* and *mecA* and certain species-specific sequences). TiO_2-reduced graphene oxide (TiO_2-rGO) composite photocatalysts proved to be efficient in complete disinfection and in ensuring no regrowth even after 24 h post-treatment. However, the total DNA concentration seemed to be resistant to photocatalysis.

Xiang et al. (Xiang et al. 2012) explained the mechanism of graphene-based TiO_2 composites as photocatalysts for efficient photocatalysis. The incident light excites electrons from valence band to conduction band, leaving behind a hole. Typically, owing to the instability of the excited electron, it comes back to the valence band and recombines with its counterpart charge carrier, the holes. This phenomenon of recombination makes photocatalysis less efficient. To overcome this limitation, Xiang et al. (Xiang et al. 2012) synthesized a graphene-based TiO_2 composite. Here, graphene acted as an efficient electron acceptor, thus preventing the recombination of charge carriers. The PEC process involves the application of electric current, which helps in separating the electrons and the holes, thereby reducing the recombination rate. In general, the effective inactivation of ARB and ARGs in •OH-based advanced treatment systems is due to the higher potential of •OH radicals (as against other oxidants) that helps them penetrate into the cells more efficiently, destroying the antibiotic resistance genes effectively (Oh et al. 2014). Jiang et al. (Jiang et al. 2017) investigated the inactivation of ARB *E. coli S1–23* and the elimination of its associated ARGs, *blaTEM-1* and *aac(3)-II*, using photoelectrocatalytic (PEC) process. It was observed that all the ARB, eARGs and iARGs were completely inactivated within 10 and 16 h PEC treatment, respectively. ARG-containing DNA extracted from *E. coli S1–23* was degraded in a few minutes across PEC, PC and EC treatment strategies. However, photocatalysis and electrochemical treatment did not display any effect towards ARB and ARGs.

3.1.6 Fenton and Related Processes

Studies on the application of Fenton process for mitigation of antimicrobial resistance transfer by ARB and ARG removal are gaining attention in recent times. The process can be briefly classified into Fenton oxidation (Fe^{2+}/H_2O_2), photo-Fenton, nano-newton and electro-Fenton. ARB inactivation by Fenton process can be extracellular oxidation or intracellular photocatalysis (Giannakis et al. 2018b). The presence of excess H_2O_2 and Fe^{2+} in the aqueous medium generates •OH radical. •OH, a powerful oxidant generated during the process, is highly reactive and non-selective in nature. Interaction of •OH with cell damages the cell membrane and inactivates the cell (Giannakis et al. 2018b). •OH interaction with ARG occurs in two ways: (i) Cell membrane damage increases the cell permeability and releases ARG along with other cell components into bulk aqueous medium where •OH interacts with the genetic material (Giannakis et al. 2018a). (ii) H_2O_2 and Fe^{2+} enter the cytoplasm via diffusion and porin transport systems, respectively. •OH is generated through intracellular Fenton reactions within the cytoplasm. Non-selective •OH interaction results in oxidative intracellular organelle and DNA damage (Giannakis et al. 2018b). Karaolia et al. (Karaolia et al. 2014) observed 5 log order of decrease in clarithromycin- and sulfamethoxazole-resistant *Enterococcus* by solar-driven Fenton oxidation. However, an increase in resistant *Enterococcus* was observed in the presence of certain antibiotics (Karaolia et al. 2014). In similar studies using solar photo-Fenton process, effective inactivation of 11 ARBs, cefotaxime-resistant bacteria and streptomycin-resistant strain was reported (Giannakis et al. 2018a; De la Obra Jiménez et al. 2019; Giannakis et al. 2018c), while Chen et al. (Chen et al. 2020) reported the removal of ARB *E. coli* SMS-3-5 and *P. aeruginosa* 01 using electro-Fenton process (Chen et al. 2020). Effective inactivation of ARB by photo-Fenton process and Fenton oxidation is also reported (Mackuľak et al. 2015; Serna-Galvis et al. 2019; Ahmed et al. 2020). ARG removal is also a widely studied application of Fenton process. The removal of both iARG and eARG using electro-Fenton process was reported (Chen et al. 2020). Chen et al. (Chen et al. 2020) also observed 3.8 and 5.2 log removal of intracellular and extracellular of *tetA* gene while 4.1 and 4.8 log removal of intracellular and extracellular *ampC* (Chen et al. 2020). Other studies on ARG removal using Fenton process, photo-Fenton process and solar photo-Fenton process have been reported (Zhang et al. 2016a; Giannakis et al. 2018a; Michael et al. 2019; Ahmed et al. 2020). 2.58–3.79 and 2.26–3.35 logs of *sul1*/*tetX* and *tetG* genes were reportedly removed at pH 3 and 7, respectively, in a Fenton oxidation process (Zhang et al. 2016a).

The disadvantages of employing a Fenton process vary depending on the type of the process. The pH of the photo-Fenton process determines the efficiency of disinfection and precipitation ability of the iron salt (Ghernaout and Elboughdiri 2020a, b).

Significant reduction in ARB resistance pattern and removal was observed only after repetitive treatment (Giannakis et al. 2018a). Regrowth after the treatment process sometimes is inevitable, which follows a similar pattern to that of non-resistant bacteria (Giannakis et al. 2018a). Moreover, degradation of ARG occurs much slower than ARB inactivation and so a prolonged treatment time is required (Ahmed et al. 2020). Hence, solar photo-Fenton process does not effectively remove ARG (Fiorentino et al. 2019). Effective ARG removal can be achieved only with long treatment durations in a photo-Fenton process (Serna-Galvis et al. 2019). On the other hand, a high dose of Fenton's reagent is required to damage iARGs compared to eARGs in a photo-Fenton process (Ahmed et al. 2020). An increase in toxicity was also observed after solar photo-Fenton process (Michael et al. 2019). Not many comparison and treatment evaluation studies are available for Fenton process on ARB and ARG removal. However, electrochemical oxidation is an effective ARB disinfection process than electro-Fenton process (Chen et al. 2020). However, Fenton process is reported to be effective in removing ARGs compared to UV/H_2O_2 process (Zhang et al. 2016a).

3.1.7 Other Advanced Oxidation Process

Application of advanced treatment technologies such as electrochemical oxidation, UV/persulfate (PS) and UV/peroxymonosulfate (PMS) for ARB and ARG removal is emerging (Rodríguez-Chueca 2019; Chen et al. 2020; Zhou et al. 2020). In the case of a UV-hybrid process, removal happens due to the interaction of free radicals with ARB and ARG in addition to UV interaction with genetic material (Zhou et al. 2020). In the case of an electrochemical oxidation process, the major free radical available for interaction is •OH. Free radicals such as •OH and $•SO_4^-$ generated during the treatment process interact with the cell membrane resulting in oxidative cell lysis rendering the cells inactive (Rodríguez-Chueca 2019). Damaged cell releases the cell components enabling interaction of free radicals with intracellular components and damaged DNA (Sharma et al. 2019). Interaction of $•SO_4^-$ is quite similar to •OH interaction with cell wall except the interaction is selective and slow (Wordofa et al. 2017). Zhou et al. (Zhou et al. 2020) reported ARB and ARG removal by UV/PS. 96.6% of macrolide-resistant bacteria, 94.7% of sulfonamide-resistant bacteria, 98.0% of tetracycline-resistant bacteria and 99.9% of quinolone-resistant bacteria were removed in 10 min of UV/PS treatment. On the other hand, 50.42% of total ARGs (*rmB*, *sul1*, *sul2*, *tetO*, *qnrS*) and integrons (*intI1* and *intI2*) was removed by UV/PS (Zhou et al. 2020). Rodríguez-Chueca (Rodríguez-Chueca 2019) reported the removal of *sul1*, *sul2*, *qnrS*, bla_{TEM}, $bla_{\text{OXA-A}}$ and *intI* from wastewater employing PMS/Fe(II)/UV-C and PMS/UV-C systems. 0.22 log removal and 0.02 log removal of total ARGs were observed with PMS/UV-C and PMS/Fe(II)/UV-C treatment in 4 sec, respectively (Rodríguez-Chueca 2019). Chen et al. (Chen et al. 2020) reported 1.7 and 2.1 log reduction of *E. coli* SMS-3-5 and *P. aeruginosa* 01, respectively, during electrochemical oxidation after 120 min. Similarly, 1.8 and 1.5 logs of extracellular *tetA* and *ampC* were removed after 120 min. However, only

0.58 and 0.72 logs of intracellular *tetA* and *ampC* genes were removed after 120 min of electrochemical oxidation, respectively (Chen et al. 2020). PMS/Fe(II)/UV-C and PMS/UV-C produce more free radicals compared to UV-C process. However, ARB and ARG removal was better when UV-C alone was employed. This is due to the competition between the DNA and the oxidants for absorption of photons generated by UV-C (Rodríguez-Chueca 2019). Zhou et al. (2020) observed better ARB and ARG removal by UV/PS compared to UV treatment. On the other hand, electrochemical oxidation showed better removal of ARB and eARGs compared to iARGs (Chen et al. 2020).

3.2 Membrane Filtration

Reverse osmosis (RO) is a pressure-driven process and is widely used for applications such as desalination and water treatment. A RO system typically houses a semi-permeable membrane that eliminates dissolved contents and emanates pure water. It functions on the following principles, namely, size exclusion, charge exclusion and solute-solvent-membrane interactions (Malaeb and Ayoub 2011). Other filtration processes commonly used in water treatment are microfiltration, ultrafiltration (UF) and nanofiltration (NF), and they vary in their pore sizes and hence their ability to remove contaminants such as microorganisms, organic species and mono- and multi-valent ions. Lu et al. (Lu et al. 2020) investigated the elimination of ARGs in an integrated membrane wastewater reclamation system and observed up to 3.8 log removal of the detected ARGs. A wastewater treatment plant effluent was subjected to UF and NF, resulting in complete removal of ARBs (Schwermer et al. 2018).

Slipko et al. (Slipko et al. 2019) investigated the removal of free DNA-containing ARGs in distilled water and a wastewater effluent using ten different membranes. These membranes differed by their charge and molecular weight cut-offs (MWCOs) (ranging from microfiltration to RO membranes). From this investigation, it was found that about 99.8% of the free DNA was rejected in the case of ultrafiltration, nanofiltration and reverse osmosis, all of which had a MWCO lesser than 5 kDa; on the other hand, microfiltration resulted in no retention. Size exclusion was the key mechanism of free DNA retention. In addition, membrane charge and adsorption of the free DNA over the membrane also played important roles. Krzeminski et al. (Krzeminski et al. 2020) investigated the removal of plasmids (cell-free DNA) containing ARGs using UF, NF and RO. Membranes with MWCO <1 kDa achieved up to 99% removal of plasmids and those with still lower MWCOs achieved complete elimination with a log reduction value greater than 6.6. The reject water obtained from the process was further exposed to UV-LED at 265 nm, which also yields good removal of ARGs. A combination of membrane filtration and UV-LED irradiation for water and concentrate yields an effective strategy to combat ARGs. A research study by Ren et al. (2018) involved TiO_2 nanoparticle functionalization of polyvinylidene fluoride (PVDF)-UF membrane for the removal of ARB and ARGs from a secondary treatment effluent. The modified TiO_2-PVDF resulted in (i) absolute retention of ARB and (ii) photocatalytic removal of integrons and ARGs. Cheng and Hong (Cheng and Hong 2017) investigated the removal of three ARBs, namely, *bla*$_{NDM-1}$-positive *Escherichia coli* PI-7, *bla*$_{OXA-48}$-positive *E. coli* UPEC-RIY-4 and *bla*$_{CTX-M15}$-positive *Klebsiella pneumoniae* L7 and their corresponding ARGs using a retro-fitted anaerobic PVDF-microfiltration membrane at different degrees of fouling. ARB removal reached 5 log removal values when the membrane was new. At sub-critical fouling, it dropped with an increase in trans-membrane pressures, and the log removal value was restored to 5 at critical fouling. A study comparing the efficacies of UF and ozonation showed that UF is way more effective in the removal of antibiotic resistance genes (Hembach et al. 2019).

3.3 Biological Reactors

Membrane bioreactors are recognized to be effective in removing the ARB and ARGs in large-scale wastewater treatment plants (Sun et al. 2016; Ben et al. 2017). Let et al. (Le et al. 2018) compared the removal of ARGs in membrane bioreactor systems along with the conventional activated sludge process (ASP). Raw influent wastewater was found to be having ARG concentration of 2.0×10^7 gene copies/mL and ARB concentration of 2.6 × 106 CFU/mL. About 2–3 order reduction in the magnitude of ARB was found at the conventional activated sludge process, whereas complete removal was observed at the MBR effluent. However, several ARGs including *bla*$_{KPC}$, *bla*$_{NDM}$, *bla*$_{SHV}$, *ermB*, *intI1*, *sul1* and *tetO* were still detected at the MBR effluent at the average concentration of ~10^3 gene copies/mL. Du et al. (Du et al. 2015) studied the removal of five ARGs (*tetG*, *tetW*, *tetX*, *sul1* and *intI1*) in the full-scale anaerobic/anoxic/aerobic-MBR process-based domestic wastewater treatment plant. The removal of ARGs was found to be occurring at the anaerobic and anoxic process, whereas the level of ARGs was found to be increasing in the aerobic process. Since the bioactivities of microorganisms are low at anaerobic and anoxic conditions, propagation and dissemination of ARGs within the microbial communities is inhibited. Further, a sharp decline in the removal of ARGs was observed at the MBR outlet. The removal of specific resistance genes in the overall process is as follows: *sul1* > *intI1* > *tetX* > *tetG* > *tetW*. ARG removal was also positively correlated with the reduction of 16S rRNA gene.

Munir et al. (Munir et al. 2011) monitored the removal of tetracycline and sulfonamide resistance genes (*tetW*, *tetO* and *sulI*) and tetracycline- and sulfonamide-resistant bacteria through different wastewater treatment processes such as MBR, conventional ASP, oxidative ditch and rotatory biological contactors. About 2.57–7.06 log reduction of ARGs and ARB was observed at the MBR process, whereas conventional processes showed the reduction in the range of 2.37–4.56 logs. The role of membrane foulants such as extracellular polymeric substance (EPS) and soluble microbial product (SMP) on the removal of ARGs in the anoxic/aerobic MBR is studied by Zhu et al. (Zhu et al. 2018). About 0.6 to 5.6 orders of magnitude removal of ARGs (*sulI*, *sulII*, *tetC*, *tetX* and *ereA*) and class 1 integron gene *int1* were reported for the MBR. About 13–25% removal of ARGs was attributed to the membrane foulants, and the denser fouling layer effectively prevents the escape of ARGs to the effluent. The removal of ARGs in the anaerobic membrane bioreactors (AnMBR) was studied by Kappell et al. (Kappell et al. 2018) while treating the primary clarifier effluent at 20 °C. About 3.3 to 3.6 log reduction was observed for the removal of ARGs and *intI1* gene at the filtrate.

Further, sequencing biological processes are reported to be exhibiting better performance in the removal of ARGs and ARB. Christgen et al. (Christgen et al. 2015) studied the removal of ARGs in anaerobic-aerobic sequence (AAS) bioreactors through metagenomic approaches. AAS showed better performance than aerobic and anaerobic reactors. AAS reduces the total ARG level to 29 ppm for the initial concentration of 198 ppm in the influent domestic wastewater, whereas aerobic and anaerobic reactor reduced the ARG level to 34 and 74, ppm respectively. Gao et al. (Gao et al. 2018) studied the long-term impact of tetracycline concentration gradient (50 μg/L to 500 μg/L) on the distribution patterns of tetracycline-resistant genes (*tetA*, *tetC*, *tetG*, *tetX*, *tetM*, *tetO* and *tetW*) and the mobile genetic element intI1 in the AAS bioreactors. The removal of tet and intI1 genes was largely observed at the aerobic unit. However, an abundance of *tetX* gene was found to be constant in the overall treatment. Strong correlation with *tet* and *intI1* genes shows that *intI1* is responsible for *tet* gene propagations in the biosystem. Li et al. (Li et al. 2019b) compared the removal of ARGs in MBR and three modified sequencing batch reactors (MSBRs). MBR exhibited 1.1–7.3 log removal of ARGs, whereas MSBRs showed 0.4–4.2 log reduction.

3.4 Constructed Wetland

Constructed wetlands are attractive for the treatment of domestic, industrial and agricultural wastewaters through natural processes occurring in semi-aquatic system categorized as surface and/or subsurface flow systems (Liu et al. 2013). The simple, cost effective, man-made wetland system is composed of aquatic plants, soil and various microbial species which collectively participate in treating the wastewater through different physical, chemical and biological process mechanisms (Huang et al. 2015). The fate and removal of ARGs in the constructed wetland system depend on environmental factors and operating conditions including plant and microbial species, filter materials, level of antibiotic and ARG/ARB contamination in the influent wastewater, flow rate and temperature in winter/summer (Miller et al. 2014; Huang et al. 2015; Song et al. 2018). The removal of ARGs in the constructed wetland is contributed by the combined adsorption and biological processes. However, biological processes contribute to complex phenomenon such as ARG exchange and ARB proliferation, while it may also eliminate the ARGs (Yang et al. 2014; Chen et al. 2016; Guo et al. 2017a, b). Further, sediment in the system can act as the reservoir of ARGs and plants providing the appropriate circumstances and oxygen supply to microbial communities which substantially could contribute to the dissemination of resistance through horizontal gene transfer mechanism (Fang et al. 2017).

Fang et al. (Fang et al. 2017) examined the removal of 14 ARGs from domestic sewage that belongs to sulfonamide (*sul1*, *sul2* and *sul3*), tetracycline (*tetA*, *tetB*, *tetC*, *tetE*, *tetH*, *tetM*, *tetO* and *tetW*) and quinolone (*qnrB*, *qnrS* and *qepA*) resistance genes in an integrated surface flow constructed wetland system. About 77.8% removal and 59.5% removal of targeted ARGs were observed in winter and summer, respectively. Constructed wetland systems provide appropriate environment composed of sediment sorbed with ARGs, populated microbial communities and carbon- and nutrient-rich wastewater for the horizontal gene transfer of genetic elements, and dissemination occurs through integrons. Strong correlations between the existence of intI1 and ARGs in the constructed wetland systems indicate the occurrence of horizontal gene transfer within the system. In sediment, ARGs, namely, *tetA*, *tetC*, *tetO* and *tetW*, were positively correlated and in water, ARGs, namely, *sul1*, *tetA*, *tetC* and *qnrB*, were correlated with the existence of *intI1* gene. The presence of ARGs in sediment was found to be higher in summer than winter, indicating summer provides suitable condition for the exchange of ARGs within microbial communities. Chen et al. (Chen et al. 2015) studied the removal of ARGs from domestic wastewater such as *sul1*, *sul2*, *tetM* and *tetO* in the integrated constructed wetland systems composed of four surface and one sub-surface flow constructed wetlands connected in series. Overall >99% removal of ARGs was observed and 1–3 orders of magnitude reduction in the gene copies were reported. Complete removal of ARGs such as *intI2*, *tetB/P*, *tetM* and *tetX* was reported and only 43% removal of *ermC* gene was observed. Chen et al. (Chen et al. 2016) examined the influence of flow configurations (surface flow, horizontal subsurface and vertical subsurface flow) and plant species (*Thalia dealbata* Fraser and *Iris tectorum* Maxim) on the removal of 12 ARGs (belonging to sulfonamide, tetracycline, macrolide and chloramphenicol resistance genes) in the mesocosm-scale constructed wetlands. Removal of ARGs varied in the range of 63.9 and 84.0% in various configurations. Subsurface flow showed better removal performance than the surface flow wetlands mainly in the removal of antibiotics. Cardinal et al. (Cardinal et al. 2014) reported that specific ARGs in outdoor shallow wetland mesocosms disappeared with half-life of 2.1 to 99 days, whereas *sulI* genes increased after 28 days.

3.5 Application of Nanomaterials

Nanomaterials offer a wide range of applications in the water and wastewater treatment sector. A variety of nanomaterials including nanocarbon and metal/metal oxides assist in combating the spread of ARB and ARG in the environment (Sharma et al. 2016; Barancheshme and Munir 2018). Nanomaterials exhibit broad-spectrum antibacterial activity through various mechanisms of actions such as (i) direct bacterial membrane disruption, (ii) production of oxidative stress through the generation of reactive oxygen species, (iii) intracellular interactions with DNA/proteins, (iv) triggering the immune response of host cells of innate or adaptive manner and (v) controlling the biofilm formation for greater exposure to antibiotics (Baptista et al. 2018). Unlike antibiotics, nanomaterials use various strategies to combat ARB; it is effective against MDR bacteria (Fig. 2). Moreover, nanomaterials are also used as a vector to deliver the antibiotic drugs to enhance its biocide activity and the drugs can be delivered through membrane interaction and penetration mechanism. The antibiotic ability of nanomaterials against MDR bacteria is instigated through the numerous interactions between nanomaterials and the MDR bacteria like electrostatic attraction and van der Waals or hydrophobic interaction (Baptista et al. 2018). Further, the intrinsic properties of nanomaterials such as large surface area, size, stability and ability to act as carriers to drugs boost the broad-spectrum antibacterial activity (Zou et al. 2016). The interaction between nanomaterials and ARBs could result in most common antibacterial mechanisms such as oxidative stress, metal ion release and non-oxidative mechanism, resulting in the inactivation of enzymes and proteins and alteration of gene expression (Baptista et al. 2018; Salas Orozco et al. 2019). Cell damage induced by oxidative stress is considered to be one of the important antibacterial activities against MDR bacteria (Wang et al. 2017). Oxidative stress is induced through the production of reactive oxygen species (ROS) within

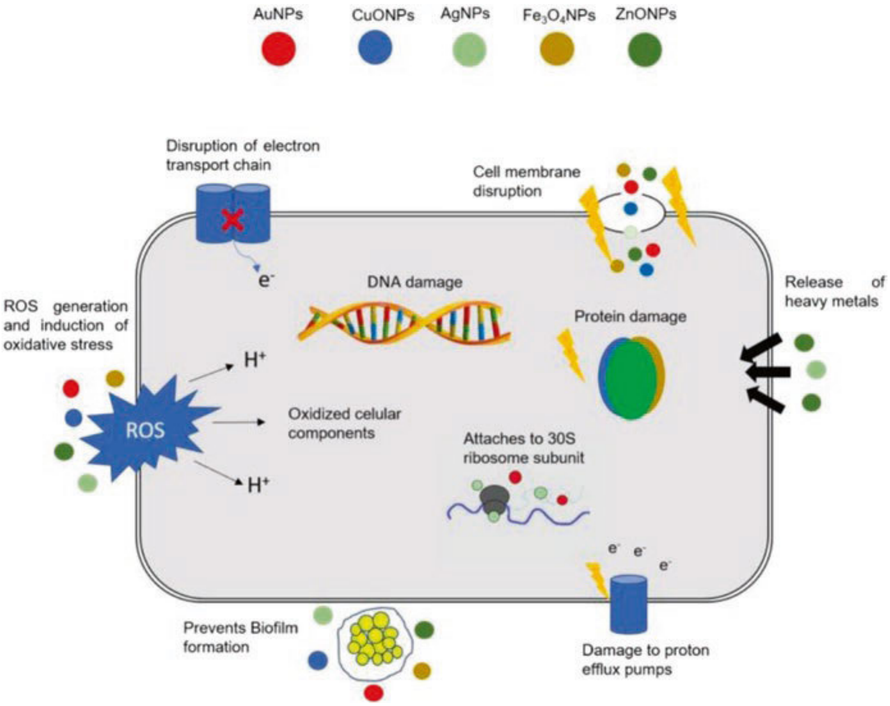

Fig. 2 Mechanisms of action of nanoparticles against bacteria. (Adapted from Baptista et al. 2018. Copyright © 2018 Baptista, McCusker, Carvalho, Ferreira, Mohan, Martins and Fernandes)

the cells, resulting in the non-selective oxidation of cell components and biomolecules, including damage to membrane lipids, DNA and intracellular proteins (Wang et al. 2017).

Nanomaterials produce different reactive species upon the interactions such as •OH, H_2O_2, O_2^- and $^1[O_2]$ (Wang et al. 2017). Further, the level of production of ROS depends on the type of nanomaterials and their intrinsic properties. Non-oxidative mechanism is due to the interaction between nanomaterial and cell membrane. Ingestion of nanomaterials into the bacterial cell results in nanomaterial binding with the cellar components and interrupts the appropriate functioning of the bacterial cells (Pruden et al. 2006; Salas Orozco et al. 2019). Broadly, nanomaterials used for combating ARBs are categorized into nanocarbons and metal/metal oxides. Nanocarbon-based materials include graphene/graphene oxide, carbon nanotubes, etc., and metal/metal oxide includes gold nanoparticles (Au NPs), silver nanoparticles (Ag NPs), copper, TiO_2, ZnO and others (Pruden et al. 2006; Bytesnikova et al. 2019; Salas Orozco et al. 2019).

3.5.1 Nanocarbon-Based Materials

Applications of graphene-based nanomaterials to remove a wide range of contaminants are reported abundantly (Divyapriya et al. 2017, 2018a, b, c, 2019; Divyapriya and Nidheesh 2020). Graphene-based materials participate in the biomolecular interactions with the genetic materials of bacteria in intracellular as well as extracellular level (Kanchanapally et al. 2015; Lee et al. 2016; Bytesnikova et al. 2019). The cell membrane of bacteria could be damaged through the physical interactions with sharp edges (Liu et al. 2011; Zheng et al. 2018a). Further oxidative stress could also be developed by the electron transfer mechanisms of π-bonding systems (Liu et al. 2011). Graphene-based nanomaterials are successfully employed for the removal of ARGs and ARB by various research groups (Zou et al. 2016; Guo and Zhang 2017; Yu et al. 2017). Abundant oxygen functionalities of graphene oxide such as hydroxyl, carboxyl and epoxide groups effectively remove the cyclic (c) and double-stranded (ds) ARGs through different adsorption mechanisms (Yu et al. 2017). The removal efficiency of ARGs depends on the length and base composition. Oxygen functional groups and the π-bonding system of GO bind to the genetic elements through chemical bonding with the aromatic structure of nucleic acids and the π-π interactions. Yu et al. (Yu et al. 2017) reported that about 3.11 and 2.88 log reduction of c-ARGs and ds-ARGs was attained for the GO dosage of 300 μg/mL. Adsorption equilibrium was attained within 15 min for both c-ARGs and ds-ARGs. Adsorption isotherm fitted well with Freundlich model. Adsorption of ARGs on GO was found to be spontaneous and exothermic. Further inhibition of antibiotic uptake and ARG propagation within the bacterial communities could be achieved in the presence of GO. Zou et al. (Zou et al. 2016) reported that uptake of sulfamethoxazole by bacteria is inhibited through the formation of GO- sulfamethoxazole complex. Moreover, sulfamethoxazole could be transported to the extracellular environment from the intracellular level in the presence of GO since GO promotes cell membrane permeability. GO reduced the abundance of *sulI* and *intI* genes by 2–3 orders of magnitude. Experiments conducted on integron transfer frequency showed that GO reduced the transfer frequency by 55 times. Guo and Zhang et al. (Guo and Zhang 2017) reported the inactivation of ARB occurs at the GO concentration of >10 mg/L through damaging the resistant plasmids. However, there was no significant inactivation observed at concentration < 1 mg/L with no damage to the resistant plasmids. Low concentrations of GO (1–10 mg/L) promoted the conjugated transfer of genetic materials, whereas high concentration of GO (100 mg/L) inhibited it.

3.5.2 Metals and Metal Oxides

Many researchers reported the antimicrobial properties of metals and metal oxides against broad-spectrum bacteria (Besinis et al. 2014). Due to the intrinsic properties of nanoparticles such as higher surface to volume ratio, high reactivity, stability and surface interactions, metals/metal oxide nanoparticles involve in different mechanistic actions against ARB and ARGs (Salas Orozco et al. 2019). Metals and metal oxides participate through electron transfer mechanisms and surface interactions between the metal/metal oxides and bacteria such as electrostatic and hydrophobic interactions and van der Waals forces of attractions (Salas Orozco et al. 2019). Antimicrobial mechanisms that are used against ARBs are membrane damage, damage to intracellular proteins and cell organelles, interactions with genetic material, release of electrons and metal ionic species and creation of oxidative stress (Besinis et al. 2014). AgNPs were largely studied for their antimicrobial properties against broad-spectrum bacteria. Miller et al. (Miller et al. 2013) reported that there was no significant change in the copy number of tetracycline resistance genes *(tetO, tetW)* in the presence of Ag NPs compared to the control which does not have Ag NPs, whereas there was a reduction in the copy numbers of *sulI*, *sulII* and *int I1* genes. Researchers also reported the enhancement in the horizontal gene transfer of ARGs upon exposure to the nanoparticles. This phenomenon occurs due to the increase in the cell membrane permeability of bacteria with the exposure to nanoparticles such as nano-Al_2O_3, nano-TiO_2, nano-ZnO, nano-SiO_2 and nano-Fe_2O_3 (Qiu et al. 2012, 2015). Qiu et al. (Qiu et al. 2015) reported that nano-TiO_2 particles could enhance the transfer of ARGs and cause significant environmental risk. It promoted the conjugation of antibiotic resistance plasmid RP4 in *E. coli* bacteria. TiO_2 nanoparticles reduced the bacterial growth rate from 0.0360 to 0.0323 min^{-1} but enhanced the conjugative gene transfer rate from 6.69×10^{-12} to 3.93×10^{-10} mL $cell^{-1}$ min^{-1}. Similarly, Qiu et al. (Qiu et al. 2012) reported up to 200 orders of increase in the conjugative transfer of RP4 between *E. coli* and *Salmonella* spp. in the presence of nano-alumina. Wang et al. (Wang et al. 2018) reported that ZnO nanoparticles could also facilitate the ARG transfer within the bacterial communities by increasing the conjugative transfer. About 24.3- and 8.3-fold increase in the conjugative transfer of antibiotic resistance plasmid RP4 in *E. coli* and mixed microbial consortium was observed, respectively.

4 Conclusion and Future Perspectives

The prevalence of ARGs and ARB in effluent wastewaters suggests the need for efficient advanced treatment methodologies. Apart from antibiotics, ARB and ARG, metal stress also enables AMR dissemination. Hence, it is crucial to consider every factor and implement treatment technologies that can tackle AMR spread. Ozonation is a commonly used tertiary treatment technology, and it becomes pragmatic to employ ozonation to remove ARB and ARGs. Ozonation in combination with other treatment processes may be more robust against regrowth issues. Photocatalysis performs better than ozonation in curtailing the regrowth of bacteria after treatment. Modified TiO_2 composite-based photocatalysis and photoelectrocatalysis effectively prevent recombination, thereby helping in the enhancement of treatment efficiency. Not all the available and hybrid Fenton processes are studied or compared with advanced treatment technologies for ARB and ARG removal. Hence, future studies can exploit different Fenton processes for better understanding, to evaluate process parameters and possible large-scale application for AMR mitigation. Similarly, limited studies are available on the application of advanced oxidation processes such as electrochemical oxidation, UV/PS and UV/PMS. There is a scope for comparison studies and innovation to bridge the research gap and possible large-scale application of these processes. Membrane filtration resulted in excellent retention of ARB and ARGs. However, it does not eliminate such emerging contaminants from the system, unlike chemical AOPs. Membrane filtration in combination with other oxidative processes will be highly effective. MBR is found to be effective in removing ARB; however, ARGs are not entirely filtered. Biofoulants in MBR act as an additional filter to remove ARGs. Sequential biological processes containing anaerobic/anoxic and aerobic arrangement are found to reduce the propagation of ARGs. Coagulation removes the ARB effectively and removes the ARGs to some extent. The interaction between nanomaterials and ARBs could result in the most common antibacterial mechanisms such as oxidative stress, metal ion release and non-oxidative mechanisms, resulting in the inactivation of enzymes and proteins and alteration of gene expression. Inhibition of antibiotic uptake and ARG propagation within the bacterial communities could be achieved in the presence of GO. Horizontal gene transfer of ARGs can be enhanced in the presence of metal oxides such as nano-Al_2O_3, nano-TiO_2, nano-ZnO, nano-SiO_2 and nano-Fe_2O_3, since the cell membrane permeability of bacteria with exposure to nanoparticles is increased. Constructed wetlands are effective in removing ARB and ARGs and could contribute to adsorption and biological processes.

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References

Aali R, Nikaeen M, Khanahmad H, Hassanzadeh A (2014) Monitoring and comparison of antibiotic resistant bacteria and their resistance genes in municipal and hospital wastewaters. Int J Prev Med 5:887–894

Ahmed Y, Lu J, Yuan Z et al (2020) Efficient inactivation of antibiotic resistant bacteria and antibiotic resistance genes by photo-Fenton process under visible LED light and neutral pH. Water Res 179:115878. https://doi.org/10.1016/j.watres.2020.115878

Alexander J, Knopp G, Dötsch A et al (2016) Ozone treatment of conditioned wastewater selects antibiotic resistance genes, opportunistic bacteria, and induce strong population shifts. Sci Total Environ 559:103–112. https://doi.org/10.1016/j.scitotenv.2016.03.154

Amador PP, Fernandes RM, Prudêncio MC et al (2015) Antibiotic resistance in wastewater: occurrence and fate of Enterobacteriaceae producers of class A and class C β-lactamases. J Environ Sci Heal - Part A Toxic/Hazardous Subst Environ Eng 50:26–39. https://doi.org/10.1080/10934529.2015.964602

Amarasiri M, Sano D, Suzuki S (2019) Understanding human health risks caused by antibiotic resistant bacteria (ARB) and antibiotic resistance genes (ARG) in water environments: current knowledge and questions to be answered. Crit Rev Environ Sci Technol 0:1–44. https://doi.org/10.1080/10643389.2019.1692611

Andersson DI, Hughes D (2012) Evolution of antibiotic resistance at non-lethal drug concentrations. Drug Resist Updat 15:162–172. https://doi.org/10.1016/j.drup.2012.03.005

Baker-Austin C, Wright MS, Stepanauskas R, McArthur JV (2006) Co-selection of antibiotic and metal resistance. Trends Microbiol 14:176–182. https://doi.org/10.1016/j.tim.2006.02.006

Baptista PV, McCusker MP, Carvalho A et al (2018) Nano-strategies to fight multidrug resistant bacteria-"a Battle of the titans". Front Microbiol 9:1–26. https://doi.org/10.3389/fmicb.2018.01441

Barancheshme F, Munir M (2018) Strategies to combat antibiotic resistance in the wastewater treatment plants. Front Microbiol 8:2603. https://doi.org/10.3389/fmicb.2017.02603

Ben W, Wang J, Cao R et al (2017) Distribution of antibiotic resistance in the effluents of ten municipal wastewater treatment plants in China and the effect of treatment processes. Chemosphere 172:392–398. https://doi.org/10.1016/j.chemosphere.2017.01.041

Besinis A, De Peralta T, Handy RD (2014) The antibacterial effects of silver, titanium dioxide and silica dioxide nanoparticles compared to the dental disinfectant chlorhexidine on Streptococcus mutans using a suite of bioassays. Nanotoxicology 8:1–16. https://doi.org/10.3109/17435390.2012.742935

Biancullo F, Moreira NFF, Ribeiro AR et al (2019) Heterogeneous photocatalysis using UVA-LEDs for the removal of antibiotics and antibiotic resistant bacteria from urban wastewater treatment plant effluents. Chem Eng J 367:304–313. https://doi.org/10.1016/j.cej.2019.02.012

Bytesnikova Z, Richtera L, Smerkova K, Adam V (2019) Graphene oxide as a tool for antibiotic-resistant gene removal: a review. Environ Sci Pollut Res 26:20148–20163. https://doi.org/10.1007/s11356-019-05283-y

Cacace D, Fatta-Kassinos D, Manaia CM et al (2019) Antibiotic resistance genes in treated wastewater and in the receiving water bodies: a pan-European survey of urban settings. Water Res 162:320–330. https://doi.org/10.1016/j.watres.2019.06.039

Cardinal P, Anderson JC, Carlson JC et al (2014) Macrophytes may not contribute significantly to removal of nutrients, pharmaceuticals, and antibiotic resistance in model surface constructed wetlands. Sci Total Environ 482–483:294–304. https://doi.org/10.1016/j.scitotenv.2014.02.095

Chang PH, Juhrend B, Olson TM et al (2017) Degradation of extracellular antibiotic resistance genes with UV254 treatment. Environ Sci Technol 51:6185–6192. https://doi.org/10.1021/acs.est.7b01120

Chen H, Zhang M (2013) Effects of advanced treatment systems on the removal of antibiotic resistance genes in wastewater treatment plants from Hangzhou, China. Environ Sci Technol 47:8157–8163. https://doi.org/10.1021/es401091y

Chen J, Liu YS, Su HC et al (2015) Removal of antibiotics and antibiotic resistance genes in rural wastewater by an integrated constructed wetland. Environ Sci Pollut Res 22:1794–1803. https://doi.org/10.1007/s11356-014-2800-4

Chen J, Ying GG, Wei XD et al (2016) Removal of antibiotics and antibiotic resistance genes from domestic sewage by constructed wetlands: effect of flow configuration and plant species. Sci Total Environ 571:974–982. https://doi.org/10.1016/j.scitotenv.2016.07.085

Chen L, Zhou Z, Shen C, Xu Y (2020) Inactivation of antibiotic-resistant bacteria and antibiotic resistance genes by electrochemical oxidation/electro-Fenton process. Water Sci Technol 81:2221–2231. https://doi.org/10.2166/wst.2020.282

Cheng H, Hong PY (2017) Removal of antibiotic-resistant bacteria and antibiotic resistance genes affected by varying degrees of fouling on anaerobic microfiltration membranes. Environ Sci Technol 51:12200–12209. https://doi.org/10.1021/acs.est.7b03798

Christgen B, Yang Y, Ahammad SZ et al (2015) Metagenomics shows that low-energy anaerobic-aerobic treatment reactors reduce antibiotic resistance gene levels from domestic wastewater. Environ Sci Technol 49:2577–2584. https://doi.org/10.1021/es505521w

Czekalski N, Imminger S, Salhi E et al (2016) Inactivation of antibiotic resistant bacteria and resistance genes by ozone: from laboratory experiments to full-scale wastewater treatment. Environ Sci Technol 50:11862–11871. https://doi.org/10.1021/acs.est.6b02640

De la Obra JI, López JLC, Ibáñez GR et al (2019) Kinetic assessment of antibiotic resistant bacteria inactivation by solar photo-Fenton in batch and continuous flow mode for wastewater reuse. Water Res 159:184–191. https://doi.org/10.1016/j.watres.2019.04.059

Destiani R, Templeton MR, Kowalski W (2017) Relative ultraviolet sensitivity of selected antibiotic resistance genes in waterborne bacteria. Environ Eng Sci 35:770–774. https://doi.org/10.1089/ees.2017.0179

Destiani R, Templeton MR, Department of Civil and Environmental Engineering, Imperial College London, London, United Kingdom (2019) Chlorination and ultraviolet disinfection of antibiotic-resistant bacteria and antibiotic resistance genes in drinking water. AIMS Environ Sci 6:222–241. https://doi.org/10.3934/environsci.2019.3.222

Di Cesare A, Eckert EM, D'Urso S et al (2016) Co-occurrence of integrase 1, antibiotic and heavy metal resistance genes in municipal wastewater treatment plants. Water Res 94:208–214. https://doi.org/10.1016/j.watres.2016.02.049

Divyapriya G, Nidheesh PV (2020) Importance of graphene in the electro-Fenton process. ACS Omega 5:4725–4732. https://doi.org/10.1021/acsomega.9b04201

Divyapriya G, Nambi IM, Senthilnathan J (2017) An innate quinone functionalized electrochemically exfoliated graphene/Fe3O4 composite electrode for the continuous generation of reactive oxygen species. Chem Eng J 316:964–977. https://doi.org/10.1016/j.cej.2017.01.074

Divyapriya G, Nambi I, Senthilnathan J (2018a) Ferrocene functionalized graphene based electrode for the electro-Fenton oxidation of ciprofloxacin. Chemosphere 209:113–123. https://doi.org/10.1016/j.chemosphere.2018.05.148

Divyapriya G, Srinivasan R, Nambi IM, Senthilnathan J (2018b) Highly active and stable ferrocene functionalized graphene encapsulated carbon felt array - a novel rotating disc electrode for electro-Fenton oxidation of pharmaceutical compounds. Electrochim Acta 283:858–870. https://doi.org/10.1016/j.electacta.2018.06.186

Divyapriya G, Thangadurai P, Nambi I (2018c) Green approach to produce a graphene thin film on a conductive LCD matrix for the oxidative transformation of ciprofloxacin. ACS Sustain Chem Eng 6:3453–3462. https://doi.org/10.1021/acssuschemeng.7b03687

Divyapriya G, Kumar K, Nambi I (2019) Development of a novel graphene / Co3O4 composite for hybrid capacitive deionization system. Desalination 451:102–110. https://doi.org/10.1016/j.desal.2018.03.023

Dodd MC (2012) Potential impacts of disinfection processes on elimination and deactivation of antibiotic resistance genes during water and wastewater treatment. J Environ Monit 14:1754–1771. https://doi.org/10.1039/C2EM00006G

Drlica K (2003) The mutant selection window and antimicrobial resistance. J Antimicrob Chemother 52:11–17. https://doi.org/10.1093/jac/dkg269

Du J, Geng J, Ren H et al (2015) Variation of antibiotic resistance genes in municipal wastewater treatment plant with A2O-MBR system. Environ Sci Pollut Res 22:3715–3726. https://doi.org/10.1007/s11356-014-3552-x

Fang H, Zhang Q, Nie X et al (2017) Occurrence and elimination of antibiotic resistance genes in a long-term operation integrated surface flow constructed wetland. Chemosphere 173:99–106. https://doi.org/10.1016/j.chemosphere.2017.01.027

Ferro G, Guarino F, Castiglione S, Rizzo L (2016) Antibiotic resistance spread potential in urban wastewater effluents disinfected by UV/H2O2 process. Sci Total Environ 560–561:29–35. https://doi.org/10.1016/j.scitotenv.2016.04.047

Fiorentino A, Ferro G, Alferez MC et al (2015) Inactivation and regrowth of multidrug resistant bacteria in urban wastewater after disinfection by solar-driven and chlorination processes. J Photochem Photobiol B Biol 148:43–50. https://doi.org/10.1016/j.jphotobiol.2015.03.029

Fiorentino A, Esteban B, Garrido-Cardenas JA et al (2019) Effect of solar photo-Fenton process in raceway pond reactors at neutral pH on antibiotic resistance determinants in secondary treated urban wastewater. J Hazard Mater 378:120737. https://doi.org/10.1016/j.jhazmat.2019.06.014

Founou LL, Founou RC, Essack SY (2016) Antibiotic resistance in the food chain: a developing country-perspective. Front Microbiol 7:1–19. https://doi.org/10.3389/fmicb.2016.01881

Frost LS, Leplae R, Summers AO, Toussaint A (2005) Mobile genetic elements: the agents of open source evolution. Nat Rev Microbiol 3:722–732. https://doi.org/10.1038/nrmicro1235

Gao P, Xu W, Ruan X et al (2018) Long-term impact of a tetracycline concentration gradient on the bacterial resistance in anaerobic-aerobic sequential bioreactors. Chemosphere 205:308–316. https://doi.org/10.1016/j.chemosphere.2018.04.135

Garrido-Cardenas JA, Esteban-García B, Agüera A et al (2020) Wastewater treatment by advanced oxidation process and their worldwide research trends. Int J Environ Res Public Health:17. https://doi.org/10.3390/ijerph17010170

Ghernaout D, Elboughdiri N (2020a) Advanced oxidation processes for wastewater treatment: facts and future trends. Open Access Library J 07:e6139. https://doi.org/10.4236/oalib.1106139

Ghernaout D, Elboughdiri N (2020b) Removing antibiotic-resistant bacteria (ARB) carrying genes (ARGs): challenges and future trends. Open Access Libr J 07:1–16. https://doi.org/10.4236/oalib.1106003

Giannakis S, Le T-TM, Entenza JM, Pulgarin C (2018a) Solar photo-Fenton disinfection of 11 antibiotic-resistant bacteria (ARB) and elimination of representative AR genes. Evidence that antibiotic resistance does not imply resistance to oxidative treatment. Water Res 143:334–345. https://doi.org/10.1016/j.watres.2018.06.062

Giannakis S, Voumard M, Rtimi S, Pulgarin C (2018b) Bacterial disinfection by the photo-Fenton process: extracellular oxidation or intracellular photo-catalysis? Appl Catal B Environ 227:285–295. https://doi.org/10.1016/j.apcatb.2018.01.044

Giannakis S, Watts S, Rtimi S, Pulgarin C (2018c) Solar light and the photo-Fenton process against antibiotic resistant bacteria in wastewater: a kinetic study with a streptomycin-resistant strain. Catal Today 313:86–93. https://doi.org/10.1016/j.cattod.2017.10.033

Gracia R, Aragües JL, Ovelleiro JL (1996) Study of the catalytic ozonation of humic substances in water and their ozonation byproducts. Ozone Sci Eng 18:195–208. https://doi.org/10.1080/01919519608547326

Grehs BWN, Lopes AR, Moreira NFF et al (2019) Removal of microorganisms and antibiotic resistance genes from treated urban wastewater: a comparison between aluminium sulphate and tannin coagulants. Water Res:166. https://doi.org/10.1016/j.watres.2019.115056

Gullberg E, Cao S, Berg OG et al (2011) Selection of resistant bacteria at very low antibiotic concentrations. PLoS Pathog 7:e1002158. https://doi.org/10.1371/journal.ppat.1002158

Guo MT, Zhang GS (2017) Graphene oxide in the water environment could affect tetracycline-antibiotic resistance. Chemosphere 183:197–203. https://doi.org/10.1016/j.chemosphere.2017.04.145

Guo M-T, Yuan Q-B, Yang J (2015) Distinguishing effects of ultraviolet exposure and chlorination on the horizontal transfer of antibiotic resistance genes in municipal wastewater. Environ Sci Technol 49:5771–5778. https://doi.org/10.1021/acs.est.5b00644

Guo J, Li J, Chen H et al (2017a) Metagenomic analysis reveals wastewater treatment plants as hotspots of antibiotic resistance genes and mobile genetic elements. Water Res 123:468–478. https://doi.org/10.1016/j.watres.2017.07.002

Guo C, Wang K, Hou S et al (2017b) H2O2 and/or TiO2 photocatalysis under UV irradiation for the removal of antibiotic resistant bacteria and their antibiotic resistance genes. J Hazard Mater 323:710–718. https://doi.org/10.1016/j.jhazmat.2016.10.041

He H, Zhou P, Shimabuku KK et al (2019) Degradation and deactivation of bacterial antibiotic resistance genes during exposure to free chlorine, Monochloramine, chlorine dioxide, ozone, ultraviolet light, and hydroxyl radical. Environ Sci Technol 53:2013–2026. https://doi.org/10.1021/acs.est.8b04393

Hegstad K, Mikalsen T, Coque TM et al (2010) Mobile genetic elements and their contribution to the emergence of antimicrobial resistant enterococcus faecalis and enterococcus faecium. Clin Microbiol Infect 16:541–554. https://doi.org/10.1111/j.1469-0691.2010.03226.x

Hembach N, Alexander J, Hiller C et al (2019) Dissemination prevention of antibiotic resistant and facultative pathogenic bacteria by ultrafiltration and ozone treatment at an urban wastewater treatment plant. Sci Rep 9:1–12. https://doi.org/10.1038/s41598-019-49263-1

Henderson R, Sharp E, Jarvis P et al (2006) Identifying the linkage between particle characteristics and understanding coagulation performance. Water Sci Technol Water Supply 6:31–38. https://doi.org/10.2166/ws.2006.005

Hendriksen RS, Munk P, Njage P et al (2019) Global monitoring of antimicrobial resistance based on metagenomics analyses of urban sewage. Nat Commun:10. https://doi.org/10.1038/s41467-019-08853-3

Hoyano Y, Bacon V, Summons RE et al (1973) Chlorination studies. IV1. The reaction of aqueous hypochlorous acid with pyrimidine and purine bases. Biochem Biophys Res Commun 53:1195–1199. https://doi.org/10.1016/0006-291X(73)90591-3

Huang J-J, Hu H-Y, Tang F et al (2011) Inactivation and reactivation of antibiotic-resistant bacteria by chlorination in secondary effluents of a municipal wastewater treatment plant. Water Res 45:2775–2781. https://doi.org/10.1016/j.watres.2011.02.026

Huang J-J, Hu H-Y, Wu Y-H et al (2013) Effect of chlorination and ultraviolet disinfection on tetA-mediated tetracycline resistance of Escherichia coli. Chemosphere 90:2247–2253. https://doi.org/10.1016/j.chemosphere.2012.10.008

Huang X, Liu C, Li K et al (2015) Performance of vertical up-flow constructed wetlands on swine wastewater containing tetracyclines and tet genes. Water Res 70:109–117. https://doi.org/10.1016/j.watres.2014.11.048

Iakovides IC, Michael-Kordatou I, Moreira NFF et al (2019) Continuous ozonation of urban wastewater: removal of antibiotics, antibiotic-resistant Escherichia coli and antibiotic resistance genes and phytotoxicity. Water Res 159:333–347. https://doi.org/10.1016/j.watres.2019.05.025

Jiang Q, Yin H, Li G et al (2017) Elimination of antibiotic-resistance bacterium and its associated/dissociative blaTEM-1 and aac(3)-II antibiotic-resistance genes in aqueous system via photoelectrocatalytic process. Water Res 125:219–226. https://doi.org/10.1016/j.watres.2017.08.050

Kanchanapally R, Nellore BPV, Sinha SS et al (2015) Antimicrobial peptide-conjugated graphene oxide membrane for efficient removal and effective killing of multiple drug resistant bacteria. RSC Adv 5:18881–18887. https://doi.org/10.1039/c5ra01321f

Kappell AD, Kimbell LK, Seib MD et al (2018) Removal of antibiotic resistance genes in an anaerobic membrane bioreactor treating primary clarifier effluent at 20 °C. Environ Sci Water Res Technol 4:1783–1793. https://doi.org/10.1039/c8ew00270c

Karaolia P, Michael I, García-Fernández I et al (2014) Reduction of clarithromycin and sulfamethoxazole-resistant enterococcus by pilot-scale solar-driven Fenton oxidation. Sci Total Environ 468–469:19–27. https://doi.org/10.1016/j.scitotenv.2013.08.027

Karaolia P, Michael-Kordatou I, Hapeshi E et al (2018) Removal of antibiotics, antibiotic-resistant bacteria and their associated genes by graphene-based TiO2 composite photocatalysts under solar radiation in urban wastewaters. Appl Catal B Environ 224:810–824. https://doi.org/10.1016/j.apcatb.2017.11.020

Kawara O (1977) Ozone and chlorine in wastewater disinfection

Köhler T, Michea-Hamzehpour M, Plesiat P et al (1997) Differential selection of multidrug efflux systems by quinolones in Pseudomonas aeruginosa. Antimicrob Agents Chemother 41:2540–2543. https://doi.org/10.1128/AAC.41.11.2540

Krzeminski P, Feys E, Anglès d'Auriac M et al (2020) Combined membrane filtration and 265 nm UV irradiation for effective removal of cell free antibiotic resistance genes from feed water and concentrate. J Memb Sci 598:117676. https://doi.org/10.1016/j.memsci.2019.117676

Kurasam J, Sihag P, Mandal PK, Sarkar S (2018) Presence of fluoroquinolone resistance with persistent occurrence of gyrA gene mutations in a municipal wastewater treatment plant in India. Chemosphere 211:817–825. https://doi.org/10.1016/j.chemosphere.2018.08.011

Lamba M, Gupta S, Shukla R et al (2018) Carbapenem resistance exposures via wastewaters across New Delhi. Environ Int 119:302–308. https://doi.org/10.1016/j.envint.2018.07.004

Le TH, Ng C, Tran NH et al (2018) Removal of antibiotic residues, antibiotic resistant bacteria and antibiotic resistance genes in municipal wastewater by membrane bioreactor systems. Water Res 145:498–508. https://doi.org/10.1016/j.watres.2018.08.060

Lee J, Yim Y, Kim S et al (2016) In-depth investigation of the interaction between DNA and nano-sized graphene oxide. Carbon N Y 97:92–98. https://doi.org/10.1016/j.carbon.2015.07.093

Li B, Yang Y, Ma L et al (2015) Metagenomic and network analysis reveal wide distribution and co-occurrence of environmental antibiotic resistance genes. ISME J 9:2490–2502. https://doi.org/10.1038/ismej.2015.59

Li L-G, Xia Y, Zhang T (2017a) Co-occurrence of antibiotic and metal resistance genes revealed in complete genome collection. ISME J 11:651–662. https://doi.org/10.1038/ismej.2016.155

Li N, Sheng GP, Lu YZ et al (2017b) Removal of antibiotic resistance genes from wastewater treatment plant effluent by coagulation. Water Res 111:204–212. https://doi.org/10.1016/j.watres.2017.01.010

Li Q, Chang W, Zhang H et al (2019a) The role of plasmids in the multiple antibiotic resistance transfer in ESBLs-producing escherichia coli isolated from wastewater treatment plants. Front Microbiol:10. https://doi.org/10.3389/fmicb.2019.00633

Li B, Qiu Y, Li J et al (2019b) Removal of antibiotic resistance genes in four full-scale membrane bioreactors. Sci Total Environ 653:112–119. https://doi.org/10.1016/j.scitotenv.2018.10.305

Liu S, Zeng TH, Hofmann M et al (2011) Antibacterial activity of graphite, graphite oxide, graphene oxide, and reduced graphene oxide: membrane and oxidative stress. ACS Nano 5:6971–6980. https://doi.org/10.1021/nn202451x

Liu L, Liu C, Zheng J et al (2013) Elimination of veterinary antibiotics and antibiotic resistance genes from swine wastewater in the vertical flow constructed wetlands. Chemosphere 91:1088–1093. https://doi.org/10.1016/j.chemosphere.2013.01.007

Liu S-S, Qu H-M, Yang D et al (2018) Chlorine disinfection increases both intracellular and extracellular antibiotic resistance genes in a full-scale wastewater treatment plant. Water Res 136:131–136. https://doi.org/10.1016/j.watres.2018.02.036

Lu J, Zhang Y, Wu J et al (2020) Fate of antibiotic resistance genes in reclaimed water reuse system with integrated membrane process. J Hazard Mater 382:121025. https://doi.org/10.1016/j.jhazmat.2019.121025

Macauley JJ, Qiang Z, Adams CD et al (2006) Disinfection of swine wastewater using chlorine, ultraviolet light and ozone. Water Res 40:2017–2026. https://doi.org/10.1016/j.watres.2006.03.021

Mackuľak T, Nagyová K, Faberová M et al (2015) Utilization of Fenton-like reaction for antibiotics and resistant bacteria elimination in different parts of WWTP. Environ Toxicol Pharmacol 40:492–497. https://doi.org/10.1016/j.etap.2015.07.002

Malaeb L, Ayoub GM (2011) Reverse osmosis technology for water treatment: state of the art review. Desalination 267:1–8. https://doi.org/10.1016/j.desal.2010.09.001

Manaia CM, Rocha J, Scaccia N et al (2018) Antibiotic resistance in wastewater treatment plants: tackling the black box. Environ Int 115:312–324. https://doi.org/10.1016/j.envint.2018.03.044

Martinez JL, Baquero F (2000) Mutation frequencies and antibiotic resistance. Antimicrob Agents Chemother 44:1771–1777. https://doi.org/10.1128/AAC.44.7.1771-1777.2000

McKinney CW, Pruden A (2012) Ultraviolet disinfection of antibiotic resistant bacteria and their antibiotic resistance genes in water and wastewater. Environ Sci Technol 46:13393–13400. https://doi.org/10.1021/es303652q

Michael SG, Michael-Kordatou I, Beretsou VG et al (2019) Solar photo-Fenton oxidation followed by adsorption on activated carbon for the minimisation of antibiotic resistance determinants and toxicity present in urban wastewater. Appl Catal B Environ 244:871–880. https://doi.org/10.1016/j.apcatb.2018.12.030

Michael-Kordatou I, Andreou R, Iacovou M et al (2017) On the capacity of ozonation to remove antimicrobial compounds, resistant bacteria and toxicity from urban wastewater effluents. J Hazard Mater 323:414–425. https://doi.org/10.1016/j.jhazmat.2016.02.023

Miller JH, Novak JT, Knocke WR et al (2013) Effect of silver nanoparticles and antibiotics on antibiotic resistance genes in anaerobic digestion. Water Environ Res 85:411–421. https://doi.org/10.2175/106143012x13373575831394

Miller JH, Novak JT, Knocke WR, Pruden A (2014) Elevation of antibiotic resistance genes at cold temperatures: implications for winter storage of sludge and biosolids. Lett Appl Microbiol 59:587–593. https://doi.org/10.1111/lam.12325

Minarini LAR, Darini ALC (2012) Mutations in the quinolone resistance-determining regions of gyrA and parC in Enterobacteriaceae isolates from Brazil. Braz J Microbiol 43:1309–1314. https://doi.org/10.1590/S1517-838220120004000010

Moreira NFF, Sousa JM, Macedo G et al (2016) Photocatalytic ozonation of urban wastewater and surface water using immobilized TiO2 with LEDs: micropollutants, antibiotic resistance genes and estrogenic activity. Water Res 94:10–22. https://doi.org/10.1016/j.watres.2016.02.003

Munir M, Wong K, Xagoraraki I (2011) Release of antibiotic resistant bacteria and genes in the effluent and biosolids of five wastewater utilities in Michigan. Water Res 45:681–693. https://doi.org/10.1016/j.watres.2010.08.033

Nybo T, Dieterich S, Gamon LF et al (2019) Chlorination and oxidation of the extracellular matrix protein laminin and basement membrane extracts by hypochlorous acid and myeloperoxidase. Redox Biol 20:496–513. https://doi.org/10.1016/j.redox.2018.10.022

Oh J, Salcedo DE, Medriano CA, Kim S (2014) Comparison of different disinfection processes in the effective removal of antibiotic-resistant bacteria and genes. J Environ Sci 26:1238–1242. https://doi.org/10.1016/S1001-0742(13)60594-X

Öncü NB, Oncu NB, Menceloğlu YZ et al (2011) Comparison of the effectiveness of chlorine, ozone, and photocatalytic disinfection in reducing the risk of antibiotic resistance pollution. J Adv Oxidat Technol 14:196–203

Oneby MA, Bromley CO, Borchardt JH, Harrison DS (2010) Ozone treatment of secondary effluent at U.S. municipal wastewater treatment plants. Ozone Sci Eng 32:43–55. https://doi.org/10.1080/01919510903482780

Pak G, Salcedo DE, Lee H et al (2016) Comparison of antibiotic resistance removal efficiencies using ozone disinfection under different pH and suspended solids and humic substance concentrations. Environ Sci Technol 50:7590–7600. https://doi.org/10.1021/acs.est.6b01340

Pang Y, Huang J, Xi J et al (2016) Effect of ultraviolet irradiation and chlorination on ampicillin-resistant Escherichia coli and its ampicillin resistance gene. Front Environ Sci Eng 10:522–530. https://doi.org/10.1007/s11783-015-0779-9

Pazda M, Kumirska J, Stepnowski P, Mulkiewicz E (2019) Antibiotic resistance genes identified in wastewater treatment plant systems – a review. Sci Total Environ 697:134023. https://doi.org/10.1016/j.scitotenv.2019.134023

Peña M, Coca M, González G, et al (2003) Chemical oxidation of wastewater from molasses fermentation with ozone. Chemosphere 51:893–900. https://doi.org/10.1016/S0045-6535(03)00159-0

Pruden A (2014) Balancing water sustainability and public health goals in the face of growing concerns about antibiotic resistance. Environ Sci Technol 48:5–14. https://doi.org/10.1021/es403883p

Pruden A, Pei R, Storteboom H, Carlson KH (2006) Antibiotic resistance genes as emerging contaminants : studies in northern Colorado. Environ Sci Technol 40:7445–7450. https://doi.org/10.1021/es060413l

Prütz WA (1996) Hypochlorous acid interactions with thiols, nucleotides, DNA, and other biological substrates. Arch Biochem Biophys 332:110–120. https://doi.org/10.1006/abbi.1996.0322

Qiu Z, Yu Y, Chen Z et al (2012) Nanoalumina promotes the horizontal transfer of multiresistance genes mediated by plasmids across genera. Proc Natl Acad Sci U S A 109:4944–4949. https://doi.org/10.1073/pnas.1107254109

Qiu Z, Shen Z, Qian D et al (2015) Effects of nano-TiO2 on antibiotic resistance transfer mediated by RP4 plasmid. Nanotoxicology 9:895–904. https://doi.org/10.3109/17435390.2014.991429

Quero-Pastor MJ, Garrido-Perez MC, Acevedo A, Quiroga JM (2014) Ozonation of ibuprofen: A degradation and toxicity study. Sci Total Environ 466–467:957–964. https://doi.org/10.1016/j.scitotenv.2013.07.067

Ren S, Boo C, Guo N et al (2018) Photocatalytic reactive ultrafiltration membrane for removal of antibiotic resistant bacteria and antibiotic resistance genes from wastewater effluent. Environ Sci Technol 52:8666–8673. https://doi.org/10.1021/acs.est.8b01888

Richardson SD, Thruston ADJ, Caughran TV, et al (1998) Chemical by-products of chlorine and alternative disinfectants. Food technology (USA)

Rodríguez-Chueca J, Varella della Giustina S, Rocha J, et al (2019) Assessment of full-scale tertiary wastewater treatment by UV-C based-AOPs: removal or persistence of antibiotics and antibiotic resistance genes? Sci Total Environ 652:1051–1061. https://doi.org/10.1016/j.scitotenv.2018.10.223

Rosal R, Rodríguez A, Perdigón-Melón JA, et al (2008) Removal of pharmaceuticals and kinetics of mineralization by O3/H2O2 in a biotreated municipal wastewater. Water Res 42:3719–3728. https://doi.org/10.1016/j.watres.2008.06.008

Sabri NA, Schmitt H, Van Der Zaan B et al (2020) Prevalence of antibiotics and antibiotic resistance genes in a wastewater effluent-receiving river in the Netherlands. J Environ Chem Eng 8:102245. https://doi.org/10.1016/j.jece.2018.03.004

Salas Orozco MF, Niño-Martínez N, Martínez-Castañón GA et al (2019) Molecular mechanisms of bacterial resistance to metal and metal oxide nanoparticles. Int J Mol Sci 20. https://doi.org/10.3390/ijms20112808

Sandegren L (2014) Selection of antibiotic resistance at very low antibiotic concentrations. Ups J Med Sci 119:103–107. https://doi.org/10.3109/03009734.2014.904457

Sasikaladevi R, Eswari VK, Nambi IM (2020) Antibiotic resistance and sanitation in India: current situation and future perspectives. In: The handbook of environmental chemistry. Springer, Berlin, Heidelberg, pp 1–28

Schwermer CU, Krzeminski P, Wennberg AC et al (2018) Removal of antibiotic resistant E. coli in two Norwegian wastewater treatment plants and by nano- and ultra-filtration processes. Water Sci Technol 77:1115–1126. https://doi.org/10.2166/wst.2017.642

Serna-Galvis EA, Vélez-Peña E, Osorio-Vargas P et al (2019) Inactivation of carbapenem-resistant Klebsiella pneumoniae by photo-Fenton: residual effect, gene evolution and modifications with citric acid and persulfate. Water Res 161:354–363. https://doi.org/10.1016/j.watres.2019.06.024

Shang C, Blatchley ER (1999) Differentiation and quantification of free chlorine and inorganic chloramines in aqueous solution by MIMS. Environ Sci Technol 33:2218–2223. https://doi.org/10.1021/es9812103

Sharma VK, Johnson N, Cizmas L et al (2016) A review of the influence of treatment strategies on antibiotic resistant bacteria and antibiotic resistance genes. Chemosphere 150:702–714. https://doi.org/10.1016/j.chemosphere.2015.12.084

Sharma VK, Yu X, McDonald TJ et al (2019) Elimination of antibiotic resistance genes and control of horizontal transfer risk by UV-based treatment of drinking water: a mini review. Front Environ Sci Eng 13:37. https://doi.org/10.1007/s11783-019-1122-7

Sillanpää M, Ncibi MC, Matilainen A, Vepsäläinen M (2018) Removal of natural organic matter in drinking water treatment by coagulation: a comprehensive review. Chemosphere 190:54–71. https://doi.org/10.1016/j.chemosphere.2017.09.113

Sivagami K, Vignesh VJ, Srinivasan R, et al (2018) Antibiotic usage, residues and resistance genes from food animals to human and environment: an Indian scenario. J Environ Chem Eng 0–1. https://doi.org/10.1016/j.jece.2018.02.029

Slipko K, Reif D, Wögerbauer M et al (2019) Removal of extracellular free DNA and antibiotic resistance genes from water and wastewater by membranes ranging from microfiltration to reverse osmosis. Water Res 164:114916. https://doi.org/10.1016/j.watres.2019.114916

Song HL, Zhang S, Guo J et al (2018) Vertical up-flow constructed wetlands exhibited efficient antibiotic removal but induced antibiotic resistance genes in effluent. Chemosphere 203:434–441. https://doi.org/10.1016/j.chemosphere.2018.04.006

Sousa JM, Macedo G, Pedrosa M et al (2017) Ozonation and UV254nm radiation for the removal of microorganisms and antibiotic resistance genes from urban wastewater. J Hazard Mater 323:434–441. https://doi.org/10.1016/j.jhazmat.2016.03.096

Srinivasan R, Nambi IM (2020) Liquid crystal display electrode-assisted bio-electroperoxone treatment train for the abatement of organic contaminants in a pharmaceutical wastewater. Environ Sci Pollut Res 27:29737–29748. https://doi.org/10.1007/s11356-019-06898-x

Sun Y, Shen YX, Liang P et al (2016) Multiple antibiotic resistance genes distribution in ten large-scale membrane bioreactors for municipal wastewater treatment. Bioresour Technol 222:100–106. https://doi.org/10.1016/j.biortech.2016.09.117

Thorpe KE, Joski P, Johnston KJ (2018) Antibiotic-resistant infection treatment costs have doubled since 2002, now exceeding $2 billion annually. Health Aff 37:662–669. https://doi.org/10.1377/hlthaff.2017.1153

Van Geluwe S, Braeken L, Van der Bruggen B (2011) Ozone oxidation for the alleviation of membrane fouling by natural organic matter: A review. Water Res 45:3551–3570. https://doi.org/10.1016/j.watres.2011.04.016

Venkobachar C, Iyengar L, Prabhakara Rao AVS (1977) Mechanism of disinfection: effect of chlorine on cell membrane functions. Water Res 11:727–729. https://doi.org/10.1016/0043-1354(77)90114-2

Virto R, Mañas P, Álvarez I et al (2005) Membrane damage and microbial inactivation by chlorine in the absence and presence of a chlorine-demanding substrate. Appl Environ Microbiol 71:5022–5028. https://doi.org/10.1128/AEM.71.9.5022-5028.2005

Wang L, Hu C, Shao L (2017) The antimicrobial activity of nanoparticles: present situation and prospects for the future. Int J Nanomedicine 12:1227–1249. https://doi.org/10.2147/IJN.S121956

Wang X, Yang F, Zhao J et al (2018) Bacterial exposure to ZnO nanoparticles facilitates horizontal transfer of antibiotic resistance genes. NanoImpact 10:61–67. https://doi.org/10.1016/j.impact.2017.11.006

Wert EC, Rosario-Ortiz FL, Snyder SA (2009) Using ultraviolet absorbance and color to assess pharmaceutical oxidation during ozonation of wastewater. Environ Sci Technol 43:4858–4863. https://doi.org/10.1021/es803524a

WHO (2014) Antimicrobial resistance: global report on surveillance. http://www.who.int/drugresistance/documents/surveillancereport/en

WHO (2017) Antibacterial agents in clinical development: an analysis of the antibacterial clinical development pipeline, including tuberculosis. World Heal Organ WHO/EMP/IAU/201711. https://apps.who.int/iris/bitstream/handle/10665/258965/WHO-EMP-IAU-2017.11-eng.pdf

Wordofa DN, Walker SL, Liu H (2017) Sulfate radical-induced disinfection of pathogenic Escherichia coli O157:H7 via iron-activated persulfate. Environ Sci Technol Lett 4:154–160. https://doi.org/10.1021/acs.estlett.7b00035

Xiang Q, Yu J, Jaroniec M (2012) Graphene-based semiconductor photocatalysts. Chem Soc Rev 41:782–796. https://doi.org/10.1039/c1cs15172j

Xu J, Xu Y, Wang H et al (2015) Occurrence of antibiotics and antibiotic resistance genes in a sewage treatment plant and its effluent-receiving river. Chemosphere 119:1379–1385. https://doi.org/10.1016/j.chemosphere.2014.02.040

Yang Y, Li B, Zou S et al (2014) Fate of antibiotic resistance genes in sewage treatment plant revealed by metagenomic approach. Water Res 62:97–106. https://doi.org/10.1016/j.watres.2014.05.019

Yin X, Deng Y, Ma L et al (2019) Exploration of the antibiotic resistome in a wastewater treatment plant by a nine-year longitudinal metagenomic study. Environ Int 133:105270. https://doi.org/10.1016/j.envint.2019.105270

Yoon Y, Chung HJ, Wen Di DY et al (2017) Inactivation efficiency of plasmid-encoded antibiotic resistance genes during water treatment with chlorine, UV, and UV/H2O2. Water Res 123:783–793. https://doi.org/10.1016/j.watres.2017.06.056

Yoon Y, Dodd MC, Lee Y (2018) Elimination of transforming activity and gene degradation during UV and UV/H2O2 treatment of plasmid-encoded antibiotic resistance genes. Environ Sci Water Res Technol 4:1239–1251. https://doi.org/10.1039/C8EW00200B

Yu W, Zhan S, Shen Z et al (2017) Efficient removal mechanism for antibiotic resistance genes from aquatic environments by graphene oxide nanosheet. Chem Eng J 313:836–846. https://doi.org/10.1016/j.cej.2016.10.107

Yuan Q-B, Guo M-T, Yang J (2015) Fate of antibiotic resistant bacteria and genes during wastewater chlorination: implication for antibiotic resistance control. PLoS One 10:e0119403. https://doi.org/10.1371/journal.pone.0119403

Zhang J, Nosaka Y (2014) Mechanism of the OH radical generation in photocatalysis with TiO2 of different crystalline types. J Phys Chem C 118:10824–10832. https://doi.org/10.1021/jp501214m

Zhang Y, Zhuang Y, Geng J et al (2015) Inactivation of antibiotic resistance genes in municipal wastewater effluent by chlorination and sequential UV/chlorination disinfection. Sci Total Environ 512–513:125–132. https://doi.org/10.1016/j.scitotenv.2015.01.028

Zhang Y, Zhuang Y, Geng J et al (2016a) Reduction of antibiotic resistance genes in municipal wastewater effluent by advanced oxidation processes. Sci Total Environ 550:184–191. https://doi.org/10.1016/j.scitotenv.2016.01.078

Zhang S, Lin W, Yu X (2016b) Effects of full-scale advanced water treatment on antibiotic resistance genes in the Yangtze Delta area in China. FEMS Microbiol Ecol 92:1–9. https://doi.org/10.1093/femsec/fiw065

Zhang T, Hu Y, Jiang L et al (2019) Removal of antibiotic resistance genes and control of horizontal transfer risk by UV, chlorination and UV/chlorination treatments of drinking water. Chem Eng J 358:589–597. https://doi.org/10.1016/j.cej.2018.09.218

Zheng H, Ma R, Gao M et al (2018a) Antibacterial applications of graphene oxides: structure-activity relationships, molecular initiating events and biosafety. Sci Bull 63:133–142. https://doi.org/10.1016/j.scib.2017.12.012

Zheng HS, Guo WQ, Wu QL et al (2018b) Electro-peroxone pretreatment for enhanced simulated hospital wastewater treatment and antibiotic resistance genes reduction. Environ Int 115:70–78. https://doi.org/10.1016/j.envint.2018.02.043

Zhou C, Wu J, Dong L et al (2020) Removal of antibiotic resistant bacteria and antibiotic resistance genes in wastewater effluent by UV-activated persulfate. J Hazard Mater 388:122070. https://doi.org/10.1016/j.jhazmat.2020.122070

Zhu Y, Wang Y, Zhou S et al (2018) Robust performance of a membrane bioreactor for removing antibiotic resistance genes exposed to antibiotics: role of membrane foulants. Water Res 130:139–150. https://doi.org/10.1016/j.watres.2017.11.067

Zhuang Y, Ren H, Geng J et al (2015) Inactivation of antibiotic resistance genes in municipal wastewater by chlorination, ultraviolet, and ozonation disinfection. Environ Sci Pollut Res 22:7037–7044. https://doi.org/10.1007/s11356-014-3919-z

Zou W, Li X, Lai Z et al (2016) Graphene oxide inhibits antibiotic uptake and antibiotic resistance gene propagation. ACS Appl Mater Interfaces 8:33165–33174. https://doi.org/10.1021/acsami.6b09981

Zuma F, Lin J, Jonnalagadda SB (2009) Ozone-initiated disinfection kinetics of Escherichia coli in water. J Environ Sci Heal - Part A Toxic/Hazardous Subst Environ Eng 44:48–56. https://doi.org/10.1080/10934520802515335

Effective Removal of Naphthalene Adsorbed on Biochar by Low-Frequency Ultrasonication in a Customized Reactor

R. Shruthi, Omkar Gaonkar, R. Mohan Kumar, Debayan Mazumdar, Peramaiah Karthik, Sunil Kumar, Neppolian Bernardshaw, and Paromita Chakraborty

Abstract Naphthalene is a ubiquitous polycyclic aromatic hydrocarbon listed as a priority pollutant by the United States Environmental Protection Agency (USEPA). In this study, we have studied adsorption of naphthalene on biochar produced from sugarcane bagasse and ultrasonically removed the adsorbed naphthalene by low-frequency ultrasonication in a customized reactor. Biochar was produced from sugarcane bagasse (SB) at a pyrolytic temperature of 400 °C. UV and HPLC results suggest that 100% adsorption of naphthalene takes place in 75 min. X-ray diffraction results showed that SB biochar particles were amorphous. A known quantity of naphthalene adsorbed on 10 mg of SB biochar was subjected to ultrasonication in a customized cylindrical reactor (10 cm depth, 5.6 cm diameter) using low-frequency (40 kHz) sonication. More than 80% of naphthalene was desorbed from the biochar in 45 min. Therefore, low-frequency ultrasonication can be used as an effective

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treatment for the removal of such trace organic pollutants present in contaminated sites.

Keywords Naphthalene · Biochar · Adsorption · Ultrasonication

1 Introduction

A large number of toxic compounds are gradually increasing in our surroundings as a result of the enormous quantity of waste generated and dumped everywhere. Rapid population growth and swift technical advancements achieved lately have led to this uncontrollable amount of waste generated. Considering the global waste generation rates, East Asian nations and Pacific regions are the biggest contributors of waste, followed by Latin America, Central and South Asia, Middle East and African nations. Improper treatment of solid waste in developing and underdeveloped regions practicing indiscriminate open dumping and burning activities is posing a great risk to environmental health by directly releasing highly dangerous toxicants (UN Centre of Human Settlements (UNCHS)). Studies have clearly highlighted the presence of persistent organic pollutants (POPs) in different environmental matrices at trace levels originating from day-to-day human activities (Chakraborty et al. 2015; Cheng et al. 2013; Devi et al. 2013; Someya et al. 2010). They pose great risk to our lives, if present, even in trace levels and can be a major threat to all organisms, if their levels go up in the future. Thus, there is a need to control any further increase in their concentrations to avoid such situations. The highly advanced treatment strategies developed earlier could rarely serve their purpose due to economic constraints.

Naphthalene is one of the most abundant polycyclic aromatic hydrocarbons (PAHs) listed as a priority pollutant by the United States Environment Protection Agency (USEPA). It is ubiquitous in sediments, soil, ground water and surface water and abundant in coal and coal tar. It is a component of refined petroleum products and chemical manufacturing processes (Guerin and Boyd 1992). Naphthalene is expected to resist its microbial exploitation due to its low water solubility and high solid-liquid dispensation ratio, which would favour their accumulation in soils and sediments (Pathak et al. 2009). The oxidation and degradation of naphthalene by chemical and biological processes release 1-naphthol into the environment (Cerniglia et al. 1983; Cerniglia et al. 1984; Crosby et al. 1965). The bioactivation of this metabolite can influence the toxicity of naphthalene, making it more cytotoxic than naphthalene (Wilson et al. 1996). In the developing world, naphthalene is abundant in different environmental matrices. Sources include industrial sources, accidental oil spills in ports or harbours, vehicular emission or incomplete combustion of solid waste in open dumpsites. To overcome the hazards associated with naphthalene, an appropriate and feasible treatment strategy must be undertaken.

Biochars are substances with commendable adsorption capabilities produced by subjecting biomass to pyrolytic temperatures. Different varieties of biochars can be produced at various degrees of carbonization that can be used for several purposes, i.e. as fuels and adsorbents, as modifier and carbon sink to reduce CO_2 emissions and in soil amendment and remediation (Mohan et al. 2014). They are effectively used in the remediation of soil and water contaminated with organic pollutants (Mohan et al. 2014; Tang et al. 2013; Zhang et al. 2013). Several feedstock materials like sugarcane bagasse, rice husk, coconut shell, corn stover, peanut shell, rice straw, sewage sludge, etc. can be used in their production. Sugarcane bagasse (SB) is generated in large quantities in tropical and subtropical regions of the globe during sugar manufacturing process (Dreher 1987). They are identified as carbon-rich biomass for biochar and biofuel production (Inyang et al. 2010). SB biochar has exhibited notable adsorption of various pollutants (Hafshejani et al. 2016; Mubarik et al. 2016). Even though biochar has many similarities with activated charcoal, unlike charcoal, they are composed of carbonized organic matter (COM) and non-carbonized organic matter (NOM) (Chen et al. 2008). The presence of NOM, COM, surface and bulk properties highly influence the sorption characteristics of biochar (Chen et al. 2008; Chun et al. 2004; Zhu et al. 2005). Thus, the distinctive features of biochar, e.g. high adsorption capacity, microporous structure, presence of various functional groups and high specific surface area, make them reliable agents for environmental applications (Ahmad et al. 2014; Mohanty et al. 2013). Moreover, low-cost technologies adopted in the production of biochar make them more versatile for real-time studies and industrial projects. Ultrasound has found its application in soil washing, electrokinetic treatment of heavy metals and organic pollutants, degradation of organic pollutants in water and pre-treatment processes (Shrestha et al. 2009). Several studies have reported the efficiency of ultrasonication in the removal of toxic organic pollutants (Shrestha et al. 2009; Thangavadivel et al. 2009). Formation and collapse of cavitation bubbles releasing high pressure and temperature are the two critical phenomena associated with ultrasonication (Mason et al. 2004).

We hypothesized that to handle liquid waste like oil spills or leachate in dumpsites, biochar can be used as a low-cost adsorbent for toxic pollutants and these concentrated pollutants can be further removed by ultrasonication. The major objectives of our study were to (i) prepare biochar from sugarcane bagasse, (ii) characterize biochar, (iii) elucidate the adsorption capacity of a known quantity of naphthalene spiked in the prepared biochar and (iii) remove naphthalene-adsorbed biochar by low-frequency ultrasonication in a customized reactor.

2 Materials and Methods

2.1 Chemicals and Reagents

Naphthalene (99% purity) standard was purchased from Sigma Aldrich, USA. HPLC grade n-hexane and methanol were used in the experimental study. Lab-grade acetone was used to wash SB.

2.2 Biochar Preparation

Sugarcane bagasse (SB) was collected from local vendors, dried and washed with acetone and shredded into pieces prior to biochar preparation. The juice was extracted properly from the sugarcane to limit the sugar content. The dried pieces of SB were filled in crucibles with tight-fitting lids and subjected to pyrolysis at 400 °C in a muffle furnace (Hotking Instruments Company Chennai (1100 °C, 240 V, 6″x6″x12″)). After the cooling period, the crucibles with biochars were removed from the furnace and stored in a desiccator to prevent entry of moisture or air.

2.3 Characterization of SB Biochar

SB biochar was characterized using scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD) and Fourier transform-infrared spectroscopy (FTIR). High-resolution field emission SEM (FEI Quanta FEG 200 SEM) was used to study the SB biochar structure, for which 0.5 g of biochar was exposed to FESEM and EDS analysis. X'Pert PRO diffractometer with CuKα1 ($\lambda = 1.5406$ Å) and 0.02 s^{-1} was used to record the X-ray diffraction patterns of SB biochar. Further, biochar was characterized using FTIR (Perkin-Elmer, Germany) within the spectrum range of 400–4000 cm^{-1} at a resolution of 4 cm^{-1}.

2.4 Adsorption of Naphthalene on SB Biochar

Naphthalene adsorption studies were carried out by batch shaking experiments. 5 mL of 20 ppm naphthalene stock solution was spiked over 10 mg of biochar in a 100 mL standard conical flask. The flasks were kept in an orbital shaker (REMI RS-12R DX orbital shaker from Remi Elektrotechnik Limited, India) at 180 rpm at room temperature. The total shaking period was 75 min, during which one flask was taken out of the shaker every 15 min. The collected samples were centrifuged to

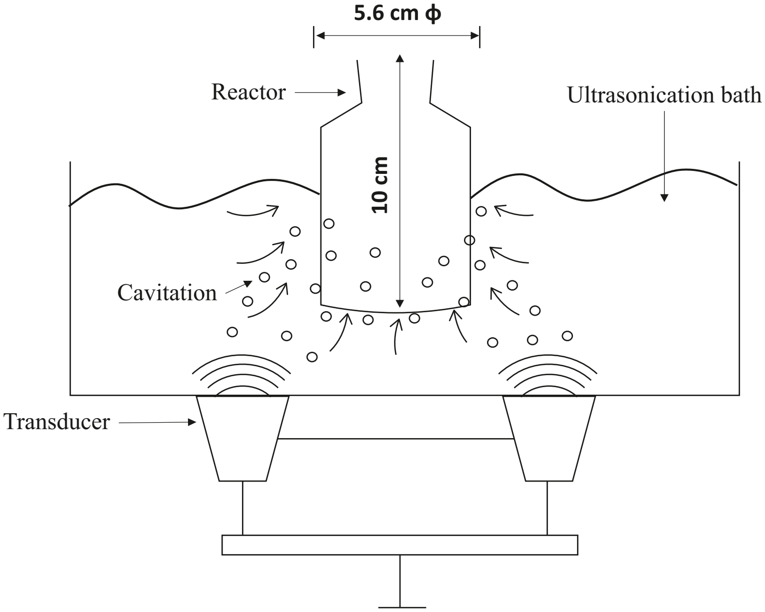

Fig. 1 Schematic representation of the customized reactor in ultrasonication bath and dissipation of vibration through the water bath to reactor

separate biochar from the liquid. The clear liquid was analysed using ultraviolet (UV) 2600 spectrophotometer (Shimadzu, Japan) by measuring its absorbance with time. UV results were further confirmed by high-performance liquid chromatography (HPLC) (Shimadzu Japan, Binary Pump: LC 20 AD).

2.5 Design of the Customized Reactor

The sonication of naphthalene-rich biochar was carried out in a cylindrical reactor (10 cm deep, 5.6 cm diameter) with a narrow neck (Fig. 1). The samples were collected and analysed in HPLC to determine the removal efficiency of naphthalene.

2.6 Enrichment and Isolation

For enrichment, Bushnell Haas broth (BHB) was used. Soil sample was taken from the oil contaminated site in Chennai city and 20 g of soil sample was suspended in 200 mL BHB (magnesium sulphate, 0.2 g L^{-1}; calcium chloride, 0.02 g L^{-1}; monopotassium phosphate, 1 g L^{-1}; dipotassium phosphate, 1 g L^{-1}; ammonium nitrate, 1 g L^{-1}; and ferric chloride, 0.05 g L^{-1}) and maintained at pH (temperature at 25 °C) of 7.0 ± 0.2. The medium was supplemented with 2000 ppm of naphthalene in dimethyl sulphoxide (DMSO) and the flasks were incubated at 25 ± 1 °C under shaking condition for 10 days. At the end of the enrichment process, the bacterial strains in the consortium were isolated by spreading tenfold serially diluted consortium on 20 mL Bushnell Haas media plate with 500 ppm of naphthalene. The plates were incubated at 25 ± 1 °C for 7 days and the bacterial colonies grown on plates were purified by repetitive streaking on nutrient agar plates. The colonies which showed maximum growth were selected, purified and maintained on slants containing 10% of naphthalene.

2.7 Utilization of Naphthalene

The flask containing 1 L BHB with an initial naphthalene concentration of 500 ppm was inoculated with 1 mL of each isolate. The samples were incubated at 25 ± 1 °C for 10 days. The broth containing 500 ppm naphthalene without inoculum was maintained as a negative (−ve) control. For quantification of the bacterial growth, the samples were aseptically collected on alternate days and assayed for optical density (OD_{600}) using UV/VIS spectrophotometer (ELICO SL159). Quantification of the residual naphthalene present in the media was performed using HPLC.

2.8 Ultrasonication

SB biochar rich in naphthalene was mixed with 5 mL of hexane in the glass reactor and sonicated in an ultrasonication bath (Digital Ultrasonic Cleaner WC series) at 40 KHz frequency and 100 W power for a total time of 45 min. After sonication, the setup was removed from the bath and allowed to settle for 3–5 min. The supernatant was then decanted and centrifuged to separate the biochar from the solvent. The clear liquid was then analysed for naphthalene using HPLC.

For HPLC analysis, the samples were extracted in hexane after which it was subjected to evaporation by rotary evaporator and the remaining solution was dissolved in methanol. 1 μL of this solution was injected to HPLC. C_{18} RP column (250 × 4.6 mm packed with 100 RP-18 (5 μm)) was used for the quantification of naphthalene. The solvent system was made of 95% methanol: 5% H_2O (v/v) and 0.1% formic acid. The run time is 30 min at a flow rate of 0.8 mL/min in isocratic mode during which the column was maintained at ambient temperature. The instrument uses a photodiode array detector (PDA).

2.9 QA/QC

After preparation, biochar was kept in the desiccator to prevent entry of moisture and air into it, which would otherwise decrease its efficiency. A method blank containing 5 mL hexane was kept alongside in the reactor which underwent ultrasonication for the same time period as the samples. Control samples were prepared by mixing 10 mg of biochar and 5 mL of hexane and were concurrently used with other samples.

3 Results and Discussions

3.1 Biochar Preparation

Pyrolytic temperature and feedstock material greatly influence the efficiency of biochar. The physical nature of biochars is highly influenced by the pyrolysis system which depends on the feedstock used for pyrolysis, with different feedstocks giving different results (Downie et al. 2009). SB biochar was prepared at 400 °C. SB biochar produced was 52% of the initial dry weight of SB. A temperature range of 350–700 °C was found appropriate for the production of efficient biochar in different studies (Chen et al. 2008; Zhang et al. 2010). But past studies have not established any conclusive relationship between the pyrolytic temperature and sorption capacity due to the complexity of biochar (Feng and Zhu 2018). In fact, the surface area of biochar was found to reduce above 400 °C in some studies (Sharma et al. 2002, 2004; Yavari et al. 2015). Thus, we used a lower pyrolytic temperature of 400 °C for biochar preparation. We also observed that the biochar turned into ash at temperatures over 600 °C.

3.2 Characterization of Biochar

3.2.1 Structure and Composition with the SEM and EDS

From the images at various magnifications (Fig. 2a–c) under scanning electron microscope, we observed that the SB biochar has honeycomb-like structure with micropores. This honeycomb-like structure may be an indication of the carbonaceous skeleton of the biochar (Hafshejani et al. 2016).

EDS analysis of SB biochar shows high carbon content (76.47%) and is consistent with a study by Ippolito et al. (2015). The other major elements present in SB biochar were N (6.15%) and O (17.16%). The O/C ratio, which is a recommended ratio for efficient biochar, was 0.22 (O/C < 0.4). The carbon content of biochar is expected to increase with the increase in temperature. It has been observed earlier

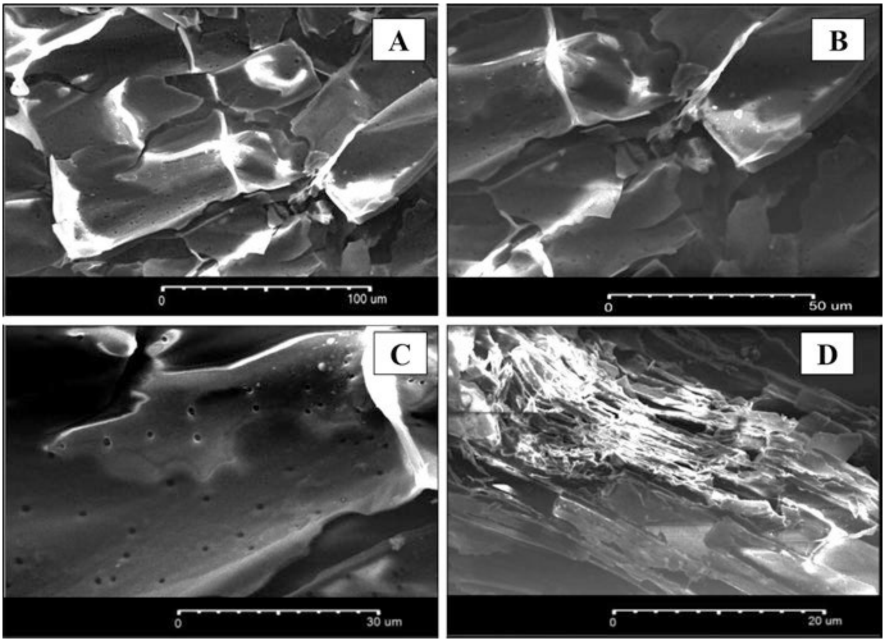

Fig. 2 SEM images of sugarcane bagasse biochar in different magnifications with pores have been developed as shown in (**a**, **b**, **c**) and disruption of biochar surface after sonication (**d**)

that at high temperatures, biochar can act as an effective adsorbent, whereas at temperatures below 350 °C, biochar showed slower adsorption rates due to the partitioning of sorbate into highly condensed organic phases (Chen et al. 2008).

3.2.2 Nature of Biochar

The absence of narrow peaks and high noise levels in powder-XRD results suggest the amorphous nature of SB biochar (Fig. 3). The broad peaks visible at 22 °C can be due to the presence of cellulose structure in biochar (Shaaban et al. 2013). At higher temperatures, the peak formed at 22 °C would disappear due to decomposition of the remaining cellulose structure (Shaaban et al. 2013).

3.2.3 FTIR Spectra

FTIR spectrum of SB biochar observed between 400 cm^{-1} and 4000 cm^{-1} (Fig. 4) indicated the presence of several functional groups. The vibrations between 3600 and 3700 cm^{-1} correspond to the vibrations of O-H group. 2924 cm^{-1} can be an

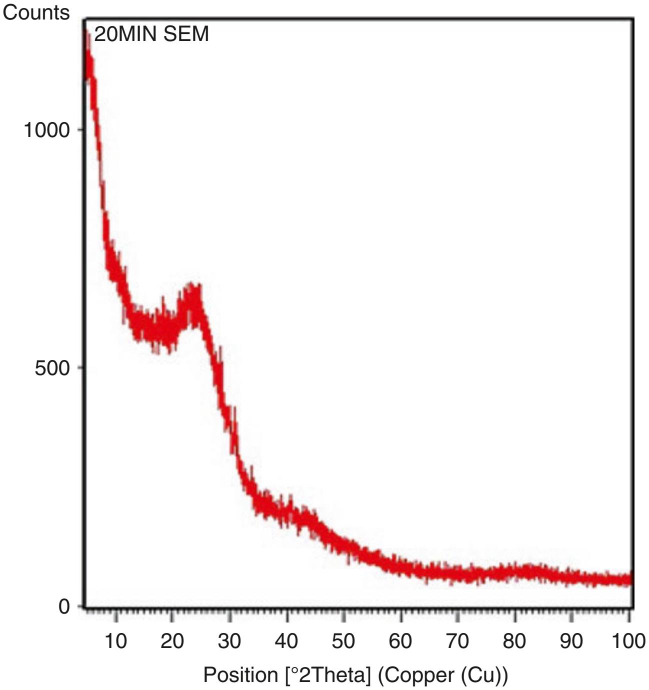

Fig. 3 Powder X-ray diffraction pattern exhibited by sugarcane bagasse biochar

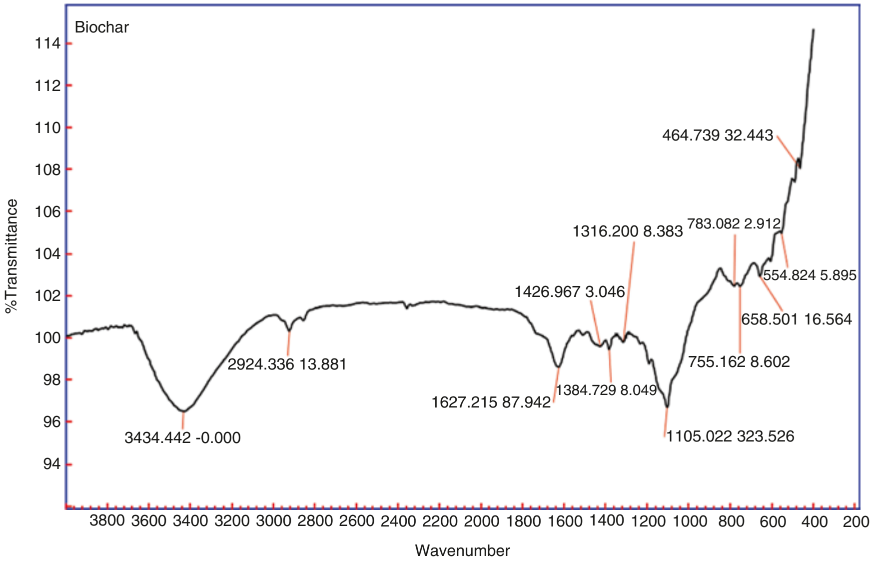

Fig. 4 Fourier transform-infrared spectroscopy (FTIR) for sugarcane bagasse biochar

indication of the stretching of C-H bond. The bands from 2954 to 2847 cm^{-1} point to the existence of CH_3 asymmetric and symmetric stretching. The vibration at 1544 cm^{-1} indicated C-N-C bending. The scissoring CH_2 vibration was observed at 1432 cm^{-1}. The removal of functional groups with O and H of C=O, –CO, –CH_2, phenolic (–OH) groups, etc., can result in an increase in the surface area of biochar produced at high temperatures (400–700 °C) (Chen et al. 2008). Thus, it can be suggested that the O-containing carboxyl group, phenolic functional groups and hydroxyl groups may interact with the pollutants (Ahmad et al. 2014).

3.3 Adsorption of Naphthalene in Biochar

In the UV spectrophotometer, naphthalene peak was observed at 275 nm. A steady decrease in naphthalene peak was observed after 15 min of adsorption by SB biochar. The adsorption of naphthalene by SB biochar was 53% for the first 15 min that increased to 100% within 45 min and steadily maintained up to 75 min. This points out the suitability of SB biochar as an adsorbent of naphthalene. Adsorption happens due to the adhesion of pollutant molecule on biochar produced at high temperatures (above 350 °C) due to surface interactions (Chen et al. 2008). For biochar produced below 350 °C, partitioning of pollutant molecules occurs due to the presence of large uncarbonized fractions which reduce the adsorption rate (Chen et al. 2008).

Adsorption was further confirmed with HPLC results where we observed naphthalene peak in samples before adsorption (Fig. 5a), whereas after adsorption, no naphthalene peak was observed, indicating complete adsorption of naphthalene in biochar (Fig. 5b). The sorption capacities of biochar derived from plant residues showed significant variation in different studies as the adsorption depends on the cellulose, hemicellulose and lignin content of the feedstock used (Chen et al. 2012b; Feng and Zhu 2018). The carbon-rich structure of SB might be a possible reason for 100% adsorption of naphthalene.

3.4 Removal of Naphthalene from SB Biochar by Ultrasonication

Ultrasonication has been extensively used for the removal of organic pollutants from soils and sediments (Collings and Gwan 2010; Shrestha et al. 2009). With the help of high-power 20 kHz ultrasound, 85% of organic pollutants like polychlorinated biphenyl (PCB Aroclor 1260) could be degraded from sand slurries within 60 min of application time (Mason et al. 2004). Similarly, around 75% of PAHs were removed from sand slurries within 5 min using ultrasound of frequency 20 kHz (Mason et al. 2004). The physical effects and thermal conditions induced by the

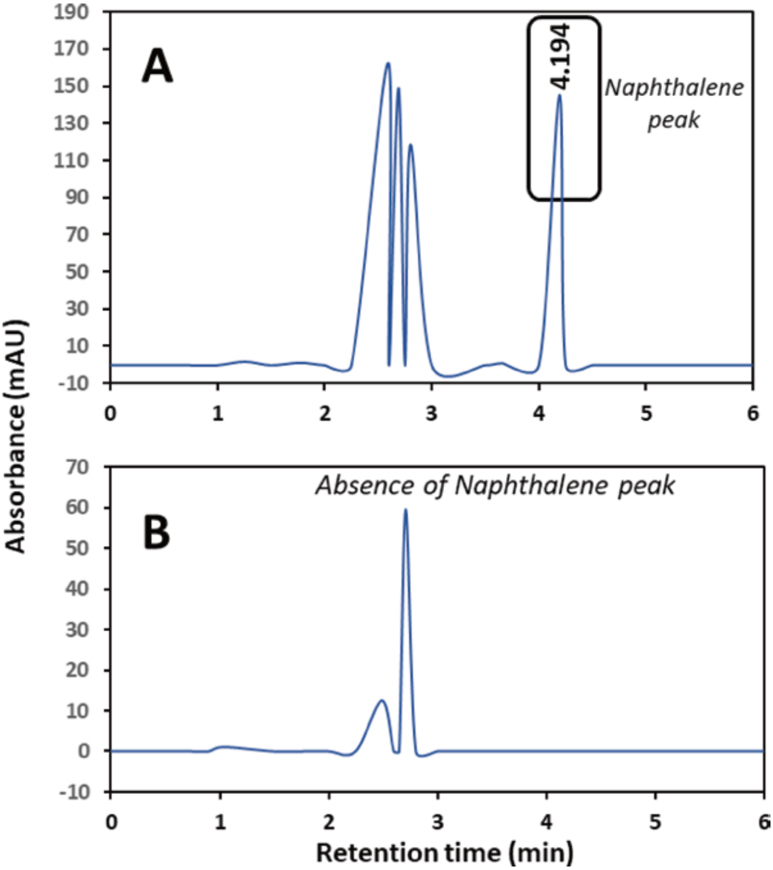

Fig. 5 **a**–**b**: HPLC chromatograms of samples at 266 nm before adsorption and after adsorption. Unit of *X*-axis is minutes; unit of *Y*-axis is milli-absorbance units detected by the photo diode array detector

acoustic cavitation on application of ultrasound are involved in the deactivation of naphthalene as observed elsewhere (Adewuyi 2001).

Customized reactor has been used for the removal of organic pollutants from slurries by high-frequency ultrasound (Thangavadivel et al. 2009). Since low-frequency ultrasonication baths are low-cost devices with less power consumption, we have used a simple ultrasonication bath for our experiments. Customized reactor used in this study was fabricated using glass reactor chamber with a diameter of 5.6 cm and a depth of 10 cm. Narrow sonication cells designed with a reaction tube of diameter 1.5 cm which can contain a low-frequency ultrasonic horn of 1.25 cm diameter were used in the treatment of pesticides from contaminated slurries (Collings and Gwan 2010). The use of custom-made reactors in ultrasonication of polluted matrices is suggested depending on the frequency and specification of

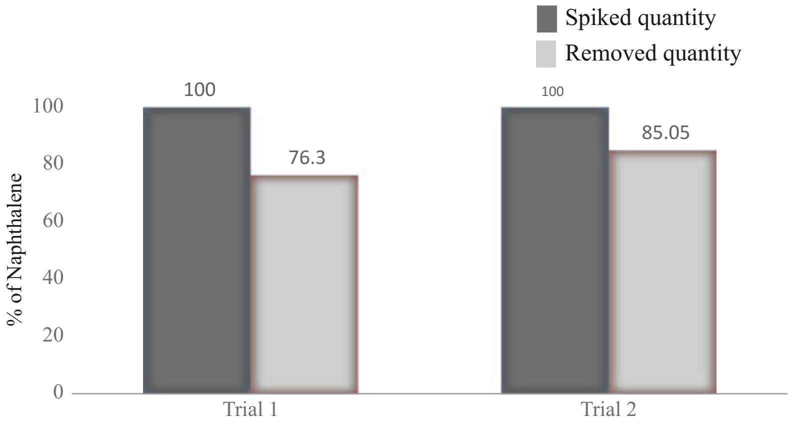

Fig. 6 Removal percentage attained for naphthalene by ultrasonication of sugarcane bagasse biochar in a customized reactor

ultrasonication device. In this study, the customized reactor had an operating volume of 100 mL. It was designed to suit low-frequency ultrasonication bath (40 KHz) used in this study. As the reactor is partially immersed in water bath during sonication, an even distribution of low-frequency ultrasound is expected from the bottom of the reactor (Fig. 1). The thin wall of the reactor facilitated proper agitation of the solvent-biochar mixture. The interference of incident and reflected ultrasonic waves in the bath and non-uniform power yield from the transducers located at the bottom of the bath can cause a variation in the intensity of ultrasound waves delivered throughout the bath (Kiani et al. 2011; Li and Sun 2002). Due to the low energy and low intensity of ultrasound in bath-type sonicators, proper positioning of reactor in the bath is very important for its stability. The flat bottom shape of our customized reactor assures its stability in the water bath ensuring an even distribution of ultrasound throughout the cylindrical structure immersed in the water bath. The removal rates for naphthalene were 76.3% and 85% in trial 1 and trial 2, respectively (Fig. 6). It is evident that the reactor could facilitate a commendable removal of naphthalene from biochar. Hence, a cylindrical reactor can be used for the treatment of low-molecular-weight PAHs like naphthalene by low-frequency ultrasonication. Sonication can possibly cause defibrillation of sugarcane bagasse fibres (de Campos et al. 2013), leading to disruption of the biochar structure as seen in Fig. 2d.

4 Scope for Field Application

There is a growing concern over the management of waste due to the huge amounts of assorted wastes generated every day across the globe. Application of biochar in the field by producing them in mass scales for concentrating the pollutants from sites and later ultrasonically removing the adsorbed pollutant in an upscaled reactor would help in arresting emergency situations without causing alarming consequences. Low-cost technologies adopted in the production of biochar make them more versatile for real-time studies and industrial projects. Less smoky, low-cost stoves and kilns developed recently are examples of such technologies (Brown 2012; Pratt and Moran 2010). The low-cost technologies and resource availability in developing regions across the globe provide higher opportunities for biochar projects compared to the developed regions which require larger capital investment and huge cost of running modern technologies (Pratt and Moran 2010).

When applying biochar for soil remediation, the soil organic matter can mimic the pollutant and occupy the micropores of biochar suppressing their adsorption ability (Pignatello et al. 2006). Moisture interference can also lead to a reduction in adsorption capability of any biochar. Also, the uncertainty surrounding the holding capacity of biochar raises doubts over the reliability of this material.

For field applications, incorporating ultrasonication technique can involve high capital investments, but they can assist in the sudden removal of organics from polluted matrices which cannot be achieved by bioremediation techniques (Adewuyi 2001; Chen et al. 2012a; Thangavadivel et al. 2009).

5 Conclusion

Anthropogenic activities release a number varieties of pollutants in different environmental matrices. Biochar produced from waste sugarcane bagasse is a low-cost and sustainable adsorbent for adsorbing PAHs in contaminated sites. SB biochar was found to be an efficient adsorbent of naphthalene exhibiting an adsorption efficiency of 100% within 30 min. The high carbon content of SB is expected to be a reason for the commendable efficiency of biochar derived from it. The customized cylindrical reactor designed for low-frequency ultrasonication device was found to be effective for the removal of more than three fourth of naphthalene adsorbed in biochar.

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References

Adewuyi YG (2001) Sonochemistry: environmental science and engineering applications. Ind Eng Chem Res 40:4681–4715

Ahmad M, Rajapaksha AU, Lim JE, Zhang M, Bolan N, Mohan D et al (2014) Biochar as a sorbent for contaminant management in soil and water: a review. Chemosphere 99:19–33

Brown R (2012) Biochar production technology. Biochar for environmental management. Routledge, pp 159–178

Cerniglia CE, Althaus JR, Evans FE, Freeman J, Mitchum RK, Yang SK (1983) Stereochemistry and evidence for an arene oxide-NIH shift pathway in the fungal metabolism of naphthalene. Chem Biol Interact 44:119–132

Cerniglia CE, Freeman J, Evans FE (1984) Evidence for an arene oxide-NIH shift pathway in the transformation of naphthalene to 1-naphthol by Bacillus cereus. Arch Microbiol 138:283–286

Chakraborty P, Zhang G, Li J, Sivakumar A, Jones KC (2015) Occurrence and sources of selected organochlorine pesticides in the soil of seven major Indian cities: assessment of air–soil exchange. Environ Pollut 204:74–80

Chen B, Yuan M, Qian L (2012a) Enhanced bioremediation of PAH-contaminated soil by immobilized bacteria with plant residue and biochar as carriers. J Soils Sediments 12:1350–1359

Chen B, Zhou D, Zhu L (2008) Transitional adsorption and partition of nonpolar and polar aromatic contaminants by biochars of pine needles with different pyrolytic temperatures. Environ Sci Technol 42:5137–5143

Chen Z, Chen B, Zhou D, Chen W (2012b) Bisolute sorption and thermodynamic behavior of organic pollutants to biomass-derived biochars at two pyrolytic temperatures. Environ Sci Technol 46:12476–12483

Cheng H, Deng Z, Chakraborty P, Liu D, Zhang R, Xu Y et al (2013) A comparison study of atmospheric polycyclic aromatic hydrocarbons in three Indian cities using PUF disk passive air samplers. Atmos Environ 73:16–21

Chun Y, Sheng G, Chiou CT, Xing B (2004) Compositions and sorptive properties of crop residue-derived chars. Environ Sci Technol 38:4649–4655

Collings A, Gwan P (2010) Ultrasonic destruction of pesticide contaminants in slurries. Ultrason Sonochem 17:1–3

Crosby DG, Leitis E, Winterlin W (1965) Carbamate insecticides, photodecomposition of carbamate insecticides. J Agric Food Chem 13:204–207

de Campos A, Correa AC, Cannella D, de Teixeira E, Marconcini JM, Dufresne A et al (2013) Obtaining nanofibers from curauá and sugarcane bagasse fibers using enzymatic hydrolysis followed by sonication. Cellulose 20:1491–1500

Devi NL, Chakraborty P, Shihua Q, Zhang G (2013) Selected organochlorine pesticides (OCPs) in surface soils from three major states from the northeastern part of India. Environ Monit Assess 185:6667–6676

Downie A, Crosky A, Munroe P (2009) Physical properties of biochar. Biochar Environ Manag Sci Technol:13–32

Dreher ML (1987) Handbook of dietary fiber. An applied approach: Marcel Dekker, Inc

Feng Z, Zhu L (2018) Sorption of phenanthrene to biochar modified by base. Front Environ Sci Eng 12:1

Guerin WF, Boyd SA (1992) Differential bioavailability of soil-sorbed naphthalene to two bacterial species. Appl Environ Microbiol 58:1142–1152

Hafshejani LD, Hooshmand A, Naseri AA, Mohammadi AS, Abbasi F, Bhatnagar A (2016) Removal of nitrate from aqueous solution by modified sugarcane bagasse biochar. Ecol Eng 95:101–111

Inyang M, Gao B, Pullammanappallil P, Ding W, Zimmerman AR (2010) Biochar from anaerobically digested sugarcane bagasse. Bioresour Technol 101:8868–8872

Ippolito JA, Spokas KA, Novak JM, Lentz RD, Cantrell KB (2015) Biochar elemental composition and factors influencing nutrient retention. Biochar Environ Manag Sci Technol Implement 139

Kiani H, Zhang Z, Delgado A, Sun D-W (2011) Ultrasound assisted nucleation of some liquid and solid model foods during freezing. Food Res Int 44:2915–2921

Li B, Sun D-W (2002) Effect of power ultrasound on freezing rate during immersion freezing of potatoes. J Food Eng 55:277–282

Mason TJ, Collings A, Sumel A (2004) Sonic and ultrasonic removal of chemical contaminants from soil in the laboratory and on a large scale. Ultrason Sonochem 11:205–210

Mohan D, Sarswat A, Ok YS, Pittman CU (2014) Organic and inorganic contaminants removal from water with biochar, a renewable, low cost and sustainable adsorbent–a critical review. Bioresour Technol 160:191–202

Mohanty P, Nanda S, Pant KK, Naik S, Kozinski JA, Dalai AK (2013) Evaluation of the physiochemical development of biochars obtained from pyrolysis of wheat straw, timothy grass and pinewood: effects of heating rate. J Anal Appl Pyrolysis 104:485–493

Mubarik S, Saeed A, Athar M, Iqbal M (2016) Characterization and mechanism of the adsorptive removal of 2, 4, 6-trichlorophenol by biochar prepared from sugarcane baggase. J Ind Eng Chem 33:115–121

Pathak H, Kantharia D, Malpani A, Madamwar D (2009) Naphthalene degradation by pseudomonas sp. HOB1: in vitro studies and assessment of naphthalene degradation efficiency in simulated microcosms. J Hazard Mater 166:1466–1473

Pignatello JJ, Kwon S, Lu Y (2006) Effect of natural organic substances on the surface and adsorptive properties of environmental black carbon (char): attenuation of surface activity by humic and fulvic acids. Environ Sci Technol 40:7757–7763

Pratt K, Moran D (2010) Evaluating the cost-effectiveness of global biochar mitigation potential. Biomass Bioenergy 34:1149–1158

Shaaban A, Se S-M, Mitan NMM, Dimin M (2013) Characterization of biochar derived from rubber wood sawdust through slow pyrolysis on surface porosities and functional groups. Proc Eng 68:365–371

Sharma RK, Wooten JB, Baliga VL, Lin X, Chan WG, Hajaligol MR (2004) Characterization of chars from pyrolysis of lignin. Fuel 83:1469–1482

Sharma RK, Wooten JB, Baliga VL, Martoglio-Smith PA, Hajaligol MR (2002) Characterization of char from the pyrolysis of tobacco. J Agric Food Chem 50:771–783

Shrestha RA, Pham TD, Sillanpää M (2009) Effect of ultrasound on removal of persistent organic pollutants (POPs) from different types of soils. J Hazard Mater 170:871–875

Someya M, Ohtake M, Kunisue T, Subramanian A, Takahashi S, Chakraborty P et al (2010) Persistent organic pollutants in breast milk of mothers residing around an open dumping site in Kolkata, India: specific dioxin-like PCB levels and fish as a potential source. Environ Int 36:27–35

Tang J, Zhu W, Kookana R, Katayama A (2013) Characteristics of biochar and its application in remediation of contaminated soil. J Biosci Bioeng 116:653–659

Thangavadivel K, Megharaj M, Smart RSC, Lesniewski PJ, Naidu R (2009) Application of high frequency ultrasound in the destruction of DDT in contaminated sand and water. J Hazard Mater 168:1380–1386

Wilson AS, Davis CD, Williams DP, Buckpitt AR, Pirmohamed M, Park BK (1996) Characterisation of the toxic metabolite (s) of naphthalene. Toxicology 114:233–242

Yavari S, Malakahmad A, Sapari NB (2015) Biochar efficiency in pesticides sorption as a function of production variables—a review. Environ Sci Pollut Res 22:13824–13841

Zhang H, Lin K, Wang H, Gan J (2010) Effect of Pinus radiata derived biochars on soil sorption and desorption of phenanthrene. Environ Pollut 158:2821–2825

Zhang X, Wang H, He L, Lu K, Sarmah A, Li J et al (2013) Using biochar for remediation of soils contaminated with heavy metals and organic pollutants. Environ Sci Pollut Res 20:8472–8483

Zhu D, Kwon S, Pignatello JJ (2005) Adsorption of single-ring organic compounds to wood charcoals prepared under different thermochemical conditions. Environ Sci Technol 39:3990–3998

Nanotechnology-Based Treatment Strategies for the Removal of Antibiotics and Their By-Products from Wastewater

Nithiya Pachamal, Rajarathnam Dharmarajan, S. Senthil Sundaram, and Selvakumar Rajendran

Abstract Antibiotic resistance has become a serious issue throughout the world due to its inappropriate use and overdosing in pharmaceutical therapies and veterinary and agricultural applications. The cause of increasing antibiotic resistance is the slow and steady exposure of sensitive microbes to antibiotics released into the wastewater. Not only the antibiotics but also the degradation products of antibiotics in wastewater are also of major concern. The higher stability of antibiotics during biodegradation and conventional chlorination process has been a major challenge to remove them from wastewater. Various technologies like photocatalysis, advanced oxidation process (AOP), biological removal, adsorption, and nanotechnology-based processes/products have been investigated to address this issue. Among these technologies, nano-based technologies have been increasingly getting attention recently owing to their advantages. This chapter addresses the suitability, efficiency, advantages, disadvantages, and other factors involved in the removal of antibiotics and their by-products from wastewater using nanotechnology. The integrated use of biotechnology and nanotechnology has also been discussed.

Keywords Antibiotics · Classification · By-product · Wastewater · Biodegradation · Antibiotic resistance · Challenges · Nanophotocatalyst · Nanoadsorption · Nanofiltration · Advanced oxidation · Nano-bio approach · Limitation

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1 Introduction

Antibiotics are recalcitrant bio-accumulative compounds and considered as potential emerging contaminants that are continuously discharged into the environment from various sources (Ahmad and Dutta 2020; Ramavandi and Akbarzadeh 2015). The antibodies are classified into various types, viz., aminoglycosides, anthracyclines, β-lactams, phenicols, glycopeptides, imidazoles, lincosamides, lipopeptides, macrolides, (fluoro)quinolones, sulfonamides, and tetracyclines (Fig.1). Among these classes, β-lactam antibiotics are the most prescribed ones (Torres-Palma et al. 2020; WHO 2018). Although in early decades, antibiotic consumption was observed to be much higher in developed countries like the United States, France, and Italy, recently developing countries like China, India, and Pakistan showed a drastic increase in antibiotic use (Riaz et al. 2020). The risk of excessive use of antibiotics in the ecological environment induces the proliferation of bacterial drug resistance which leads to loss of antibiotic efficiency in controlling infectious disease and dysbacteriosis in humans (Li et al. 2019; Kupolati et al. 2020; Wu 2020). The World Health Organization (WHO) and several environmental protection agencies such as US EPA are concerned about both environmental and health impacts of antibiotic misuse/overuse (Cerro-Lopez and Mendez-Rojas 2017).

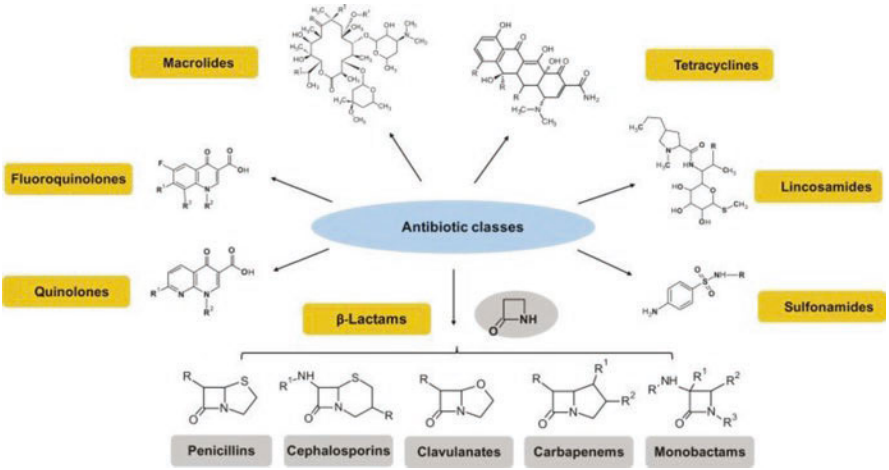

Fig. 1 Different classes of antibiotics. (Source: Torres-Palma et al. 2020; Copyright 2021, Elsevier)

2 Emerging Pollutant – Antibiotics in Wastewater

Antibiotics were first identified in surface and wastewaters in the United States and Europe in the 1960s. However, antibiotics in wastewater was considered as a potential risk to public health safety mostly after 1999 (Kyzas et al. 2018). The occurrence of antibiotics or their intermediates in waste water treatment plant (WWTP) effluents, in surface waters, and less frequently, in ground and drinking water has been reported all over the world (Kyzas et al. 2018). The entry of antibiotics into the environment was through various sources (Fig. 2). Among them, WWTP are considered to be a potential source through which antibiotic spread was found to be maximum (Eniola et al. 2019). Therefore, the treatment of these antibiotics, antibiotic residues, and their degradation by-products present in wastewater and pharmaceutical effluents has significant importance in protecting the environment. The treatments of antibiotics and their degradation products from wastewater were conventionally carried out with various biological, physical, and chemical methods. However, the inability of conventional treatment in the total or complete removal of antibiotics from wastewater is of primary concerns. Such ineffectiveness in antibiotic remediation from wastewater by conventional treatment is due to three main reasons. Firstly, the biodegradation-based treatments are not suitable as the antibiotics are inherently toxic to the employed biological species during treatment. The

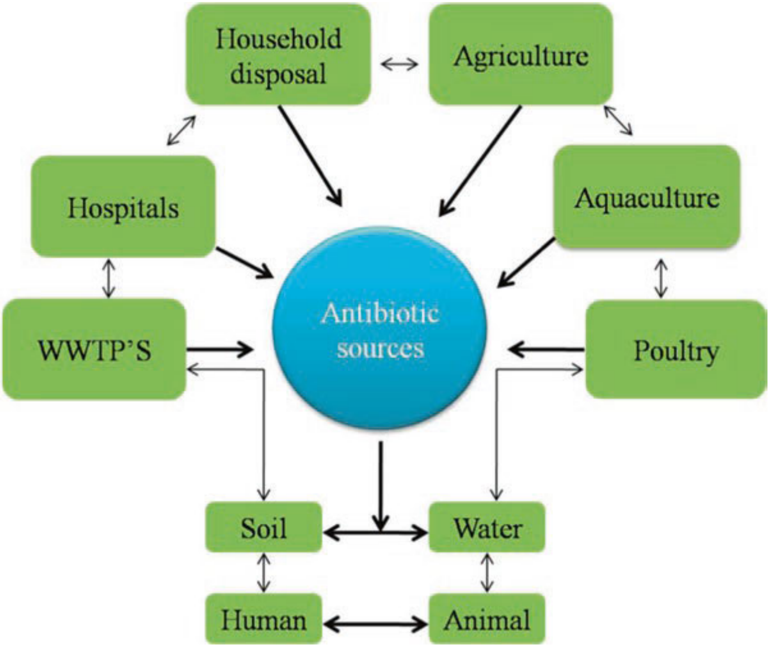

Fig. 2 Various sources of antibiotic contamination. (Adopted from Kumar et al. 2019; Copyright 2021, Elsevier)

presence of antibiotics in wastewater affects some of the naturally occurring beneficial microflora (Cerro-Lopez and Mendez-Rojas 2017). Secondly, the sorption ability of antibiotics gets affected by the physicochemical properties of sludge during sorption-based treatment. Lastly, antibiotics are less susceptible to simple oxidation or photocatalytic treatments as they are chemically very stable due to the presence of complex aromatic rings, heteroatoms, and functional groups (Chauhan et al. 2019). Hence, there is an urgent need to develop a promising technology to effectively remove antibiotics from wastewater.

2.1 COVID Pandemic-Related Antibiotic Stress in Wastewater

Coronaviruses are influenza viruses that infect humans, cows, birds, bats, rodents, and other fauna's respiratory tract, gastrointestinal tract, liver, and central nervous system. The first case of the current pandemic was reported in early December 2019 with an unknown origin at Wuhan, Hubei Province, China. The prevalent acute respiratory syndrome is known as COVID-19, the new emerging coronavirus considered as the seventh member of the coronavirus family (Dindarloo et al. 2020). Various disinfectants and pharmaceuticals were aggressively used to control the spread of coronavirus disease. Disinfectants such as alcohols, chlorine, formaldehyde, glutaraldehyde, ortho-phthalaldehyde, hydrogen peroxide, iodophors, peracetic acid, phenolics, and quaternary ammonium compounds were employed alone or in specific composition on public health by authorities. Although there were many training programs and guidance for the usage of disinfectants against the virus by the World Health Organization to reduce their adverse effect on human health, the mass production and significant pharmaceuticals particularly antibiotics were administrated without any regulations to control the infectious disease. For example, in the United States alone around 250 million antibiotic prescriptions were employed, whereas in China 96 million kg of antibiotics was used. Since the specific treatment and medications are not identified, the usage of disinfectants and antibiotics was high. Although the antibiotics cannot be used to treat the virus, it is overused in the urge to control and treat co-infections. Above 30–90% of these administrated antibiotics would be excreted as the elimination of body to the waste system. The pharmaceuticals and their metabolites were not completely removed by the traditional wastewater treatment which may cause the release of antibiotics and disinfectants to the environment. As per the report, these antibiotics and disinfectants were observed in surface water, groundwater, sediments, wetlands, and soil with the amount of 1 mg/L which can cause a severe impact on the environment and public health. Before the current pandemic, it is estimated that by 2050 the death rate due to AMR will be ten million per year, but in this situation as a result of the continuous increased usage and misuse of antibiotics, lack of effective antibiotic degradation and removal process lead to new AMR's arrival and adverse impact on the environment (Chen et al. 2021).

3 Current Technology for Antibiotic Removal from Wastewater

There are no specific or special processes designed separately for the treatment of antibiotics in water and wastewater practiced so far. For years conventional wastewater methods are being used in wastewater treatment plants mostly to remove pathogens and undesired products. This treatment process generally includes three processes involving physical, biological, and chemical methods. The physical treatment process comprises the preliminary and primary treatment such as bar screening and sedimentation basins to remove most of the suspended solids. As the secondary treatment, biological treatment processes, such as the activated sludge process, biological filter process, and rotating biological contactor process, are the principal technologies in WWTPs that aim to degrade the complex organic compounds into non-toxic substances via microbial metabolism, while tertiary treatment includes disinfection, sand filtration, constructed wetland, soil aquifer treatment, etc. (Pei et al. 2019). Thus, conventional methods are not specifically configured to address the mitigation of antibiotic pollutants. Although a significant reduction has been achieved in the WWTP, it is not up to the desired levels, as these methods don't remove antibiotic pollutants completely. The existing wastewater treatment processes and removal efficiencies were observed to be typically 12.5% (Balakrishna et al. 2017). Table 1 projects the methods that have been carried out and their efficiencies in antibiotic removal at wastewater treatment plants. Among the various upcoming technologies, nanotechnology is considered a vital means through the development of multi-functional nanomaterials affording highly efficient and superior processes for antibiotic remediation in wastewater treatment plants (Amin et al. 2014). Recently researchers are also developing remediation techniques coupled with nanotechnology platforms to improve the removal of antibiotics.

4 Nanotechnology in the Removal of Antibiotics

To remove the chemically stable and persistent antibiotic pollutants from wastewater, one of the most reliable and efficient methods is through nanotechnology-based technique. Nanotechnology is promising, with a large potential to utilize its high reactivity due to the large surface-to-volume ratio that can aid in the complete removal of antibiotics (Adegoke and Stenström 2019). Latest advancements in the field of nanotechnology have led to the development of novel nanomaterials with attractive properties that broaden the range of utilization in the removal of antibiotics from wastewater. The nanotechnology-based treatment majorly includes nanoadsorption, nanophotocatalysis, advanced oxidation process, and nanofiltration methods which are discussed in detail in this chapter. The forthcoming sections will focus on the explored nanotechnology methods and materials in the effective removal of antibiotics along with their advantages and disadvantages (Table 2).

Table 1 Current treatment methods for antibiotic removal in WWTPs. (Anjali and Shanthakumar 2019; Copyright 2021, Elsevier)

Country	Classification	Name	Influent	Effluent	Treatment methods
Greece	β-Lactams	Amoxicillin	ND	ND	Screening; grit removal; primary sedimentation; chemical and biological treatment
		Ampicillin	1243	151	
	Fluoroquinolones	Ciprofloxacin	152	199	
		Moxifloxacin	425	85	
	Sulfonamides	Sulfamethoxazole	904.2[a]	30.6[a]	
	Trimethoprim	Trimethoprim	138[a]	59.8[a]	
United States	Sulfonamides	Sulfamethoxazole	3800[a]	304[a]	Secondary treatment plants; oxidation ditches
	Trimethoprim	Trimethoprim	1170[a]	586[a]	Bar screen; two aerated lagoons; filtration
Spain	Fluoroquinolones	Ciprofloxacin	–	52	Tertiary treatment; ultrafiltration; reverse osmosis; UV disinfection
		Ofloxacin	–	341	
	Macrolides	Erythromycin	–	39	
	Sulfonamides	Sulfamethazine	–	74.33	
		Sulfamethoxazole	–	102.5	
		Sulfapyridine	–	54	Primary sedimentation; secondary; UV disinfection
China	Fluoroquinolones	Ofloxacin	200	150	
	Tetracyclines	Oxytetracycline	91	20	
		Tetracycline	48	14	
	Sulfonamides	Sulfamethoxazole	25	9	
	Others	Cyclophosphamide	13	14	
		Glibenclamide	1.4	1.9	
Korea	Lincosamides	Lincomycin	16700[a]	14200[a]	Conventional treatment processes
	Sulfonamides	Sulfamethazine	164[a]	144[a]	
		Sulfamethoxazole	120[a]	57[a]	
		Sulfachloropyridazine	30	14	
		Sulfamonomethoxine	ND	ND	
		Sulfamerazine	48	33	
		Sulfathiazole	131	345	
	Trimethoprim	Trimethoprim	261[a]	96[a]	
UK	Macrolides	Erythromycin	274	–	
Singapore[a]	Trimethoprim	Trimethoprim	880	–	
Finland	Fluoroquinolones	Ciprofloxacin	600	60	Conventional activated sludge (CAS) treatment
		Norfloxacin	120	ND	
		Ofloxacin	100	14	

(continued)

Table 1 (continued)

Country	Classification	Name	Influent	Effluent	Treatment methods
India	β-Lactams	Amoxicillin	172.6	62.5	Conventional treatment methods
		Ampicillin	104,200	12,680	
	Fluoroquinolones	Ciprofloxacin	20,060	8000	
		Gatifloxacin	2740	1220	
		Levofloxacin	107900[a]	–	
		Norfloxacin	18200[a]	–	
		Ofloxacin	–	285	
		Sparfloxacin	22,490	140	
	Macrolides	Azithromycin	176900[a]	–	
	Sulfonamides	Sulfamethoxazole	2260[a]	637[a]	
	Cephalosporin	Cefuroxime	3420	220	
	Lincosamides	Clindamycin	1870[a]	952[a]	
		Lincomycin	730[a]	430[a]	
	Trimethoprim	Trimethoprim	4010[a]	2469[a]	
	Others	Miconazole	1410[a]	1020[a]	
		Tiabendazole	123[a]	79[a]	
Germany[b]	Chloramphenicol	Chloramphenicol	–	560	
	Macrolides	Clarithromycin	–	240	
		Erythromycin-H_2O	–	6000	
		Roxithromycin	–	1000	
	Sulfonamides	Sulfamethoxazole	–	2000	
	Trimethoprim	Trimethoprim	–	660	

(continued)

Table 1 (continued)

Country	Classification	Name	Influent	Effluent	Treatment methods
Canada[b]	β-Lactams	Cloxacillin	50	50	Facultative lagoon; chemically assisted primary treatment; secondary activated sludge; biological nutrient removal; aerated lagoon
		Penicillin V	64	27	
	Fluoroquinolones	Ciprofloxacin	2500	620	
		Enrofloxacin	15	5.3	
		Ofloxacin	2800	210	
	Macrolides	Azithromycin	2500	1300	
		Clarithromycin	8000	7000	
		Erythromycin	600	270	
		Roxithromycin	4.4	9.3	
		Tylosin	–	47	
	Sulfonamides	Sulfadiazine	42	–	
		Sulfamerazine	9.3	–	
		Sulfamethazine	45	–	
		Sulfamethizole	6.5	87	
		Sulfamethoxazole	3100	1800	
	Tetracyclines	4-Epitetracycline	120	46	
		Doxycycline	78	53	
		Tetracycline	120	36	
	Lincosamide	Lincomycin	110	65	
	Trimethoprim	Trimethoprim	810	580	
	Others	Carbadox	–	78	
		Miconazole	43	27	
		Tiabendazole	220	140	
Sweden	Fluoroquinolones	Ciprofloxacin	320	31.5	Conventional activated sludge (CAS) treatment
		Norfloxacin	18	< LOQ	
		Ofloxacin	22.5	10	
Italy	Fluoroquinolones	Ciprofloxacin	2200	630	
		Norfloxacin	210	150	
		Ofloxacin	980	400	
	Macrolides	Azithromycin	120	130	
		Clarithromycin	200	280	
		Erythromycin	46	15	
		Roxithromycin	66	290	
	Trimethoprim	Trimethoprim	59	40	
	Imidazoles	Metronidazole	42	28	

[a] – mean concentration (max); <LOQ – below detection limit; ND – not detected. [a] – concentration range. [b] – maximum value; concentrations are in ng L^{-1}

Table 2 Advantages and disadvantages of nanotechnology-based processes

Method	Advantage	Disadvantage
Nanoadsorption	High specific surface area More binding sites Short intraparticle diffusion distance Tunable surface chemistry Tailorable pore size	Aggregation of nanomaterials limits binding sites Non-destructive (transfer the antibiotics from wastewater to adsorbent) Secondary pollution Separation of nanoadsorbents
Nanophotocatalysis	Quantum size effect Enhanced energy gap Chemical stability	Poor recovery of catalyst Recombination of electron and hole pairs
Advanced oxidation process	Proficient technique Produces high oxidizing species	Partial oxidation Produces intermediates Formation of highly toxic by-products Complex operation High cost
Nanofiltration	Easy operation High efficacy Better removal capacity Filters hard ions High retention of multivalent anion salts	Demands high energy Expensive cleaning process Membrane fouling

4.1 Nanoadsorbent

Adsorption is one of the powerful technologies with a strong binding ability of an adsorbent and removal of pharmaceutical compounds like antibiotics (Eniola et al. 2019). Among the adsorbents, nanoadsorbents have significant properties and advantages over conventional adsorbents. The surface functionalization possibility and high surface energy of nanoadsorbents pave the way for high adsorption sites besides selectivity (Qu et al. 2013). It has been demonstrated that various antibiotics can be adsorbed from water using functionalized nanomaterials. Ciprofloxacin (CIP) adsorbs up to 80% strongly onto the nano-magnetite surface through an inner-sphere coordination complex mediated through carboxylic acid groups. The COOH moiety and C=O group of CIP likely form a bridging bidentate surface complex with nano-Fe_3O_4 (Rakshit et al. 2013). The agricultural material pistachio shell coated with ZnO nanoparticles subjected to tetracycline antibiotic adsorption showed a maximum adsorption capacity of 95.06 mg/g. Adsorption isotherm and adsorption kinetics of tetracycline removal showed best fit with the Freundlich model and pseudo-second order, respectively (Mohammed and Kareem 2019). A new magnetic nanocomposite ($FeNi_3/SiO_2/CuS$) adsorbent was synthesized for the removal of metronidazole with an adsorption capacity of 147 mg/g. The Langmuir isotherm and pseudo-second-order kinetic models favorably described the experimental data attributing the adsorption process to be spontaneous and exothermic (Nasseh et al. 2019). Liu et al. (2020) prepared garlic skin-derived porous biomass carbon (GSP-BC) using KOH-based activation exhibiting ultra-high surface area (3686 m^2g^{-1}) with a total pore volume of 1.96 cm^3g^{-1}. They have shown that garlic skin waste is a feasible precursor to use for the preparation of porous biomass carbon. GSP-BC showed an adsorption capacity of 1911.8 mg/g toward tetracycline hydrochloride. The adsorption process followed a pseudo-second-order model which agreed well with Freundlich isotherm. It adsorbs on the surface of sorbent GSP-BC with the most possible mechanism of pore filling, hydrogen bonding, π-π electron donor-acceptor interactions, and electrostatic interactions.

A new concept of triple-network hydrogel carbon nanotubes/L-cysteine@graphene oxide/sodium alginate (CNTs/L-cys@GO/SA) was synthesized with more pores and antibiotic adsorption sites for the removal of antibiotic ciprofloxacin depicted in Fig. 3. The maximum adsorption capacity of ciprofloxacin adsorbed onto CNTs/L-cys@GO/SA was 181 mg/g. Ciprofloxacin being an unsaturated molecule, the mechanism behind adsorption includes π-π electron donor-receptor interaction, π-π stacking, and electrostatic adsorption. The electrostatic interaction occurs with the negatively charged electron-rich surface of graphene and electropositive ciprofloxacin hydrochloride (Ma et al. 2020). Other available adsorbents for antibiotic removal are given in Table 3.

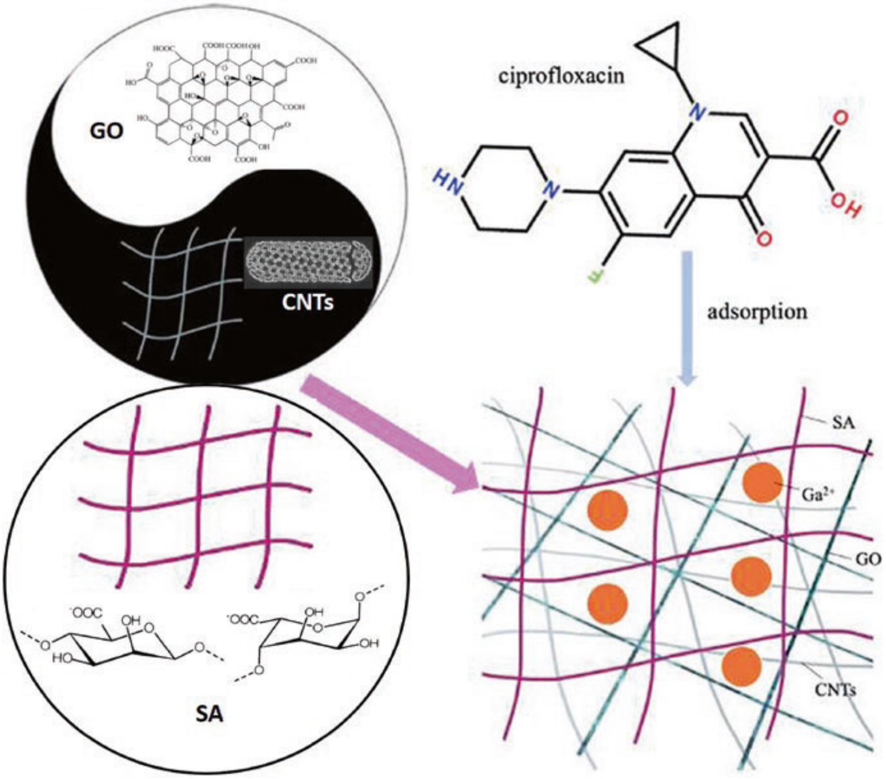

Fig. 3 Schematic diagram of the adsorption of ciprofloxacin on CNTs/L-cys@GO/SA. (Adopted from Ma et al. 2020; Copyright 2021, Elsevier)

Table 3 Nanoadsorbents for antibiotic removal (Eniola et al. 2019)

Antibiotic	Adsorbent	pH	Temperature °C	BET mg^2/g	Adsorption capacity mg/g
Polymer sorbents					
Penicillin V	Amberlite XAD-16	2.7	25	904	1401
Cephalexin	Amberlite XAD-16	3	25	800	116
Erythromycin	Amberlite XAD-4	–	30	725	358
Tetracycline	CS 15	–	–	–	4.710
Ciprofloxacin	CS 15	–	–	–	4.413
Carbonaceous sorbents					
Amoxicillin	ZnO/carbon Nanofibers	7.5	–	–	156
Amoxicillin	MAC-1	–	50	–	245.03
Amoxicillin	MAC-2		50	–	414.03
Amoxicillin	AC	4.98	–	1092.95	221.8
Penicillin G	SWCNTs	5	10	–	141
Penicillin G	MWCNTs	5	10	–	119
Amoxicillin	MWCNT	7	60	712.9	159.4
Clay based sorbents					
Amoxicillin	Bentonite	3.8	30	91.6	49.9
Amoxicillin	DK 1	–	20	3.79	26.1
Ciprofloxacin	Fe-PILL	10	20	206	122
Ciprofloxacin	Si-PILL	10	20	519	100
Ciprofloxacin	Clay	10	20	67	80.8
Ciprofloxacin	Zr-PILL	10	20	231	25.2
Ciprofloxacin	AL-PILL	10	20	322	17.7
Ciprofloxacin	Bentonite	4.5	–	–	147

CS chitosan starch hydrogel, *MAC* modified activated carbon, *AC* activated carbon, *SWCNT* single-walled carbon nanotube, *MWCNT* multiwalled carbon nanotube, *DK* organobentonite, *PILL* pillared clay

4.2 *Nanophotocatalyst*

In recent times, nanophotocatalysis has gained enormous research attention and emerged as a proficient technology for the degradation of antibiotic pollutants. Photocatalysis is generally considered a promising green technique for addressing environmental pollutant issues (Siedlecka 2020). Photocatalyst upon excitation by a photon with greater energy than its bandgap energy produces an electron-hole pair (i.e., excitation of an electron from the valence band to the conduction band) (Fig. 4). The electrons either drive the reduction of an organic molecule (R) or react with O_2 for the formation of superoxide radical anion O_2^-. The developed holes promote the oxidation reaction of adsorbed molecules on the photocatalyst surface. The oxidation process of R from R^+ or reaction with OH^- or H_2O to produce $^{\bullet}OH$

radicals is called mineralization with the formation of CO_2, H_2O, inorganic salts, etc. (Cerro-Lopez and Méndez-Rojas 2017).

Following these mechanisms, many antibiotics have been studied for the possibility to be photocatalytically degraded. The photocatalytic degradation of levofloxacin (LEVO) using crystalline TiO_2 nanoparticles was carried out under UV illumination. It was observed that intermediates formed during the process reduced with increased irradiation, whereas no significant degradation was observed while the same process was performed under dark conditions even after 120 mins of exposure. The photocatalytic efficiency of prepared TiO_2 nanoparticles and commercially available TiO_2 (P25 & PC-50) photocatalyst was compared for their abilities to degrade LEVO at known catalyst dosage (1 g L^{-1}), LEVO concentration (25 mg L^{-1}), pH (6), and irradiation time (120 mins). After 120 min of irradiation, 90% of levofloxacin were removed by the as-prepared TiO_2 nanoparticles, while 80% and 78% were degraded by P25 and PC-50 commercial TiO_2 photocatalyst, respectively. The prepared TiO_2 nanoparticles possessed significant photocatalytic performance in the degradation of levofloxacin even after three cycles of reuse (Kansal et al. 2014).

Multiwalled carbon nanotube (MWCNT)/bismuth vanadate ($BiVO_4$) nanofiber photocatalyst was prepared using electrospinning technology for the removal of OTC. The modification of bismuth vanadate with MWCNT possessed a narrower bandgap that absorbs wider wavelength from sunlight and generates e^-/h^+ pairs which in turn enhances the photocatalytic activity and efficiency. The synergistic effect and calcination temperature of MWCNT/$BiVO_4$ played a vital role in increasing the separation rate of photogenerated electron-hole pairs. The degradation rate

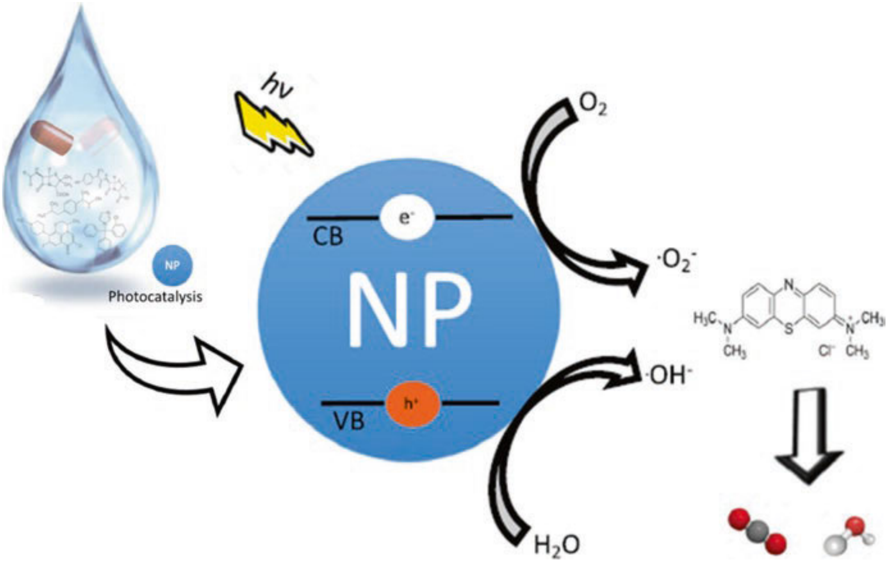

Fig. 4 Representation of photocatalytic process. (Adopted from Fanourakis et al. 2020)

of OTC by MWCNT/BiVO_4 nanofiber photocatalysts was 88.7%. The mechanism of OTC degradation by MWCNT/BiVO_4 nanofiber photocatalyst is given in Fig. 5a (Ye et al. 2019). Likewise, graphene quantum dots decorated graphitic carbon nitride nanorods (GQDs/g-CNNR) photocatalyst was synthesized using the hydrothermal treatment and tested for the removal of oxytetracycline (OTC) in water. The OTC was found to be adsorbed on the photocatalyst in the dark but decomposed OTC (~80%) under visible light. The possible OTC removal mechanisms by GQDs/g-CNNR photocatalyst are schematically represented in Fig. 5b. The chemical oxygen demand (COD) and total organic carbon (TOC) removal during the photocatalytic process were observed to be 56.4% and 68.1%, respectively, through mineralization of OTC. The catalyst was effectively reused for 5 cycles with a degradation efficiency between 70% and 80% and the photocatalyst was highly stable. High utilization efficiency of visible light and the significantly enhanced transportation along with migration rate of photogenerated charges were the reasons behind the excellent photocatalytic activity of GQDs/g-CNNR photocatalyst. Further GQDs/g-CNNR photocatalyst showed ~80% tetracycline removal exhibiting the universality of

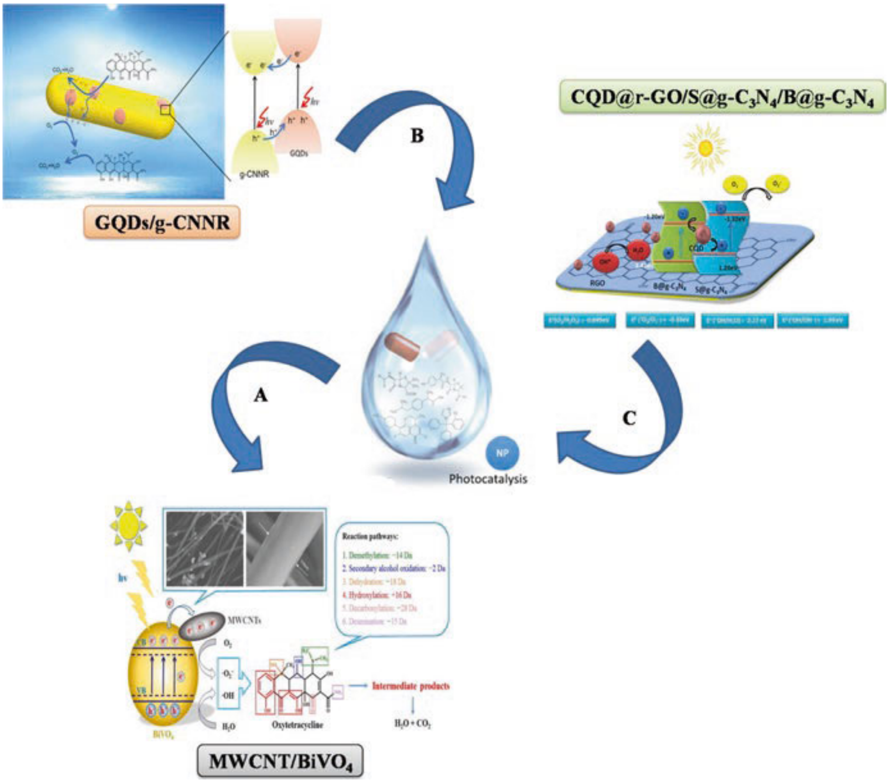

Fig. 5 Nanophotocatalyst mechanism of (**a**) MWCNT/BiVO_4, (**b**) GQDs/g-CNNR, and (**c**) CQD@r-GO/S@g-C_3N_4/B@g-C_3N_4. (Adopted from Ye et al. 2019; Copyright 2021, Elsevier; Yuan et al. 2019; Copyright 2021, Elsevier; Kumar et al. 2020; Copyright 2021, Elsevier)

photocatalyst for antibiotics removal (Yuan et al. 2019). Carbon quantum dots and reduced graphene oxide-modified self-assembled S@C_3N_4/B@C_3N_4 metal-free nanophotocatalyst (CRSB) were synthesized for degradation of chloramphenicol (CMP). The CMP molecules adsorbed to the photocatalyst and got simultaneously degraded by free radicals generated on the surface of CQD@r-GO/S@g-C_3N_4/B@g-C_3N_4 under visible light exposure. The removal efficiency was found to be 99.11%. The mechanisms behind CMP degradation were C-N bond cleavage, dechlorination by radical attack, and finally, the ring opening that resulted in the formation of low molecular weight compounds like HCl, C_2H_5OH, Cl_2, water, CO_2, etc. (Fig. 5c). During the degradation process, dopants boron and sulfur reduced electron recombination, while RGO sheets helped in easy diffusion of e^- and adsorption of CMP molecules to the pollutant (Kumar et al. 2020). Malakootian et al. (2019) synthesized TiO_2-doped Fe^{3+} heterogeneous nanocatalyst for effective removal of metronidazole antibiotic from synthetic solution and pharmaceutical wastewater. Doping of Fe^{3+} ions with TiO_2 nanoparticles traps electrons and pores generated from radiation over the surface of the TiO_2 network. Both the photocatalytic and quantum efficiencies are enhanced through a decrease in electron recombination and pore development. The influences of different factors pH, concentration of nanophotocatalyst, and contact time were studied to obtain optimum parameters (pH 11, catalyst dose 500 mg/L, and contact time 120 mins) for 80 mg/L metronidazole degradation process. The removal efficiency of metronidazole with Fe^{3+}-TiO_2/UV-C photocatalyst in synthetic solution and pharmaceutical wastewater under optimum condition was 97% and 69.85%, respectively (Malakootian et al. 2019).

4.3 Advanced Oxidation Process

Ozonation is a type of advanced oxidization process in which a powerful oxidizing agent, ozone, reacts with organic pollutants to form small molecules. The complex ozone oxidation mechanism can be through direct oxidation reaction with dissolved ozone (O_3) or indirect oxidation through the formation of radicals ($OH^{\cdot}$). The direct oxidation of organic pollutants occurs when the molecular ozone reacts with $OH^{\cdot}$ radical under acidic condition (1).

$$3O_3 + OH^- + H^+ \rightarrow 2OH^{\cdot} + 4O_2 \tag{1}$$

During alkaline condition, indirect oxidation occurs with ozone decomposition in reaction with hydroxide ions forming superoxide anion radical O_2 and hydroperoxyl radical HO_2^- (2). Further reaction of indirect oxidation can be depicted as follows (Sivashankar et al. 2016; Cuerda-Correa et al. 2020) (3–7):

$$O_3 + OH^- \rightarrow O_2 + HO_2^- \tag{2}$$

$$O_3 + HO_2^- \rightarrow HO_2 + O_3^- \quad (3)$$

$$HO_2 \rightarrow H^+ + O_2^- \quad (4)$$

$$O_2^- + O_3 \rightarrow O_2 + O_3^- \quad (5)$$

$$O_3^- + H^+ \rightarrow HO_3 \quad (6)$$

$$HO_3 \rightarrow HO^\bullet + O_2 \quad (7)$$

Remarkable ciprofloxacin degradation efficiency was achieved using carbon nanotube supported manganese oxide in the presence of ozone (Sui et al. 2012). The MnOx/MWCNT acts as a catalyst for generating hydroxyl radicals to improve the O_3 oxidation for degrading ciprofloxacin. Similarly, the antibiotic metronidazole was also degraded in the process of catalytic ozonation. The MgO nanocrystals acted as a radical formation initiator and catalyzed the disintegration process through several active radicals as the ozone adsorbed over the surface of MgO. The complete degradation of metronidazole occurred within 20 mins of the ozonation process (Kermani et al. 2016). Zhu et al. (2017) successfully prepared nano-MgO using a homogenous precipitation method for biodegradability of wastewater containing quinoline. The coal gasification wastewater having quinolone was treated with biological and nano-MgO catalytic ozonation process. During ozonation, the ozone decomposition process was accelerated with the help of nano-MgO catalyst through the generation of hydroxyl radical which readily converted quinolone to biodegradable compound. The proposed mechanism of quinolone degradation by nano-MgO is schematically represented in Fig. 6 (Zhu et al. 2017). Bai et al. (2018a,b) synthesized Fe_3O_4/MWCNTs and iron-doped fibrous structured silica nanosphere (Fe-KCC-1) catalysts for catalytic ozonation process to degrade sulfamethazine (SMT) antibiotics having 90% and 96% degradation efficiency, respectively. During the Fe-KCC-1 catalytic process, it was suggested that O_3 with its dipole property adsorbs onto the catalyst's hydroxylated surface which acts as an electrophile and a nucleophile generating ·OH that in turn degraded SMT (Bai et al. 2018a, b). A nano-$Mg(OH)_2$ catalyst was prepared through chemical precipitation which degraded various antibiotics like sulfamide, fluoroquinolone, tetracycline, metronidazole, tinidazole, and dimetridazole within 10 mins of reaction time. Ozonation occurs with promising radical type oxidation, by forming a hydrogen bond with the hydroxyl group of nano-$Mg(OH)_2$. The bound ozone molecules partially decompose into atomic oxygen which accelerates the catalytic ozonation process for the degradation of antibiotics (Sun et al. 2019a, b). Hence, advanced oxidation process shows high degradation efficiency that can be exploited as a promising tool for the degradation of antibiotics in water and wastewater (Wang and Zhuan 2020).

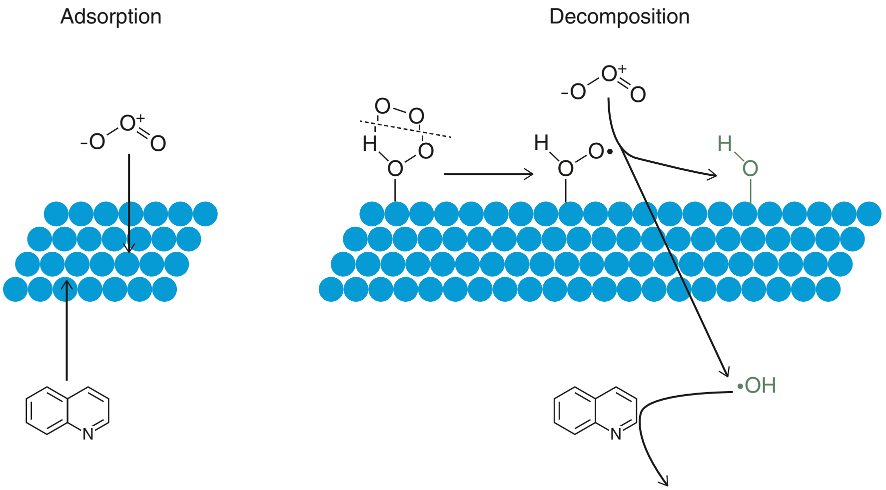

Fig. 6 Catalytic ozonation mechanism for quinolone degradation by Nano-MgO. (Adopted Zhu et al. 2017; Copyright 2021, Elsevier)

4.4 Nanofiltration

Nanofiltration is a pressure-driven separation technique first acknowledged in the late 1980s that falls between reverse osmosis and ultrafiltration that can be used for the separation/removal of antibiotic pollutants. A driving force is generated by exerting pressure on the solution at one side to separate retentate and permeate (Chauhan et al. 2019). The two significant mechanisms of nanofiltration membranes are simple screening and the Donnan effect. Screening effect retains the low molecular weight molecules, whereas the Donnan effect deals with electrostatic interaction of ions to the membrane (Yang and Wang 2015). Nanofiltration membranes are widely used for concentrating antibiotics from the aqueous system similar to different membrane types (Bagheri et al. 2016). In 2016, Lu-Lu Qu et al. synthesized silver nanoparticle/carbon nanotube (Ag NPs/CNT) intercalated graphene oxide (GO) membrane for filtration and enrichment of antibiotic molecules and detected the enrichment using surface-enhanced Raman spectroscopy (SERS). High antibiotic enrichment by membrane was achieved through π-π stacking and electrostatic interactions of GO over antibiotics which also enhanced the sensitivity of SERS detection (Qu et al. 2016). A novel 3D all-carbon nanofiltration (NF) membrane that consists of multiwalled carbon nanotubes (MWCNTs) interposed between GO nanosheets was developed by Yang et al. (2018). The antifouling property of the membrane was achieved through grafting a cationic polyelectrolyte polydiallyldimethylammonium chloride (PDDA) over the MWCNT. This membrane with a thickness of 4.26 μm showed high adsorption of 99.23% for tetracycline hydrochloride (TCH). This was achieved through sieving of antibiotic molecules through electrostatic interaction with a high water permeation of 16.12 L m^{-2} h^{-1} bar^{-1}

which makes this membrane a promising tool for pollutant separation (Yang et al. 2018). Cheng et al. (2015) developed a green membrane technology with m-phenylenediamine/trimesoyl chloride (MPDA/TMC), polyethylene glycol (PEG) 600-NH_2, and PEG-4arm-NH_2 thin film composite nanofiltration membranes using interfacial polymerization for the removal of antibiotics clindamycin phosphate, tobramycin, and cephalexin as illustrated in Fig. 7. The negatively charged high molecular weight clindamycin phosphate was highly rejected (98.6%) by MPDA/TMC. The PEG-based membranes were hydrophilic and rejected over 80% of all tested antibiotics which also exhibited high fouling and chlorine resistance (Cheng et al. 2015). The polyamide thin film composite membrane with piperazine (PIP)-TMC was prepared by interfacial polymerization. The prepared membrane was covalently anchored with 1-aminoethyl-3-methylimidazolium bromide (AMIB) molecules that exhibited high water flux. PIP-TMC-AMIB thin film composite membrane was exploited to filter solutions containing various antibiotics such as ciprofloxacin, tetracycline, oxytetracycline, levofloxacin, and erythrocin with effective rejection of >90% and high water permeance ($22.5\ \mathrm{L\ m^{-2}\ h^{-1}\ bar^{-1}}$). The membrane also possessed good antibacterial activity in addition to the high separation of antibiotics (He et al. 2020). Recently, Li et al. (2020) developed laminated titanium carbide ($Ti_3C_2T_x$ (T_x = O, OH, F)) membranes with regular slit-shaped nanochannels assembled with ultra-large $Ti_3C_2T_x$ sheets on polyethersulfone support. A series of antibiotics such as bacitracin, azithromycin, erythromycin, tetracycline, penicillin, rifampicin, and chloramphenicol with varying sizes were used to analyze the separation efficiency of the membrane. Over >90% removal of all the analyzed antibiotics was achieved with the membrane. The mechanism behind the antibiotic removal of the $Ti_3C_2T_x$ membrane is mainly based on size-selective sieving supported by the electrostatic interaction between the membrane and antibiotic molecules. $Ti_3C_2T_x$ nanosheet membrane with the regular slit-shaped parallel interlayer space also improved the permeance (Li et al. 2020).

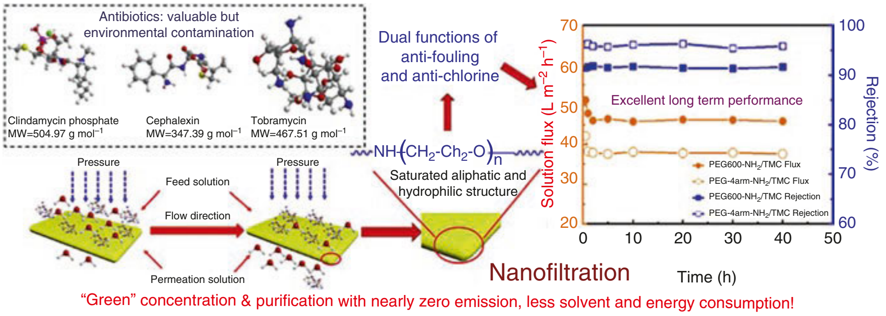

Fig. 7 PIP-TMC-AMIB TFCM nanofiltration membrane mechanism. (Source: Cheng et al. 2015; Copyright 2017, Elsevier)

4.5 Nano-Bio Approach

In recent years, a new approach involving integrated nano-bio systems toward the degradation/removal of antibiotics has been investigated. Gopal et al. (2019) synthesized a novel bio-nanocomposite (BNC)-loaded alginate bead using fortified titanium dioxide (TiO_2) (P25) catalyst with iron oxide nanoparticles and dead biomass of *Acinetobacter* sp. for tetracycline (TC) adsorption and degradation with UV-C irradiation. BNC-loaded alginate bead removed 71.09 ± 0.2% of TC from natural water. These beads were easily separable after the process and possess an increased reusability range, whereas cefdinir antibiotic was degraded and removed from aqueous solution using combined treatment with cefdinir degrading yeast *Candida* sp. SMN04 and MgO nanoparticles. Faster degradation (88%) of cefdinir was achieved in 2.97 days along with a reduced half-life of 1.46 days. This was due to the MgO nanoparticle coating which increased the permeability of transmembrane system of yeast cells for antibiotic transport through the intracellular matrix. The synergistic effect of the integrated system stimulated the biotic process which enhanced the activities of other enzymes (cytochrome P450, NADPH reductase, amylase, and manganese peroxidase) in microbial cells and involvement of β-lactamase enzyme in cefdinir degradation (Adikesavan and Nilanjana 2016). Similarly, degradation of cefdinir using the integrated nano-bio system was observed with yeast *Candida* sp. SMN04 and nanoscale zero-valent ion (nFe^0). Compared to the above investigation the degradation was higher with 91% over 2.68 days with a reduced half-life of 1.34 days. The magnetic separation technique easily recovers nFe^0 (Selvi and Das 2016). Hence, a nano-bio integrated system will serve as an effective remediation tool for antibiotic removal from wastewater.

5 Limitation and Challenges

Nanotechnology, an emerging area, has several advantages, challenges, and shortcomings. The level of sustainability of nanotechnology use in wastewater treatment applications for the removal of antibiotic pollutants is always a primary concern that restricts down the large-scale commercialization. Some of the major limitations are (1) dispersion issues, (2) low retention and recovery, (3) loss of activity over time, (4) realistic efficacy condition, (5) cost balance, and (6) lesser known downhill toxicity of nanoparticles (Saikia et al. 2019). Currently, research is underway for the synthesis of several nanotechnology-based products for remediation of antibiotics in wastewater but rarely very few products are commercialized. The challenges in exploiting nanoparticles include (1) handling of toxicity-related issues of nanomaterials, (2) technical and economic barriers, (3) regulatory policies for nanomanufacturing processes, (4) deployment of scale-up procedures, and (5) life cycle analysis (Khan 2020). Among the mentioned limitations, the major concern is the environmental fate of nanomaterial toxicity. It is suspected that leached out nanoparticles possess a high risk of toxicity that harms human health. The potentiality of nanoparticles is always overwhelmed with its properties like smaller size, high surface area, high reactivity, etc. Due to the same properties, they are found to exhibit health effects in living beings. The disposal of generated nanomaterial wastes and its risk assessment has not been addressed systematically in the majority of published scientific literature. Exploitation of potential hazard management plans and risk assessment of leached out nanomaterial in the removal of antibiotics from wastewater are the real challenges for the research community (Baruah et al. 2019).

6 Conclusion

Antibiotics, a major global threat, have a short life span but their properties like hydrophobicity and lipophilic nature make them environmentally persistent and cause increased antibiotic resistance. The commercially existing WWTP is not efficient enough to completely degrade antibiotic pollutants and their residues from wastewater. In recent years, advancements in novel nanomaterials have shown good potential and are highly exploited to overcome the drawbacks of conventional wastewater treatment techniques. Although the efficiency of nanomaterials for antibiotic removal/degradation is high, their inherent toxic nature hampers the commercialization of the product. To generate promising nanotechnology for the remediation of antibiotic pollutants, the challenges and limitations mentioned in this chapter have to be addressed with in-depth studies. Even though antibiotic technologies will be further improved in the future, control measures for the safe use of antibiotics should be adopted.

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References

Adegoke AA, Stenström TA (2019) Metal oxide nanoparticles in removing residual pharmaceutical products and pathogens from water and wastewater. In: Nanoparticles in pharmacotherapy. William Andrew Publishing, pp 561–589

Adikesavan S, Nilanjana D (2016) Degradation of cefdinir by *Candida Sp.* SMN04 and MgO nanoparticles—an integrated (Nano-bio) approach. Environ Prog Sustain Energy 35(3):706–714

Ahmad A, Dutta J (2020) The role of combination beads for effective removal of antibiotic cefixime from water: towards of better solution. J Phys Confer Ser 1531(1):012092

Amin MT, Alazba AA, Manzoor U (2014) A review of removal of pollutants from water/wastewater using different types of nanomaterials. Adv Mater Sci Eng 2014

Anjali R, Shanthakumar S (2019) Insights on the current status of occurrence and removal of antibiotics in wastewater by advanced oxidation processes. J Environ Manag 246:51–62

Bagheri H, Afkhami A, Noroozi A (2016) Removal of pharmaceutical compounds from hospital wastewaters using nanomaterials: a review. Analytical Bioanalytical Chem Res 3(1):1–18

Bai Z, Yang Q, Wang J (2018a) Catalytic ozonation of sulfamethazine antibiotics using Fe_3O_4/multiwalled carbon nanotubes. Environ Prog Sustain Energy 37(2):678–685

Bai Z, Wang J, Yang Q (2018b) Iron doped fibrous-structured silica nanospheres as efficient catalyst for catalytic ozonation of sulfamethazine. Environ Sci Pollut Res 25(10):10090–10101

Balakrishna K, Rath A, Praveenkumarreddy Y, Guruge KS, Subedi B (2017) A review of the occurrence of pharmaceuticals and personal care products in Indian water bodies. Ecotoxicol Environ Saf 137:113–120

Baruah A, Chaudhary V, Malik R, Tomer VK (2019) Nanotechnology based solutions for wastewater treatment. In: Nanotechnology in water and wastewater treatment. Elsevier, pp 337–368

Cerro-Lopez M, Méndez-Rojas MA (2017) Application of nanomaterials for treatment of wastewater containing pharmaceuticals. In: Ecopharmacovigilance. Springer, Cham, pp 201–219

Chauhan A, Sillu D, Agnihotri S (2019) Removal of pharmaceutical contaminants in wastewater using nanomaterials: a comprehensive review. Curr Drug Metab 20(6):483–505

Chen Z, Guo J, Jiang Y, Shao Y (2021) High concentration and high dose of disinfectants and antibiotics used during the COVID-19 pandemic threaten human health. Environ Sci Eur 33(1):1–4

Cheng XQ, Liu Y, Guo Z, Shao L (2015) Nanofiltration membrane achieving dual resistance to fouling and chlorine for "green" separation of antibiotics. J Membr Sci 493:156–166

Cuerda-Correa EM, Alexandre-Franco MF, Fernández-González C (2020) Advanced oxidation processes for the removal of antibiotics from water. An overview. Water 12(1):102

Das N, Madhavan J, Selvi A, Das D (2019) An overview of cephalosporin antibiotics as emerging contaminants: a serious environmental concern. 3 Biotech 9(6):231

Dindarloo K, Aghamolaei T, Ghanbarnejad A, Turki H, Hoseinvandtabar S, Pasalari H, Ghaffari HR (2020) Pattern of disinfectants use and their adverse effects on the consumers after COVID-19 outbreak. J Environ Health Sci Eng 18(2):1301–1310

Eniola JO, Kumar R, Barakat MA (2019) Nanomaterials for the adsorptive removal of antibiotics from aqueous solution: a minireview. General Chem. https://doi.org/10.21127/yaoyigc20190018

Fanourakis SK, Peña-Bahamonde J, Bandara PC, Rodrigues DF (2020) Nano-based adsorbent and photocatalyst use for pharmaceutical contaminant removal during indirect potable water reuse. npj Clean Water 3(1):1–15

Gopal G, Roy N, Chandrasekaran N, Mukherjee A (2019) Photo-assisted removal of tetracycline using bio-nanocomposite-immobilized alginate beads. ACS Omega 4(17):17504–17510

He B, Peng H, Chen Y, Zhao Q (2020) High performance polyamide nanofiltration membranes enabled by surface modification of imidazolium ionic liquid. J Membrane Sci 118202

Kansal SK, Kundu P, Sood S, Lamba R, Umar A, Mehta SK (2014) Photocatalytic degradation of the antibiotic levofloxacin using highly crystalline TiO 2 nanoparticles. New J Chem 38(7):3220–3226

Kermani M, Bahrami Asl F, Farzadkia M, Esrafili A, Salahshour Arian S, Khazaei M et al (2016) Heterogeneous catalytic ozonation by Nano-MgO is better than sole ozonation for metronidazole degradation, toxicity reduction, and biodegradability improvement. Desalin Water Treat 57(35):16435–16444

Khan SH (2020) Green nanotechnology for the environment and sustainable development. In: *Green materials for wastewater treatment*. Springer, Cham, pp 13–46

Kumar M, Jaiswal S, Sodhi KK, Shree P, Singh DK, Agrawal PK, Shukla P (2019) Antibiotics bioremediation: perspectives on its ecotoxicity and resistance. Environ Int 124:448–461

Kumar A, Kumari A, Sharma G, Du B, Naushad M, Stadler FJ (2020) Carbon quantum dots and reduced graphene oxide modified self-assembled S@ C3N4/B@ C3N4 metal-free nanophotocatalyst for high performance degradation of chloramphenicol. J Mol Liq 300:112356

Kupolati KW, Busari AA, Sadiku ER et al (2020) Inhibition of bacterial growth and removal of antibiotic-resistant bacteria from wastewater. In: Antibiotics materials in healthcare. Elsevier, pp 159–170

Kyzas GZ, Deliyanni EA, Matis KA, Lazaridis NK, Bikiaris DN, Mitropoulos AC (2018) Emerging nanocomposite biomaterials as biomedical adsorbents: an overview. Composite Interfaces 25(5–7):415–454

Li MF, Liu YG, Zeng GM, Liu N, Liu SB (2019) Graphene and graphene-based nanocomposites used for antibiotics removal in water treatment: a review. Chemosphere 226:360–380

Li ZK, Wei Y, Gao X, Ding L, Lu Z, Deng J et al (2020) Antibiotics separation with MXene membranes based on regularly stacked high-aspect-ratio nanosheets. Angew Chem Int Ed 59(24):9751–9756

Liu S, Pan M, Feng Z, Qin Y, Wang Y, Tan L, Sun T (2020) Ultra-high adsorption of tetracycline antibiotics on garlic skin-derived porous biomass carbon with high surface area. New J Chem 44(3):1097–1106

Ma J, Jiang Z, Cao J, Yu F (2020) Enhanced adsorption for the removal of antibiotics by carbon nanotubes/graphene oxide/sodium alginate triple-network nanocomposite hydrogels in aqueous solutions. Chemosphere 242:125188

Malakootian M, Olama N, Nasiri A (2019) Photocatalytic degradation of metronidazole from aquatic solution by TiO 2-doped Fe 3 PLUS_SPI nano-photocatalyst. Int J Environ Sci Technol 16(8):4275–4284

Mohammed AA, Kareem SL (2019) Adsorption of tetracycline fom wastewater by using pistachio shell coated with ZnO nanoparticles: equilibrium, kinetic and isotherm studies. Alex Eng J 58(3):917–928

Nasseh N, Barikbin B, Taghavi L, Nasseri MA (2019) Adsorption of metronidazole antibiotic using a new magnetic nanocomposite from simulated wastewater (isotherm, kinetic and thermodynamic studies). Compos Part B 159:146–156

Pei M, Zhang B, He Y, Su J, Gin K, Lev O et al (2019) State of the art of tertiary treatment technologies for controlling antibiotic resistance in wastewater treatment plants. Environ Int 131:105026

Qu X, Brame J, Li Q, Alvarez PJ (2013) Nanotechnology for a safe and sustainable water supply: enabling integrated water treatment and reuse. Acc Chem Res 46(3):834–843

Qu LL, Liu YY, Liu MK, Yang GH, Li DW, Li HT (2016) Highly reproducible Ag NPs/CNT-intercalated GO membranes for enrichment and SERS detection of antibiotics. ACS Appl Mater Interfaces 8(41):28180–28186

Rakshit S, Sarkar D, Elzinga EJ, Punamiya P, Datta R (2013) Mechanisms of ciprofloxacin removal by nano-sized magnetite. J Hazard Mater 246:221–226

Ramavandi B, Akbarzadeh S (2015) Removal of metronidazole antibiotic from contaminated water using a coagulant extracted from Plantago ovata. Desalin Water Treat 55(8):2221–2228

Riaz L, Anjum M, Yang Q, Safeer R, Sikandar A, Ullah H et al (2020) Treatment technologies and management options of antibiotics and AMR/ARGs. In: Antibiotics and antimicrobial resistance genes in the environment. Elsevier, pp 369–393

Saikia J, Gogoi A, Baruah S (2019) Nanotechnology for water remediation. In: Environmental nanotechnology. Springer, Cham, pp 195–211

Selvi A, Das N (2016) Nano-bio hybrid system for enhanced degradation of cefdinir using *Candida sp.* SMN04 coated with zero-valent iron nanoparticles. J Appl Pharm Sci 6(09):009–017

Siedlecka EM (2020) Application of bismuth-based photocatalysts in environmental protection. In: Nanophotocatalysis and environmental applications. Springer, Cham, pp 87–118

Sivashankar R, Sathya AB, Sivasubramanian V (2016) Wastewater treatment technologies and recent developments. Environ Sustain Green Technol 1:1

Sui M, Xing S, Sheng L, Huang S, Guo H (2012) Heterogeneous catalytic ozonation of ciprofloxacin in water with carbon nanotube supported manganese oxides as catalyst. J Hazard Mater 227:227–236

Sun Q, Lu J, Wu J, Zhu G (2019a) Catalytic ozonation of sulfonamide, fluoroquinolone, and tetracycline antibiotics using nano-magnesium hydroxide from natural bischofite. Water Air Soil Pollut 230(3):1–15

Sun Q, Zhu G, Wu J, Lu J, Zhang Z (2019b) Catalytic ozonation of nitroimidazole antibiotics using nano-magnesium hydroxide as heavy-metals free catalyst. Desalin Water Treat 161:216–227

Torres-Palma RA, Serna-Galvis EA, Ávila-Torres YP (2020) Photochemical and photocatalytical degradation of antibiotics in water promoted by solar irradiation. In: Nano-materials as photocatalysts for degradation of environmental pollutants. Elsevier, pp 211–243

Wang J, Zhuan R (2020) Degradation of antibiotics by advanced oxidation processes: an overview. Sci Total Environ 701:135023

World Health Organization. (2018) WHO report on surveillance of antibiotic consumption: 2016–2018 early implementation

Wu B (2020) Human health hazards of wastewater. In: High-risk pollutants in wastewater. Elsevier, pp 125–139

Yang H, Wang X (2015) Mechanism of removal of pharmaceuticals and personal care products by nanofiltration membranes. Desalin Water Treat 53(10):2816–2824

Yang GH, Bao DD, Zhang DQ, Wang C, Qu LL, Li HT (2018) Removal of antibiotics from water with an all-carbon 3D nanofiltration membrane. Nanoscale Res Lett 13(1):1–8

Ye S, Zhou X, Xu Y, Lai W, Yan K, Huang L et al (2019) Photocatalytic performance of multi-walled carbon nanotube/BiVO4 synthesized by electro-spinning process and its degradation mechanisms on oxytetracycline. Chem Eng J 373:880–890

Yuan A, Lei H, Xi F, Liu J, Qin L, Chen Z, Dong X (2019) Graphene quantum dots decorated graphitic carbon nitride nanorods for photocatalytic removal of antibiotics. J Colloid Interface Sci 548:56–65

Zhu H, Ma W, Han H, Han Y, Ma W (2017) Catalytic ozonation of quinoline using nano-MgO: efficacy, pathways, mechanisms and its application to real biologically pretreated coal gasification wastewater. Chem Eng J 327:91–99

Phenoxy Herbicides in Aquatic Ecosystems: Environmental Levels, Toxicological Effects, and Remediation Methods

Elżbieta Mierzejewska and Magdalena Urbaniak

Abstract Inappropriate storage and application practices may lead to the wide dispersal of phenoxy herbicides, including 2,4-D (2,4-dichlorophenoxyacetic acid) and MCPA (4-chloro-2-methylphenoxyacetic acid), and their metabolites throughout the environment. Worldwide data have identified increased levels of 2,4-D and MCPA in wetlands, marine water, stormwater, rivers, groundwater, and sources of drinking water. Ecotoxicological studies showed that those herbicides can exert a negative effect on aquatic organisms. A growing body of literature has investigated physicochemical methods of phenoxy herbicide removal from water systems using various adsorbent materials and photocatalysis. Biodegradation is an in situ environmentally friendly method which takes advantage of autochthonous soil bacteria activity. Phytoremediation and rhizoremediation can serve as an effective barrier for phenoxy acids due to interactions between plants and microorganisms. This chapter deals with the current status of selected phenoxy herbicide production, their commercial sale and use, mode of action, legislation, physical and chemical properties

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and their fate in the environment, levels observed in water ecosystems, effects on biota, and remediation technologies. This chapter also identifies critical challenges in handling these compounds and future research needs in order to prevent exposure and to protect living resources on a global scale.

Keywords Phenoxy herbicides · 2,4-D · MCPA · Water contamination · Ecotoxicology · Water treatment · Remediation · Bioremediation · Phytoremediation · Rhizoremediation · Constructed wetlands

1 Introduction

Contamination of freshwater ecosystems with residuals of herbicides has become a major concern for science. A great deal of attention has been paid to an effect of several herbicides (e.g., organophosphates – chlorpyrifos and glyphosate – atrazine, paraquat) on biota and methods of their removal (Loganathan et al. 2020). Often these compounds are replaced by new formulations of commercial products and new, synthetic organic compounds. For several years herbicides based on phenoxy phytohormones, such as 2,4-D (2,4-dichlorophenoxyacetic acid) and MCPA (4-chloro-2-methylphenoxyacetic acid), were considered to be safe for natural environment. However, recent data and research has shown that there is a need to verify and question their effect on environment, measure levels of their residuals in water, and develop methods of their removal (Loganathan et al. 2020).

Phenoxy herbicides, including 2,4-D and MCPA, have been the most commonly used herbicides in agriculture since the 1940s (Gupta and Crissman 2013). 2,4-D and related compound 2,4,5-T (which is banned in majority of countries) were used during the Vietnam War as a defoliant commonly known as Agent Orange (Gupta and Crissman 2013). 2,4-D is the fifth most extensively used active ingredient in the USA. In agricultural and home/garden market sector, over 46 mln kg of 2,4-D alone is applied annually (DeQuattro and Karasov 2016). In Europe 6.5 mln kg of herbicides based on phenoxy-phytohormones (i.e., 2,4-D and MCPA) was sold in 2016, including ~2 mln kg sold in Poland. Rapid economic growth and development caused a substantial increase of herbicide use worldwide: for example, overall pesticide use per area of cropland increased worldwide from 1.5 kg ha^{-1} in 1990 to 2.63 kg ha^{-1} in 2017; in Poland, in 1990, an average of 0.37 kg/ha of herbicides was used, while in 2017 the use of plant protection agents increased around sixfold to 2.22 kg/ha (FAO). According to Statistics Poland (2018), in 2017 herbicides based on phenoxy phytohormones accounted for around 13% of total herbicide sales in Poland. Additionally, phenoxy acids are also widely used as aquatic herbicides for the control of invasive aquatic plants in lakes, ponds, and natural waterways. There are various registered commercial formulations of soil and aquatic herbicides containing phenoxy herbicides (Table 1) alone or together with other active ingredients, e.g., dicamba, sulfuron-methyl-sodium, or aminopyralid. Phenoxy herbicides are typically applied as commercial products in the form of amines, salts, or esters.

Table 1 Trade names of commercial products containing 2,4-D and MCPA registered in the USA and Poland

Country	a.i.	Trade names
USA (U.S. EPA, 2020)	2,4-D	Hi-Dep, Weedar 64, Weed RHAP, Aquakleen, Aquasweep, Aquacide Pellets, Hivoll 44, 2,4-D DMA-DEA LDV, Acme Hi-Dep Herbicide, Gordon's Brush Killer for Large Property
	MCPA	Agroxone, Bison, Commando M, Dandelion Destroyer, HM-1144 Herbicide, EH1154 Weed and Feed, Chiptox, Horsepower Concentrate/Granular Weed Killer/Selective Herbicide/Spot Weed Killer/Weed and Feed, MCPA Lawn Weed Killer, Bromox MCPA, Curtail M, Maestro Advanced Herbicide/Advanced Selective Herbicide/MA Herbicide
Poland (Institute of Plant Protection, 2016)	2,4-D	Aminopielik D Maxx 430 EC/Standard 600 SL/Super 464 SL, Deresz 306 SE, Diablo 306 SE, Dicopur 600 SL/ Top 464 SL, Dresz 306 SE, Esteron 600 EC, Feniks 306 SE, Gold 450 EC, Horse 306 SE, Huzar Activ 387 OD, Kantor Forte 195 SE, King 306 SE, Kojot 306 SE, Kojot Forte 195 SE, Muskato 306 SE, Mustang 306 SE/ Forte 195 SE, Pielik 85 SP, Tarpan 306 SE, Tayson 464 SL
	MCPA	Agritox 500 SL,/Turbo 750 SL, Agroxone Max 750 SL/Turbo 750 SL, Ceridor MCPA 750 S, ChwasTech Turbo 750 SL, Chwastox 500 SL/750 SL/AS 600 EC/D 179 SL/Extra 300 SL/Trio 540 SL/Turbo 340 SL, Dicoherb 750 SL/Turbo 750, Fastoxin 300 SL, MCPA 300 SL, Nutox Turbo 750 SL, The-Tox Turbo 750 SL, Weed-Tox Turbo 750 SL, Weedox 300 SL/ Plus 340 SL

a.i. – active ingredient

These compounds control the growth of dicotyledonous broadleaf weeds (e.g., *Cirsium arvense*, *Cirsium vulgare*, *Convolvulus arvensis*, *Apocynum cannabinum*, *Amaranthus* spp., *Vicia* spp., *Lemna* spp., *Myriophyllum* spp.) in monocotyledonous grass cereal grains (e.g., rice and wheat). The tools of genetical engineering enabled the transfer of genetic resistance to 2,4-D to soybeans, which created an alternative to glyphosate-resistant cereals (Gupta and Crissman 2013).

The modes of action of phenoxy herbicides are similar to that of phytohormones (IAA, auxins) by participating in the regulation of plant growth/physiological processes (Skiba and Wolf 2017). Auxins are phytohormones which stimulate growth and developmental processes in plants. When the concentration of auxins exceeds standard values, it can cause severe malformations and eventually lead to lethal damage to sensitive plant tissues. If the concentration of natural auxins is too high, they can be readily deactivated by cell mechanisms, whereas synthetic auxins (including 2,4-D and MCPA) are more stable, long-lasting, and hence more effective as herbicides. They are applied to the foliage of weeds as post-emergence agents and transported to meristems, causing uncontrolled growth and consequently damaging the structure of plant tissues. It has been stated that the phytotoxic activity of auxins is determined by the charge of the carboxyl group together with the aromatic ring structure. The effects of phenoxy herbicides can be observed as discoloration of foliage and deformations in new growth, the spontaneous formation of cambial cell regions, and unstructured cell division (Grossmann 2003).

Inappropriate storage and application practices may lead to the wide dispersal of active ingredients and their metabolites throughout the environment, especially in soil and water ecosystems, resulting in disturbances of ecological sustainability. After herbicides are applied to land, they are spread in the environment through several processes such as sorption/desorption, leaching, runoff, plant uptake, and volatilization. Phenoxy acid herbicides and their metabolites can reach surface- and groundwater through surface runoff and leaching processes. The persistence of acidic herbicides is increased in a temperate climate characterized by low winter temperatures and, in many regions, by depleted soil organic carbon content and acidic pH (Paszko 2011). Additionally, phenoxy acids can sink into the bottom sediments and be adsorbed onto solid particles. Hence, extensive use of phenoxy herbicides may promote the contamination of environmental matrices and consequently can generate a threat to surface- and groundwater ecosystems. There are high levels of uncertainty when assessing the distribution of phenoxy herbicides in the environment. Data from several sources have identified increased levels of MCPA and 2,4-D in wetlands, marine water, stormwater outlets, rivers, groundwater, and sources of drinking water. Phenoxy herbicides and their metabolites are one of the most frequently detected pollutants in water reservoirs in many European countries. Thus, they are considered to be emerging contaminants, especially because of their significant usage.

Since the 1990s we have observed a growing number of scientific publications (Fig. 1) including articles and reviews, concerned about different aspects of the pollution of aquatic ecosystems with phenoxy herbicides (mainly 2,4-D and MCPA):

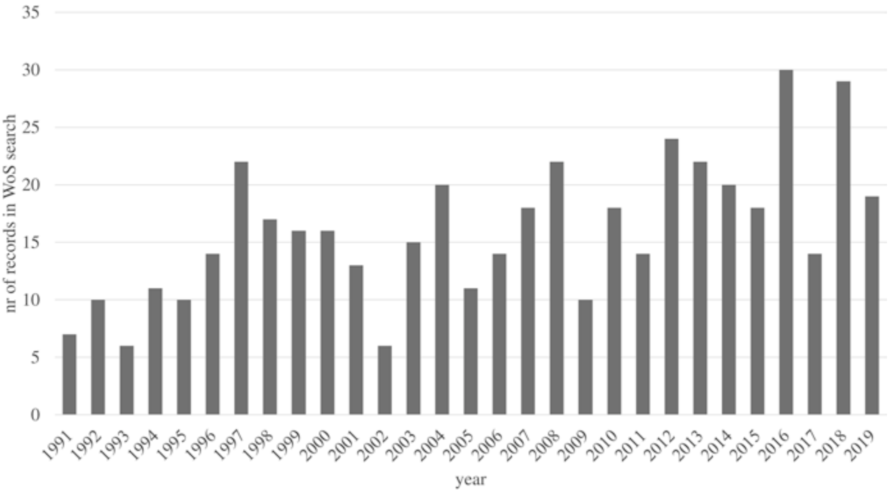


Fig. 1 The number of records in Web of Science (WoS) search: TOPIC (phenoxies OR “phenoxy herbicide*” OR “phenoxyalkanoic acid*” OR “phenoxy acid*” OR 2,4-D OR “2,4-dichlorophenoxy acid” OR “MCPA” OR “4-chloro-2-methylphenoxy acid”) AND TOPIC (freshwater OR “fresh water” OR “fresh-water” OR “river” OR “lake” OR “wetland*” OR “dam reservoir” OR “estuary” OR “transitional water*” OR “seawater*” OR “sediment*”)

mode of action, monitoring the levels of phenoxy herbicides in water sources, establishing the maximum permissible limits of phenoxy herbicides in drinking water, ecotoxicological effect on aquatic organisms (animals and plants), and methods of phenoxy herbicide removal from the environment. According to *Web of Science Categories*, a large number of publications on phenoxy herbicides were classified in the following fields: Environmental Science (184 records), Analytical Chemistry (58 records), and Toxicology (50 records). However, it is still necessary to continue the interdisciplinary research and implement decisive legislative actions which can prevent and mitigate the risk posed by the contamination of water with phenoxy herbicides.

Until now, reviews considering phenoxy herbicides were focused mainly on the following: monitoring the concentration and the effect of single compounds, i.e., MCPA and mecoprop (Caux et al. 1995; Buss et al. 2006), on the surrounding environment; the effect of pesticides (including phenoxy compounds) on saltmarsh sediments (Scrimshaw and Lester 1996); analytical methods of phenoxy herbicide concentration determination in environmental matrices (El Rassi 1997; Dabrowska et al. 2005); the potential endocrine-disrupting effect of herbicides on aquatic organisms (i.e., endemic species of the *Goodeinae* subfamily in the Mexican Central Plateau) (Guerrero-Estevez and Lopez-Lopez 2016) and humans (Buranatrevedh and Roy 2001) (i.e., the cause of hormonal cancers in human); and methods of phenoxy acid removal from environmental matrices (especially soils) (Haggblom 1992; Veeh et al. 1996; Paszko 2011).

Therefore, the major objective of this chapter is to build up an interdisciplinary approach to the problem of water contamination with phenoxy acid herbicides through integrating available literature data on two model phenoxy compounds: 2,4-D and MCPA, with regard to their properties, levels in the environment, toxicity to organisms from different trophic levels, and possible ways of removing them using physicochemical methods and nature-based solutions.

2 Worldwide and European Legislation for 2,4-D and MCPA

Setting the limit values for pesticide residuals in drinking water is very often a complex problem and depends on economic, political, setting, and technological standards. Therefore, different states establish their maximum permissible limits (MPLs) of single and total pesticide concentration based on various factors (Table 2).

The US Environmental Protection Agency (US EPA) permits aquatic 2,4-D applications as spot treatments up to 4000 μg/L and permits whole-lake treatments up to 2000 μg/L with allowances of follow-up treatments 21 days after the initial application. The drinking water MPLs of pesticides (Table 2) are currently established under the Safe Drinking Water Act and include the maximum concentrations of phenoxy herbicides in treated water to be used as a supply of human drinking water. These criteria were established according to several factors such as the potential adverse effects of contaminants on human health, their frequency and level of

Table 2 Maximum levels of MCPA and 2,4-D (μg/L) in drinking water according to the World Health Organization (WHO), US Environmental Protection Agency (US EPA), Health Canada and CDW (CHC), Australian Government, National Health and Medical Research Council (AG), Ministry of Health in New Zealand 2017 (NZ), The Council of the European Union (EU), and the Polish Ministry of Health (PMH)

Organization	WHO	EPA US	CHC	BrMH	AG	NZ	EU	PMH
2,4-D (μg/L)	30	70	100	30 (+2,4,5-T)	30	40	0.1	0.1
MCPA (μg/L)	2	nd	100	nd	40	2	0.1	0.1

nd – not defined

occurrence in public water supply systems, the available treatment technologies, and whether the cost of regulation of the substance will represent a significant opportunity to reduce risks to public health (Barbosa et al. 2015).

In Canada, the guidelines (Health Canada and CDW 2019) for 2,4-D and MCPA in drinking water were established based on potential adverse effects of phenoxy herbicides on health (2,4-D, kidney effects; MCPA, kidney, systemic, liver, testicular, reproductive/developmental, and nervous system effects) and on operational considerations (e.g., the fate of herbicides in the environment: groundwater leach, runoff, use as a weed controller, release from industrial effluents).

In Brazil, Ordinance 2914/2011 from the Brazilian Ministry of Health only includes 27 pesticide active ingredients (<10% of currently used active ingredients in Brazil), which have to be monitored every 6 months in drinking water supplies (Barbosa et al. 2015). MPL is only defined for 2,4-D together with 2,4,5-T, and it is not set for MCPA.

The limit values in Australia are often not based on health issues and toxicological data but rather on the quantification limit of the analytical method, unless the analytical quantification limit is too high (Barbosa et al. 2015).

A set of regulations on pesticide levels in drinking water has been prepared by the Ministry of Health in New Zealand (Ministry of Health in New Zealand 2017), who calculated the MPL of both 2,4-D and MCPA in drinking water basing on:

- No-observable-adverse-effect level (2,4-D, body weight per day for effects on the kidney in chronic studies in rats and mice; 1 mg/kg, MCPA: 0.15 mg/kg body weight per day based on liver and kidney toxicity observed in a 1-year feeding study in dogs).
- Average weight of an adult (70 kg).
- Average quantity of water consumed by an adult (2 L/day).
- Proportion of tolerable daily intake allocated to drinking water (0.1).
- Uncertainty factor (2,4-D, 100 for inter- and intra-species variation; MCPA, 300 and 100 for inter- and intra-species variation and 3 for the inadequacy of the database).

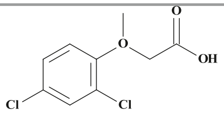
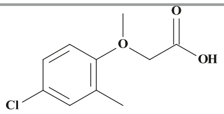
The European Commission Directive No. 2005/57/EC and Regulation No. 540/2011 and 2015/2033 (European Commission 2005, 2011, 2015) imply the legal use of 2,4-D and MCPA as active substance only as herbicides within the European Union. Additionally, both documents emphasize that Member States cit. *Should pay* *particular attention to the potential for groundwater contamination, when the active substance is applied in regions with vulnerable soil and/or climatic conditions. Conditions of authorization should include risk mitigation measures, where appropriate* (e.g., buffer zones). For MCPA, Member States should also emphasize the protection of aquatic organisms, whereas for 2,4-D it is specified that the dermal absorption should be monitored and non-target arthropods should be protected. The maximum residue levels (mg/kg) of 2,4-D and MCPA as well as 2,4,5-T, for products sold within the European Union, are described in Annex II of Regulation No. 149/2008 and No. 491/2014 (European Commission 2008, 2014). In contrast to other states and recommended values by the WHO, the EU strictly reduced the MPL of individual pesticides and their total amount in order to almost completely remove their residuals from drinking water.

The MPLs of phenoxy herbicides in drinking water, which are established by different organizations and governments, can vary significantly (Table 2). Before Poland implemented EU directives, the total pesticide content in surface water used to supply people with drinking water had been defined for three water classes (Polish Ministry of Environment 2012): 1 μg/L for A1 class (water requiring simple physical treatment, in particular filtration and disinfection), 2.5 μg/L for A2 class (water requiring physical and chemical treatment, in particular pre-oxidation, coagulation, flocculation, decanting, filtration, disinfection – final chlorination), and 5 μg/L for A3 class (water requiring high-efficiency physical and chemical treatment, in particular oxidation, coagulation, flocculation, decantation, filtration, adsorption on active carbon, disinfection – ozonation, final chlorination).

3 Fate of Phenoxy Herbicides in Water Bodies and Weathering Processes

An increase in the use of pesticides affects most countries where agriculture is an important branch of the economy. Phenoxy herbicides are readily absorbed by target organisms (i.e., dicotyledonous weeds). However, often a significant part of their residuals (*a.i.* and metabolites) does not reach their primary targets, but instead non-target organisms. Phenoxy acids are all based on ring-like structures and have at least one chlorine atom attached to the ring at different positions (Kamrin 1997). For agricultural applications, they are usually used as ammonium salts or esters, because they can be more readily taken up by plants (Plimmer 2001). Herbicides released into the environment in the form of commercial products containing phenoxy acid amines, salts, or esters immediately hydrolyze to their corresponding anionic or neutral forms (Paszko et al. 2016) – pKa values indicate that both 2,4-D and MCPA mostly occur in soils in their anionic forms (Table 3). The standard dosage of phenoxy acid used is in the range of 0.8 kg to 1.8 kg of a.i. per ha. The retention and translocation of herbicides in the soil profile strictly depend on their chemical and physical properties, which are described by pK_a (acid dissociation

Table 3 Physical and chemical properties of 2,4-D and MCPA

Properties	2,4-D	MCPA
Chemical structure		
IUPAC name	(2,4-Dichlorophenoxy)acetic acid	(4-Chloro-2-methylphenoxy) acetic acid
Molar mass (g/mol)	220.04	200.62
Solubility in H_2O (mg/L)	450	720
pK_a	2.73–2.87	3.73
K_{oc} (mg/L)	5–212	10–157
logP	2.50/2.58 ± 0.36	2.41/2.49 ± 0.27
GUS[a]	1.62	2.94
Henry's law constant (Pa x m^3/mol)	1.30×10^{-5}	5.50×10^{-5}
$t_{1/2}$ in water	1–5 days	15 days
$t_{1/2}$ in soil	2–4 weeks	3–4 weeks

[a] GUS – Groundwater Ubiquity Score

constant), logP (octanol-water partition coefficient), and K_{oc} (organic carbon normalized adsorption coefficient) (Table 3). Based on $K_{oc,}$2,4-D has a higher affinity to soil particles than MCPA; however, both compounds in most soil types are expected to leach and subsequently adsorb to soil particles or reach groundwater sources. The relation between pesticide half-life and K_{oc} is described by the Groundwater Ubiquity Score (GUS), which classifies 2,4-D as a transient pesticide and MCPA as a leacher (Paszko et al. 2016). Adsorption and desorption processes depend on time, the physicochemical properties of soil, and soil depth (K_{oc} increases with soil profile). The adsorption of acidic herbicides is positively correlated with organic matter content and negatively correlated with soil pH (Paszko et al. 2016). The remaining particles can either be exposed to spontaneous biodegradation in the soil profile or remain adsorbed to soil particles. Phenoxy herbicides are rather weakly volatilized due to low values of Henry's law constant (Table 3). The residuals of phenoxy herbicides can be partitioned between the aqueous phase and solid soil particles; thus, they can be transported together with soil particles and surface runoff and reach surface water sources. The amount of herbicide residuals transported to water reservoirs via surface runoff depends on several factors such as the quantity of herbicide, commercial formulations, and the presence of both artificial and natural barriers to the transfer of soil/sediment particles (Rheinheimer dos Santos et al. 2020). Intensified runoff and the accumulation of high amounts of pesticides in water reservoirs can be caused by high rainfall (because it causes high pollutant mobilization due to soil erosion during rainy seasons), inadequate plant cover, and soil management and use. The highest levels of phenoxy herbicides in surface water can occur as pulses in response to late spring and early summer (Rheinheimer dos Santos et al. 2020). The transportation of phenoxy herbicides

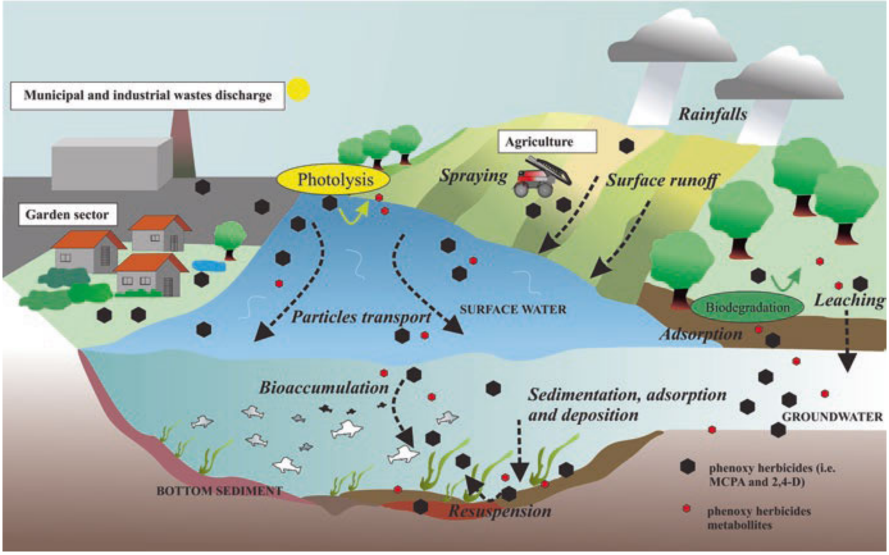


Fig. 2 Fate of phenoxy herbicides in the environment

with surface runoff is determined by the climatic conditions, rates of soil erosion, irrigation, precipitation, and half-life of compounds. A fraction of phenoxy herbicides can be either degraded by natural light (photolysis) or transported and reach the bottom sediment. Phenoxy herbicides can be retained adsorbed to sediment particles and deposited for a long time or absorbed by living organisms and bioaccumulated in trophic chains (Fig. 2).

4 Levels of Phenoxy Herbicides in Water Ecosystems

Data from several sources have identified increased levels of MCPA and 2,4-D in the soil, ground-, surface-, and drinking water (Table 4). Studies by Ignatowicz and Struk-Sokołowska (2004) showed that the concentration of phenoxy herbicides in the Narew River (Poland) fluctuated seasonally from 0 to 150 μg/L. The EU established the MPL of an individual pesticide in drinking water as 0.1 μg/L and the total pesticide concentration as 0.5 μg/L (The Council of the European Union 1998). Of the various pesticides analyzed, 2,4-D was the only compound detected in the Rolante River (Brazil), especially in the summer, which was probably caused by the diffused source of contamination associated with extensive agriculture in the region (Bianchi et al. 2017). Although the level of 2,4-D was below the permitted maximum level in Brazil (Table 2), its presence was associated with a potential genotoxic and cytotoxic effect on aquatic organisms. The group of Harrahy et al. (2014) measured the concentrations of 2,4-D in two Wisconsin lakes: Delavan and Beulah

Table 4 Concentration of phenoxy acids observed in various environments

Compound	Concentration (μg/L)	Environment	Source
2,4-D	0.51	Lebo drain	Metcalfe et al. (2019)
	1.68	McGregor Creek	Metcalfe et al. (2019)
	103–329	Rice field water	Ismail et al. (2015)
	0.8	Sinos River (Rolante, Brazil)	Bianchi et al. (2017)
	0.99	Surface water samples from El Crespo watershed (Argentina)	Perez et al. (2017)
	2.7–36.9	Delavan and Beulah Lakes	Harrahy et al. (2014)
	0.0006	Yamuna River at Okhla (Delhi), India	Aleem and Malik (2005)
	<LD -0.176	Concentration measured in epilithic biofilms	Rheinheimer dos Santos et al. (2020)
	2.2	Minnesota lakes (sites impacted by domestic wastewater)	Guyader et al. (2018)
MCPA	0.08–4.24	Rhône delta (southern France)	Chiron et al. (2009)
	82.8–354	Rice field water	Ismail et al. (2015)
	0.58	Brejo of Cagarrão stream (Portugal)	Palma et al. (2018)
	0.07	Czarna Przemsza River	Janoska and Gruszecka-Kosowska (2020)
	0.052–0.31	Danish surface waters	Matamoros et al. (2012a)
	6.29	Pilica basin	Jarosiewicz et al. (2018)
MCPA, MCPP, 2,4-D	0–150	Narew River	Ignatowicz and Struk-Sokołowska (2004)

(USA), where phenoxy herbicides are used to control the growth of *Myriophyllum spicatum*. Different commercial formulations of herbicide were used in those two locations: DMA (salt) and BEE (ester). The measured concentration did not exceed the public health groundwater preventative action limit of 70 μg/L according to the US EPA (Table 2). The authors hypothesized that 2,4-D, if applied during cold spring periods, can persist in the water column and affect non-target organisms. The results indicated that although 2,4-D is not persistent in the water column, it can influence the abundance of selected groups of macroinvertebrates. The immediate reduction of its concentration in both lakes was probably caused by its dissipation into untreated areas and degradation processes, which are dependent on the trophic status of the lake and bottom type. The concentration of phenoxy herbicides is often dependent on the season: the 2,4-D concentration was higher in the spring/summer than in the autumn/winter, probably due to the phase of development of soybean, corn, and tobacco plants and the period of pesticide application (Rheinheimer dos Santos et al. 2020).

Trace levels of emerging contaminants (i.e., phenoxy herbicides) were noted in sewage released by on-site wastewater treatment systems, which are commonly used by rural communities for water purification. The average concentration of 2,4-D in several sampling sites in Minnesota lakes (USA) impacted by domestic wastewater was 2.2 μg/L (Guyader et al. 2018). These results showed that the household application of herbicides (i.e., for gardening) can contribute more to the contamination of lakes than discharge from an on-site wastewater treatment system.

A national monitoring study on pesticide residuals in selected Vistula tributaries (Poland) showed that MCPA was present in 32.6% of the studied sites; however, its level did not exceed 1 μg/L (Zagibajło et al. 2017). In another monitoring study, MCPA was detected in more than 60% of samples from the Pilica basin. MCPA had the highest noted concentration of all the studied pesticides in the surface water samples (Jarosiewicz et al. 2018). The highest noted concentration of MCPA in the Brejo of Cagarrão stream (Portugal) was 0.58 μg/L (Palma et al. 2018). The high level of MCPA was detected in the summer, probably due to intensive agricultural practices. Although throughout the year the concentration of the studied pesticide was considered to be low, some populations of benthic macroinvertebrates were affected by the presence of organic pollutants. In the studies of Janoska and Gruszecka-Kosowska (2020), water quality was estimated using 62 indicators, including the concentration of phenoxy herbicides (2,4-D and MCPA). MCPA was detected in the Czarna Przemsza River (Poland) and the estimated hazard index indicated a very high total non-carcinogenic risk in a residential exposure scenario. The Danish surface water monitoring of emerging contaminant concentration in rivers showed that MCPA was one of the most abundant pollutants, and its concentration was positively correlated with the increase in rainfall events. The level of MCPA in the majority of surface water reservoirs was higher than the maximum limit of individual pesticides for drinking water in Europe (0.1 μg/L). These results showed that agricultural runoff during rainy seasons contributes significantly to the increase of MCPA in surface waters (Matamoros et al. 2012a).

Sun et al. (2020) monitored the concentration of phenoxy herbicides in tap water throughout China. The detection frequency of phenoxy herbicides in the studied tap water samples ranged from 44.9% to 90.5%. MCPA was more often detected than 2,4-D; however, the highest noted concentrations of MCPA were an order of magnitude lower than those of 2,4-D, i.e., the maximum concentration of 2,4-D amounted to 0.0662 μg/L (detected in samples from South China), whereas the maximum concentration of MCPA amounted to 0.124 μg/L (noted in Southwest China). Additionally, the authors observed that the total concentration of phenoxy herbicides was higher in urban than rural areas, and conventional water treatment was not effective enough to remove the residues of 2,4-D and MCPA. MCPA and 2,4-D were also detected in stormwater: the level of MCPA in 4 out of 62 studied samples exceeded the standard value of 2 μl/L established by Queensland public health standards for recycled water in Australia (Rippy et al. 2017).

5 Toxicological Effects on Aquatic Organisms

Although the *WHO Recommended Classification of Pesticides by Hazard* classified both active ingredients 2,4-D and MCPA as class II pesticides (moderately hazardous) (World Health Organization 2019), their accumulating residuals in environment matrices may cause an adverse effect on living organisms, especially in aquatic ecosystems (Table 5, Fig. 2). Studies of the ecotoxicological effect of phenoxy acids are essential to select species that are sensitive and universal enough to serve as biological biomarkers for biomonitoring the possible adverse effects of selected pollutants. The majority of research on the negative effects of phenoxy acids on non-target organisms is concerned with 2,4-D, whereas other compounds (i.e., MCPA, metabolites) are often neglected.

The experiments of Alves and Oliveira (2014) were focused on the elaboration of the effect which 2,4-D exerts on biomineralization processes in *Anodonta cygnea*, because there is still little known about the molecular mechanism of the toxic effect of phenoxies on aquatic bivalves. *Anodonta cygnea* is a bivalve species which has a wide geographical distribution and is mostly dominant in aquatic habitats; thus, its biological parameters can serve as bioindicators. The applied dose of 22 mg/L of 2,4-D disturbed its shell formation, because it affected the membrane ion transport mechanism essential for biomineralization. The exposure of *Orconectes rusticus* to sublethal doses of 2,4-D for 96 h decreased the fitness of the population and body weight of organisms due to an inability to locate and sense food (Browne and Moore 2014). The studies showed that even lower levels of 2,4-D can cause an impairment of chemoreceptors (the olfactory system), because they are directly exposed to water-soluble compounds such as 2,4-D. Lindsay et al. (2010) observed different responses of various developmental stages of *Mya arenaria* to a commercial formulation of 2,4-D. Veligers were more sensitive than pediveligers, whereas the observation of a long-term effect of 2,4-D on juvenile clams after 21 months showed a hermetic effect. The survival and growth of juvenile clams was enhanced by 2,4-D in comparison to the control. The authors indicated the necessity of ecotoxicological studies on different developmental stages of organisms, because they can be very different.

The effects of phenoxy herbicides have been extensively studied in fish malformations and behavioral changes to fish (i.e., *Cyprinus carpio*; *Danio rerio*) (Sarikaya and Yilmaz 2003; Li et al. 2017). Often the application of phenoxy herbicides coincides with the fish breeding period. Even though no morphological changes were observed, the exposure of embryonic and early larval fish stages to 2,4-D caused a decreased viability of fish progeny due to reduced neural activity within the optic tectum, which is necessary for prey capture and survival (Dehnert et al. 2019). According to recent research, the predicted no-effect concentration (PNEC) for aquatic organisms is 500 μg/L for 2,4-D and 0.022 μg/L for MCPA (López-Roldán et al. 2013). Studies by Sarikaya and Yilmaz (2003) showed that 2,4-D (66 mg/L) caused internal hemorrhage and behavioral changes in *C. carpio*. The presence of 2,4-D in river water probably influenced the increased genetic damage in fish

Table 5 Toxic effects of 2,4-D and MCPA on selected organisms

Dose of 2,4-D or MCPA	Period of exposure	Analyzed organism	Effect on organism	Source
IC50 1353.80 mg/L µ2,4-D	96 h	*Ankistrodesmus falcatus*	External morphological alterations	Martínez-Ruiz and Martínez-Jerónimo (2018)
IC50 71.20 mg/L 2,4-D	96 h	*Microcystis aeruginosa*	Stimulation of the production of cyanotoxins	
LC50 66 mg/L 2,4-D	96 h	*Cyprinus carpio* L.	Behavioral changes	Sarikaya and Yilmaz (2003)
25 and 50 mg/L		*Danio rerio*	Cardiotoxicity, altered transcriptional levels of stress- and cardiac-related genes; accumulation of 2,4-D in embryos	Li et al. (2017)
0.24 mg/L MCPA (both commercial formulations and active ingredient)	0, 24, 48, and 72 h	Crustaceans and algae	Commercial formulations were more toxic than solutions of active ingredient	Pereira and Cerejeira (2000)
50, 75, and 100 mg/L 2,4-D commercial formulation	10 days	*Biomphalaria glabrata*	Development of nonviable embryos	Estevam et al. (2006)
32.69, 14.07, and 7.65 mg/L 2,4-D	96 h	*Orconectes rusticus*	Behavioral changes, lower body weight, decreased fitness of population	Browne and Moore (2014)
LC509.06 and 7.76 mg/L 2,4-D	96 h and 168 h	*Rhinella arenarum*	Reduced body size, delayed development, microcephaly, agenesis of gills, and abnormal cellular proliferation processes	Aronzon et al. (2011)
0.75–8 mg/L 2,4-D	21 days	*Danio rerio* and *Perca flavescens* (embryonic and larval zebrafish)	Disturbance of visual neural activity within the optic tectum	Dehnert et al. (2019)
9 mg/L-1 2,4-D	7 days	*Astacus leptodactylus*	Histopathological alterations in hepatopancreas and gill tissue	Benli et al. (2016)

(continued)

Table 5 (continued)

Dose of 2,4-D or MCPA	Period of exposure	Analyzed organism	Effect on organism	Source
1, 10, 100 mg/L 2,4-D	96 h	*Carassius auratus* L.	Oxidative stress development in the liver and kidney	Husak et al. (2014)
1, 10, 100 mg/L 2,4-D	96 h	*Carassius auratus* L.	Increased level of plasma proteins, changes in leukocyte number, and increase in selected plasma enzyme activity	Kubrak et al. (2013)
112 kg/ha 2,4-D (commercial formulation; water from two lakes)	28–42 days	Benthic macroinvertebrates	Decline in abundance of some groups of macroinvertebrates	Harrahy et al. (2014)
0.00–2.00 mg/L of 2,4-D (commercial formulations)	28 days	*Pimephales promelas*	Endocrine disruption	DeQuattro and Karasov (2016)
252–756 mg/L 2,4-D	48–96 h	*Cnesterodon decemmaculatus*	Increased genetic damage index	Ruiz de Arcaute et al. (2016)
25, 50, 75 mg/L 2,4-D	48–96 h	*Clarias batrachus*	Dose-dependent genotoxicity	Ateeq et al. (2005)
22 mg/L 2,4-D	15 days	*Anodonta cygnea*	Disturbance of shell formation	Alves and Oliveira (2014)
Phytoplankton experiment L 0.3, 3, and 6 mg/L of glyphosate and 0.135, 1.35, and 2.7 mg/L of 2,4-D; periphyton experiment: 3 mg/L of glyphosate and 1.35 mg/L 2,4-D	7 days	Freshwater phytoplankton and periphyton	Additive, synergistic, and antagonistic effects of two compounds on phytoplankton and periphytic communities; periphyton was more resistant to contaminants	Lozano et al. (2018)
0, 0.5, 5, 10, or 50 mg/L 2,4-D commercial formulations (Agway super BK 32)	24 h, 21 months post-exposure experiment	*Mya arenaria* (veliger, pediveligers, and juvenile clams)	Initial growth delay, increased veliger mortality	Lindsay et al. (2010)
0–2.0 mg/L of MCPA (alone and in mixture with glyphosate and bentazone)	3-day exposure for *Z. marina* 2 h exposure for phytoplankton	*Zostera marina and natural communities of phytoplankton from Roskilde Fjord*	Herbicide mixtures: Decreased growth rate, RNA-DNA, chlorophyll *a–b*	Nielsen and Dahllof (2007)

confirmed by comet assay (Scalon et al. 2010; Bianchi et al. 2017). A dose-dependent genotoxic effect of 2,4-D in fish erythrocytes was also confirmed by comet assay (Ateeq et al. 2005). The short-term exposure of fish to 2,4-D caused changes in the number of leukocytes (twofold increase in promyelocytes and sevenfold increase in metamyelocytes), the level of carbonyl proteins (which are a known marker of oxidative damage to proteins), increase in the plasma triacylglycerol, and an increased activity of alanine transaminase and lactate dehydrogenase activity (which are indicators of tissue damage) (Kubrak et al. 2013). However, the majority of the studied parameters returned to control values after 96 h of recovery time, indicating the ability of organisms to recover after short-term exposure to 2,4-D. The microcosm study by Lozano et al. (2018) showed various responses of phytoplankton and periphytic communities to two herbicides: 2,4-D and glyphosate, which are commonly used as mixtures in agriculture. Generally, glyphosate was more toxic; however, glyphosate and 2,4-D applied together could exert an additive, synergistic, or even antagonistic effect on the studied organisms, depending on several factors. Periphyton proved to be more resistant to the applied contaminants.

It has been also demonstrated that the spread of phenoxy herbicides in the environment can result in significant damage to aquatic organisms, leading to the cellular deformation of green algae (i.e., *Ankistrodesmus falcatus*) (Martínez-Ruiz and Martínez-Jerónimo 2018); abnormal cellular proliferation in amphibians (*Rhinella arenarum*) (Aronzon et al. 2011); negative effects on freshwater organisms such as the crustaceans *Daphnia magna*, *Thamnocephalus platyurus*, and *Artemia franciscana* and algae *Selenastrum capricornutum* (Pereira and Cerejeira 2000); and the development of nonviable embryos in invertebrates (*Biomphalaria glabrata*) (Estevam et al. 2006), where effects were directly connected to the doses.

The contamination of water sources with phenoxy herbicides is not only a threat to aquatic organisms but also to humans. According to the International Agency for Research on Cancer, phenoxy acids are classified as “possibly carcinogenic to humans.” According to Hugh-Jones et al. (2020), the significant usage of 2,4-D in rural areas was probably the main cause of an increasing number of Parkinson disease cases among the human population living in areas of moderate and high aquifer-recharge potential.

6 Technologies for Phenoxy Herbicide Removal from Water Ecosystems

6.1 Physicochemical Methods

Conventional water treatments are often ineffective at removing micropollutants, including phenoxy herbicides. Although most of these solutions are low cost, it is still necessary to develop novel, environmentally friendly methods to prevent the spread of pollutants or degrade them on site. Thus, there is an increasing amount of scientific research considering different removal methods of phenoxy herbicides from contaminated water (Fig. 4).

It has been shown that phenoxy herbicides are prone to degrade under the influence of natural sunlight in seawater; thus, some of the developed methods use photocatalysis, which accelerates a photoreaction in the presence of a catalyst. Ye et al. (2018) proposed the application of a membrane-free photocatalytic fuel cell composed of a TiO_2 nanotube array photoanode and a Cu cathode (TNA-Cu PFC system) for the removal of MCPA residuals from pretreated water which is planned to be used as drinking water. The photocatalytic system enhanced the removal of MCPA and exhibited good stability for repeated use. Martinez et al. (2016) studied the removal of a phenoxy herbicide (mecoprop) using advanced oxidation processes (including the ultraviolet/hydrogen peroxide process, e.g., UV/H2O2, the Fenton process, photo-Fenton). Their research showed that optimized photo-Fenton was the most effective process in terms of removing mecoprop from surface water.

The adsorption of phenoxy herbicides by different matrices can also enhance the removal of contaminants from water reservoirs. Sorption is a time-dependent phenomenon and depends on matrix properties (e.g., pH and organic matter content). The adsorption of phenoxy acids is negatively correlated with pH and positively correlated with organic matter content. Some minerals such as ferrihydrite, goethite, and lepidocrite can effectively adsorb phenoxy acids (Paszko et al. 2016). The effectiveness of water treatment in terms of the removal of MCPA and mecoprop was studied by Petrie et al. (1993). Among the different adsorbents, activated carbon, clay, and peat were effective sorption materials at removing herbicides; however, sand filtration did not significantly improve the removal of the studied compounds. The removal of MCPA using constructed wetlands can be enhanced by the application of special sorption materials, i.e., lightweight expanded clay aggregates (LECA) (Dordio et al. 2007). This material can support the matrix in constructed wetlands by enhancing MCPA sorption. A promising alternative adsorbent is also biochar, a porous material produced via biomass pyrolysis. The performance of pine and biosolid biochar (in terms of physicochemical characteristics and sorption properties) can be enhanced by ash pretreatment (Bentley and Summers 2020). Such a modification can increase the sorption of 2,4-D by an order of magnitude from surface water, which is a promising method for improving the treatment of stormwater and wastewater.

6.2 *Biological Methods*

6.2.1 Biodegradation and Bioremediation

Although a great deal of studies showed that phenoxy herbicides can be removed efficiently using physicochemical processes, residuals of the produced metabolites can cause an increase in the ecotoxicity of the studied matrices (Mierzejewska et al. 2019b). Therefore, there is a growing interest in biological transformation and mineralization of organic compounds. Before phenoxy herbicides reach aquatic ecosystems, they are often adsorbed to soil particles, where they are exposed to inter alia microbial degradation (biodegradation). Biological processes are primarily involved in the elimination of phenoxy herbicides from the environmental matrices (Paszko et al. 2016). The biodegradation process is dependent on several factors such as oxygen availability, microbial biomass, and temperature (Paszko et al. 2016). Successful biodegradation is achieved especially by bacteria harboring the functional genes which are involved in the degradation pathway of phenoxy acids (Fig. 3). Various bacteria belonging to different classes and genera which can degrade phenoxies were isolated from both pristine and contaminated environments and this was influenced by anthropogenic activities (Urbaniak and Mierzejewska 2019). Since over the last few decades there has been an increasing interest in biodegradation studies, bacteria equipped with a metabolic apparatus that enables them to utilize phenoxy herbicides have been exhaustively described (Fig. 3), although much more attention has been paid to 2,4-D than other related compounds (e.g., MCPA). The classification of bacteria degrading phenoxy herbicides was established based on their physiology, degrading enzymes, and evolutionary origin (Kamagata et al. 1997). The first group of bacteria degrading phenoxy herbicides is characterized as fast-growing copiotrophic bacteria belonging to beta- and gamma-proteobacteria (Fig. 3) harboring the *tfdA* gene (e.g., *Cupriavidus necator* JMP134, *Burkholderia* sp. strain RASC, and *Rhodoferax* sp. strain P230). The second group

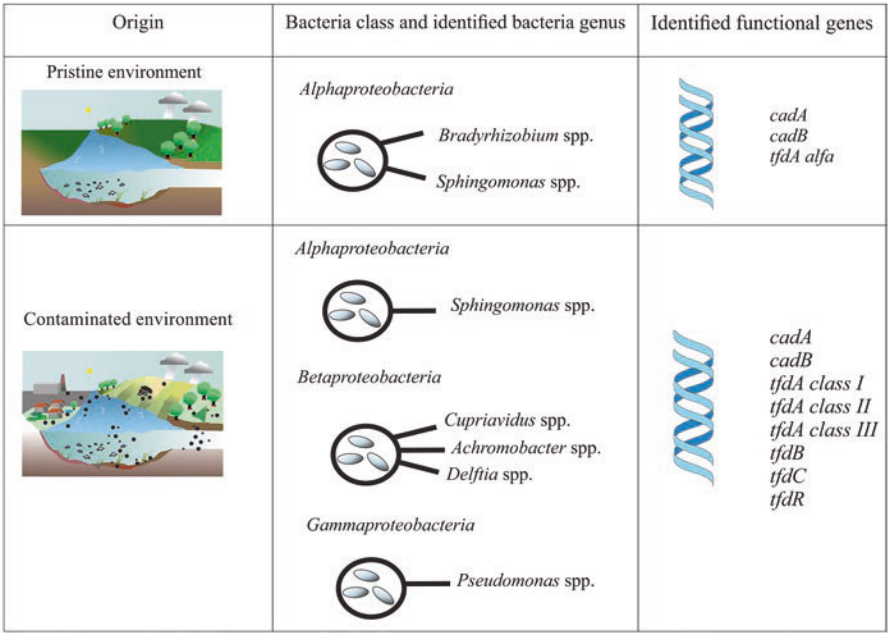


Fig. 3 The identified genus of bacteria isolated from pristine and contaminated environments together with the identified functional genes

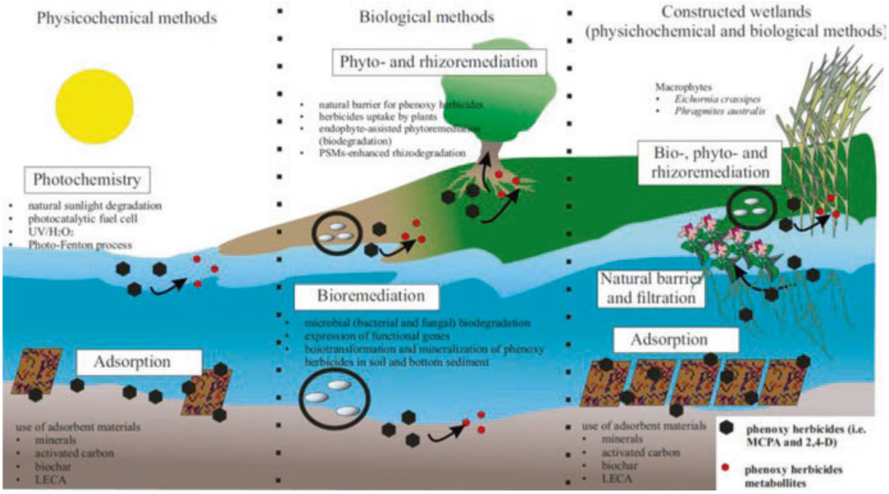


Fig. 4 Physicochemical and biological methods for the removal of phenoxy herbicides from freshwater ecosystems

consists of slow-growing oligotrophic bacteria belonging to alphaproteobacteria, mainly *Bradyrhizobium* harboring the *tfdAa* and *cadA* genes. The third group of bacteria belongs to alphaproteobacteria, mainly *Sphingomonas*.

The first step in the phenoxy herbicide biodegradation pathway is initiated by alpha ketoglutarate-dependent dioxygenase encoded by *tfdA* genes. The *tfdA* gene is located in the *tfdA*BCDEF gene cluster (Kitagawa et al. 2002). Based on the similarities between the *tfdA* sequences, bacteria were classified into subclasses including *tfdA* Classes I, II, and III (Mcgowan et al. 1998; Poll et al. 2010a) and *tfdA alpha* (Kitagawa et al. 2002). One of the most extensively studied 2,4-D degraders is *Cupriavidus necator* JMP134, harboring a 80 kb plasmid pJP4, which carries all of the structural and regulatory genes needed to convert phenoxy herbicides to 2-chloromaleylacetic acid (Bælum et al. 2006). Primarily, the *tfdA* fragment is responsible for the conversion of 2,4-D to 2,4-DCP (2,4-dichlorophenol) (Fukumori and Hausinger 1993) and the compound is further degraded via a pathway encoded by *tfdBCDEF* genes. MCPA degradation is preceded by the expression of *tfdA* genes, followed by the formation of the major metabolite – MCP (4-chloro-2-methylphenol) – through the cleavage of the ether linkage, yielding MCP and acetic acid.

A wide range of bacteria, capable of degrading phenoxy acids in the environment, harbors *tfdA* genes. Due to the high degree of homology between strains, the *tfdA* genes have been selected as biomarkers for the capability of bacteria to metabolize 2,4-D and MCPA (Kitagawa et al. 2002). Hence, they are frequently used in studies on phenoxy acid biodegradation.

Another potential to degrade MCPA and 2,4-D is found in bacteria which carry the *cadA* and *cadB* genes (encoding the nonheme iron oxygenase) and the *rdpA* and *sdpA* genes. Proteins encoded by these genes exhibit a different mode of action and structural and functional differences in substrate preferences from *tfdA* genes.

The enzymes encoded by both *cad* and *tfd* genes are aromatic ring hydroxylation dioxygenases (RHDO), which are widely distributed in a number of microorganisms and might be transferred through horizontal gene transfer (Nojiri et al. 2014). However, the exact role of *cadA*, *cadB*, *rdpA*, and *sdpA* genes has not been fully understood yet.

The spread of phenoxy herbicides in aquatic organisms can be reduced due to the adsorption of residuals on soil particles and subsequent degradation of contaminants; however, it is dependent on the retention time, properties of soil/contaminants, and climatic conditions (i.e., temperature and rainfalls). The study of Mierzejewska et al. (2018) showed that microorganisms present in soil contaminated with a commercial product containing MCPA exhibited biodegradation potential via the presence of *tfdA alpha* and *tfdA* Class III genes. Culture-dependent methods of microorganism identification showed that the use of 2,4-D in agriculture at the recommended level enhances the growth of the copiotrophic 2,4-D-degrading microbial population (Zabaloy and Gómez 2014). In addition, the structure of soil microfauna can also profoundly affect the biodegradation of organic contaminants. Earthworms, which move around in the soil, cause better aeration and increase the soil moisture. This can influence the microorganism population structure and favor microorganism communities that can enhance the process of phenoxy herbicide aerobic degradation (Liu et al. 2013).

Research on the bioremediation of environments contaminated with phenoxy herbicides mostly focuses on bacterial degradation, whereas the fungal activity (mycoremediation) has often been neglected in the majority of environmental research. Studies by Vroumsia et al. (2005) showed that up to 20% of 2,4-D and its metabolite 2,4- DCP can be degraded using the majority of active strains of fungi, i.e., *Aspergillus penicillioides*, *Mortierella isabellina*, *Chrysosporium pannorum*, and *Mucor genevensis*. Studies on Vietnamese soils, heavily contaminated with Agent Orange during the war, showed that the group of *Eupenicillium* spp. can adapt to a high concentration of 2,4-D and 2,4,5-T and coexist with bacterial communities (Itoh et al. 2013). The degradative activity of the filamentous fungi *Umbelopsis isabellina* not only decreased the level of 2,4-D but also reduced the toxic effect of herbicide on *Artemia franciscana* larvae (Nykiel-Szymańska et al. 2018). In contrast to bacteria, there is no described specific pathway of phenoxy herbicide degradation by fungi. Del Pilar Castillo et al. (2001) indicated that fungi can excrete non-specific enzymes involved in lignin degradation (e.g., lignin peroxidase, manganese peroxidase/laccase), which enhance the degradation of phenoxy substances. This statement was subsequently confirmed by other research (Poll et al. 2010b), which showed that the addition of litter stimulated the development of fungal communities and hence the excretion of non-specific enzyme-degrading MCPA. Fungal-based technologies (mycoremediation) of phenoxy herbicide removal from the environment are promising tools for effective biodegradation; however, they have not been developed yet and thus different aspects of these issues need to be tested.

6.2.2 Phyto- and Rhizoremediation

Phytoremediation is another biological method which is a steadily developing strategy for the in situ treatment of contaminated soils (Fig. 4). Phenoxy herbicides can be transformed and subsequently mineralized using plants that are tolerant to high concentrations of these contaminants (Gerhardt et al. 2009). Plants can also contribute to the removal of contaminants indirectly, because they play a crucial role in the development of soil structure and the stabilization of fundamental soil ecosystem functions such as water flow (Machado et al. 2018). Plants produce an array of catabolic enzymes and a range of compounds (e.g., plant secondary metabolites – PSMs) which act to protect the host organisms, stimulate and attract beneficial microorganism, and detoxify xenobiotic compounds (Singer et al. 2003). Successful phytoremediation is determined by several abiotic factors: climate conditions and soil and pollutant characteristics (Reshma and Krishna 2012) and biotic factors – plant cover (selection of an appropriate plant species and cultivars) (Siwek 2008; Posmyk and Urbaniak 2014).

Until now, little attention has been paid to phenoxy acid removal using phytoremediation due to the pollutants' leaching potential and short residence time in soil. However, the development of diversified plant cover (e.g., buffer zones) around an agricultural field could constitute a natural barrier for contaminants before they enter the aquatic ecosystems. The studies of Ramborger et al. (2017) evaluated the phytoremediation potential of *Plectranthus neochilus* exposed to the commercial pesticide Aminol (containing 2,4-D) in soil and water. The removal rate for 2,4-D reached 49% over 60 days, and the herbicide was not detected in plant leaves. The plant was resistant to the applied concentration of herbicide; however, its removal efficiency was not sufficient to consider this method as a potential removal solution.

The coexistence of plants and microorganisms determines the efficient and successful detoxification of contaminated sites. Additionally, this prevents the spread of phenoxy herbicide in the environment. Microbe-assisted phytoremediation (rhizoremediation) is extensively studied, especially in terms of the removal of persistent organic pollutants from environmental matrices. Existing interactions between plant roots, root exudates, soil, and microorganisms are naturally occurring processes within the plant root zone (rhizosphere). The growth of microorganisms and their degradative activity are stimulated by root exudates enriched with PSMs, such as phenolics, flavonoids, coumarins, and terpenes. Plant-derived compounds can influence soil chemical and physical properties, enhance plant health, act as allelochemicals, protect plants against pathogens, serve as substrates or inducers of contaminant catabolic pathways of rhizospheric microorganisms, or enhance the bioavailability of contaminants (Musilova et al. 2016). The microcosm study showed that the biodegradative activity of soil microbiota towards MCPA removal can be enhanced by syringic acid (a PSM excreted by cucurbits) (Urbaniak et al. 2019; Mierzejewska et al. 2019a).

Endophytic bacteria that reside inside the plant tissues are also known to play a crucial role in the removal of organic compounds both directly and indirectly: they can degrade organic contaminants and enhance plant growth (Eevers et al. 2016).

Bacterial endophyte-enhanced phytoremediation was studied by Germaine et al. (2006) on the example of *P. sativum*, which was inoculated with genetically tagged endophytic bacteria, which naturally possess the ability of 2,4-D biodegradation. They not only showed the inoculated plants to have a higher efficiency of herbicide removal but also demonstrated no 2,4-D accumulation in the aerial parts of plants.

6.2.3 Constructed Wetlands

When contaminants enter the aquatic ecosystems, it is necessary to reduce their concentration and prevent their further spread and accumulation in sediments. Recently, more and more studies showed that constructed wetlands (CWs) are effective alternatives to traditional water treatments and can also successfully remove trace micropollutants (Fig. 4). The study on microcosm wetland system investigated the efficiency of the following plants: *Salvinia molesta*, *Lemna minor*, *Ceratophyllum demersum*, and *Elodea canadensis* at removing MCPA from water (Matamoros et al. 2012b). After 38 days, the removal of MCPA was negligible (less than 20%) in comparison to other studied contaminants, which indicated a low efficiency of the selected plants to take up the MCPA from water. Experimental observations were subsequently confirmed by field studies by Matamoros et al. (2012a, b), who studied the effect of a restored wetland system on the mitigation capacity of an emerging contaminant, i.e., MCPA. The average concentration of MCPA in the studied rivers ranged between 0.052 and 0.311 μg/L, whereas in the restored wetland outlet it was 0.133 μg/L. This indicates that the removal efficiency of MCPA was low, and the restored wetland system was not effective enough to remove contaminant residuals. The authors suggested that this was caused by a relatively short water residence time in the restored wetland and the climate conditions (i.e., the low sunlight radiation and low temperature). Rodríguez-Espinosa et al. (2018) studied the feasibility of a constructed wetland planted with *Eichhornia crassipes* to absorb organic compounds (i.e., 2,4-D). In contrast to the previously described studies, the efficiency of 2,4-D removal from water using water hyacinth was 99.1%; thus, this macrophyte can be used in constructed wetlands to remove traces of phenoxy herbicides. The efficiency of LECA (as the bed's substrate in a constructed wetland mesocosm system for the treatment of olive mill wastewater) in terms of MCPA removal was enhanced by vegetation of *Phragmites australis* (up to 28% higher), indicating the importance of synergism between the abiotic and biotic factors (Dordio and Carvalho 2013).

7 Recommendations and Conclusions

There are a growing number of publications which consider phenoxy herbicides as water contaminants; however, they do not provide an interdisciplinary description of the problem. Thus, this chapter collectively describes different aspects of model phenoxy herbicide compounds, i.e., 2,4-D and MCPA, including the following: their effect on aquatic environments, worldwide legislation, toxicological studies, and remediation methods.

Phenoxy herbicides are widely used in the agricultural, industrial, and gardening sectors. Their extensive use, inappropriate storage, and misuse can cause a severe effect on non-target aquatic organisms. Due to their physicochemical characteristics, their retention time in soil is limited and they can leach into groundwater or reach surface waters together with rainfall and intensified surface runoff. According to worldwide monitoring data, the concentration of 2,4-D and MCPA exceeds the limits for drinking water established by various state bodies. The toxicological studies showed that phenoxy herbicides can cause many developmental, systemic, and behavioral changes and act as endocrine disruptors, which is dependent on the time of application, dose of herbicides, and the organism's developmental stage. However, many of these studies were performed under laboratory conditions; thus, it is important to study the toxicological effect in situ. The standardized values of phenoxy herbicide MPLs in drinking water are often based on different factors such as health issues or analytical method; thus, the limit values are significantly different (by orders of magnitude) in the abovementioned states.

Since conventional treatments are often not effective enough to remove trace contaminants (such as phenoxy herbicides), many studies are focused on the development and enhancement of existing environmentally friendly methods. Physicochemical methods such as photodegradation and adsorption can improve the treatment of pretreated water, stormwater, and wastewater. Other methods are based on biological processes such as bio- (bacterial and fungal biodegradation), phyto-, and rhizoremediation, which can be enhanced by the activity of endophytes and PSMs released into the rhizosphere. Also, constructed wetlands can be effective at removal of phenoxy herbicides from surface waters due to a multitude of synchronized processes: filtration, uptake by macrophytes, microbial activity, and adsorption onto optimized matrices.

On the basis of this chapter, it is possible to imply that it is necessary to monitor the level and effect of phenoxy herbicides in water sources. Additionally, various water treatment methods might be developed because of the differences in legislation in individual states. In conclusion, it is essential to gather information from various fields in order to establish and implement decisive, risk-mitigating, preventive, legislative actions which can reduce the risk posed by the contamination of water with phenoxy herbicides.

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References

Aleem A, Malik A (2005) Genotoxicity of the Yamuna River water at Okhla (Delhi), India. Ecotoxicol Environ Saf 61:404–412. https://doi.org/10.1016/j.ecoenv.2004.09.001

Alves MG, Oliveira PF (2014) 2,4-Dichlorophenoxyacetic acid alters intracellular pH and ion transport in the outer mantle epithelium of the bivalve Anodonta cygnea. Aquat Toxicol 154:12–18. https://doi.org/10.1016/j.aquatox.2014.04.029

Aronzon CM, Sandoval MT, Herkovits J, Pérez-Coll CS (2011) Stage-dependent toxicity of 2,4-dichlorophenoxyacetic on the embryonic development of a South American toad, Rhinella arenarum. Environ Toxicol 26:373–381. https://doi.org/10.1002/tox.20564

Ateeq B, Abul Farah M, Ahmad W (2005) Detection of DNA damage by alkaline single cell gel electrophoresis in 2,4-dichlorophenoxyacetic-acid- and butachlor-exposed erythrocytes of Clarias batrachus. Ecotoxicol Environ Saf 62:348–354. https://doi.org/10.1016/j.ecoenv.2004.12.011

Australian Government, National Health and Medical Research Council (2011) National water quality management strategy. Australian Drinking Water Guidelines

Bælum J, Henriksen T, Christian H et al (2006) Degradation of 4-Chloro-2-Methylphenoxyacetic acid in top- and subsoil is quantitatively linked to the class III tfdA gene. Appl Environ Microbiol 72:1476–1486. https://doi.org/10.1128/AEM.72.2.1476

Barbosa AMC, de LM SM, de Umbuzeiro GA (2015) Pesticides in drinking water – the Brazilian monitoring program. Front Public Heal 3. https://doi.org/10.3389/fpubh.2015.00246

Benli ACK, Sahin D, Selvi M et al (2016) The sublethal effects of (2,4-Dichlorophenoxy) acetic acid (2,4-D) on narrow-clawed crayfish (Astacus leptodactylus Eschscholtz, 1823). Arh ZA Hig RADA I Toksikol Ind Hyg Toxicol 67:289–296. https://doi.org/10.1515/aiht-2016-67-2793

Bentley MJ, Summers RS (2020) Ash pretreatment of pine and biosolids produces biochars with enhanced capacity for organic micropollutant removal from surface water, wastewater, and stormwater. Environ Sci Res Technol 6:635–644. https://doi.org/10.1039/c9ew00862d

Bianchi E, Lessing G, Brina KR et al (2017) Monitoring the genotoxic and cytotoxic potential and the presence of pesticides and hydrocarbons in water of the Sinos River Basin, Southern Brazil. Arch Environ Contam Toxicol 72:321–334. https://doi.org/10.1007/s00244-016-0334-0

Brazilian Ministry of Health (2011) Ordinance No 2914/2011 (Portaria N° 2914, de 12 de Dezembro de 2011, Ministério da Saúde). Brazil

Browne AM, Moore PA (2014) The effects of sublethal levels of 2,4-Dichlorophenoxyacetic acid herbicide (2,4-D) on feeding behaviors of the crayfish O-rusticus. Arch Environ Contam Toxicol 67:234–244. https://doi.org/10.1007/s00244-014-0032-8

Buranatrevedh S, Roy D (2001) Occupational exposure to endocrine-disrupting pesticides and the potential for developing hormonal cancers. J Environ Health 64:17–29

Buss SR, Thrasher J, Morgan P, Smith JWN (2006) A review of mecoprop attenuation in the subsurface. Q J Eng Geol Hydrogeol 39:283–292. https://doi.org/10.1144/1470-9236/04-081

Caux P-Y, Kent RA, Bergeron V et al (1995) Environmental fate and effects of MCPA: a Canadian perspective. Crit Rev Environ Sci Technol 25:313–376. https://doi.org/10.1080/10643389509388483

Chiron S, Comoretto L, Rinaldi E et al (2009) Pesticide by-products in the Rhône delta (Southern France). The case of 4-chloro-2-methylphenol and of its nitroderivative. Chemosphere 74:599–604. https://doi.org/10.1016/j.chemosphere.2008.09.012

Dabrowska D, Kot-Wasik A, Namiesnik J (2005) Pathways and analytical tools in degradation studies of organic pollutants. Crit Rev Anal Chem 35:155–176. https://doi.org/10.1080/10408340500207565

Dehnert GK, Karasov WH, Wolman MA (2019) 2,4-Dichlorophenoxyacetic acid containing herbicide impairs essential visually guided behaviors of larval fish. Aquat Toxicol 209:1–12. https://doi.org/10.1016/j.aquatox.2019.01.015

Del Pilar CM, Andersson A, Ander P et al (2001) Establishment of the white rot fungus Phanerochaete chrysosporium on unsterile straw in solid substrate fermentation systems intended for degradation of pesticides. World J Microbiol Biotechnol 17:627–633. https://doi.org/10.1023/A:1012420422111

DeQuattro ZA, Karasov WH (2016) Impacts of 2,4-dichlorophenoxyacetic acid aquatic herbicide formulations on reproduction and development of the fathead minnow (Pimephales promelas). Environ Toxicol Chem 35:1478–1488. https://doi.org/10.1002/etc.3293

Dordio A, Carvalho AJP (2013) Constructed wetlands with light expanded clay aggregates for agricultural wastewater treatment. Sci Total Environ 463–464:454–461. https://doi.org/10.1016/j.scitotenv.2013.06.052

Dordio AV, Teimão J, Ramalho I et al (2007) Selection of a support matrix for the removal of some phenoxyacetic compounds in constructed wetlands systems. Sci Total Environ 380:237–246. https://doi.org/10.1016/j.scitotenv.2007.02.015

Eevers N, Hawthorne JRR, White JCC et al (2016) Exposure of Cucurbita pepo to DDE-contamination alters the endophytic community: a cultivation dependent vs a cultivation independent approach. Environ Pollut 209:147–154. https://doi.org/10.1016/j.envpol.2015.11.038

El Rassi Z (1997) Capillary electrophoresis of pesticides. Electrophoresis 18:2465–2481. https://doi.org/10.1002/elps.1150181236

Estevam EC, Nakano E, Kawano T et al (2006) Dominant lethal effects of 2,4-D in Biomphalaria glabrata. Mutat Res Genet Toxicol Environ Mutagen 611:83–88. https://doi.org/10.1016/j.mrgentox.2006.07.001

European Commission (2005) Commission Directive 2005/57/EC of 21 September 2005 amending Council Directive 91/414/EEC to include MCPA and MCPB as active substances

European Commission (2008) Commission regulation No 149/2008 of 29 January 2008 amending regulation (EC) No 396/2005 of the European Parliament and of the council by establishing Annexes II, III and IV setting maximum residue levels for products covered by Annex I thereto

European Commission (2011) Commission Implementing Regulation (EU) No 540/2011 of 25 May 2011 implementing Regulation (EC) No 1107/2009 of the European Parliament and of the Council as regards the list of approved active substances

European Commission (2014) Commission Regulation (EU) No 491/2014 of 5 May 2014 amending Annexes II and III to Regulation (EC) No 396/2005 of the European Parliament and of the Council as regards maximum residue levels for ametoctradin, azoxystrobin, cycloxydim, cyfluthrin, dinotef

European Commission (2015) Commission Implementing regulation (EU) 2015/2033 of 13 November 2015 renewing the approval of the active substance 2,4-D in accordance with Regulation (EC) No 1107/2009 of the European Parliament and of the Council concerning the placing of plant protect

FAO Pesticide indicators (2020) http://www.fao.org/faostat/en/#data/EP/visualize. Accessed 8 Jul 2020

Fukumori F, Hausinger RP (1993) Alcaligenes eutrophus JMP134 “2,4-dichlorophenoxyacetate monooxygenase” is an alpha-ketoglutarate-dependent dioxygenase. J Bacteriol 175:2083–2086. https://doi.org/10.1128/JB.175.7.2083-2086.1993

Gerhardt KE, Huang X, Glick BR, Greenberg BM (2009) Phytoremediation and rhizoremediation of organic soil contaminants: potential and challenges. Plant Sci 176:20–30. https://doi.org/10.1016/j.plantsci.2008.09.014

Germaine KJ, Liu X, Cabellos GG et al (2006) Bacterial endophyte-enhanced phytoremediation of the organochlorine herbicide 2,4-dichlorophenoxyacetic acid. FEMS Microbiol Ecol 57:302–310. https://doi.org/10.1111/j.1574-6941.2006.00121.x

Grossmann K (2003) Mediation of herbicide effects by hormone interactions. J Plant Growth Regul 22:109–122. https://doi.org/10.1007/s00344-003-0020-0

Guerrero-Estevez SM, Lopez-Lopez E (2016) Effects of endocrine disruptors on reproduction in viviparous teleosts with intraluminal gestation. Rev Fish Biol Fish 26:563–587. https://doi.org/10.1007/s11160-016-9443-0

Gupta RC, Crissman JW (2013) Agricultural chemicals. In: Haschek and rousseaux’s handbook of toxicologic pathology. Elsevier, pp 1349–1372

Guyader ME, Warren LD, Green E et al (2018) Trace organic contaminant (TOrC) mixtures in Minnesota littoral zones: effects of on-site wastewater treatment system (OWTS) proximity and biological impact. Sci Total Environ 626:1157–1166. https://doi.org/10.1016/j.scitotenv.2018.01.123

Haggblom MM (1992) Microbial breakdown of halogenated aromatic pesticides and related compounds. FEMS Microbiol Lett 103:29–72. https://doi.org/10.1111/j.1574-6968.1992.tb05823.x

Harrahy EA, Edwards DS, Hedman CJ (2014) Persistence of 2,4-D and its effects on benthic macroinvertebrates following spring treatment of Eurasian watermilfoil, Myriophyllum spicatum L. in two lakes in Southeastern Wisconsin, USA. Bull Environ Contam Toxicol 92:404–409. https://doi.org/10.1007/s00128-014-1206-9

Health Canada, Federal-Provincial-Territorial Committee on Drinking Water (2019) Guidelines for Canadian drinking water quality – summary table. Ottawa, Canada

Hugh-Jones ME, Peele RH, Wilson VL (2020) Parkinson's disease in Louisiana, 1999-2012: based on hospital primary discharge diagnoses, incidence, and risk in relation to local agricultural crops, pesticides, and aquifer recharge. Int J Environ Res Public Health 17. https://doi.org/10.3390/ijerph17051584

Husak VV, Storey KB, Lushchak VI et al (2014) Tissue-specific induction of oxidative stress in goldfish by 2,4-dichlorophenoxyacetic acid: mild in brain and moderate in liver and kidney. Environ Toxicol Pharmacol 37:861–869. https://doi.org/10.1016/j.etap.2014.02.007

Ignatowicz K, Struk-Sokołowska J (2004) Sezonowe wahania zanieczyszczeń agrotechnicznych w rzece Narwi ze szczególnym uwzględnieniem herbicydów fenoksyoctowych. Środkowo-Pomorskie Tow Nauk Ochr Środowiska 4:189–205

Institute of Plant Protection (2016) List of herbicides used for the protection of agricultural plants (in polish). In: Plant Protection Program. Poznań

Ismail BS, Prayitno S, Tayeb MA (2015) Contamination of rice field water with sulfonylurea and phenoxy herbicides in the Muda irrigation scheme, Kedah, Malaysia. Environ Monit Assess 187:406. https://doi.org/10.1007/s10661-015-4600-9

Itoh K, Kinoshita M, Morishita S et al (2013) Characterization of 2,4-dichlorophenoxyacetic acid and 2,4,5-trichlorophenoxyacetic acid-degrading fungi in Vietnamese soils. FEMS Microbiol Ecol 84:124–132. https://doi.org/10.1111/1574-6941.12043

Janoska O, Gruszecka-Kosowska A (2020) Water quality and human Health risk assessment: a case study of the Czarna Przemsza River source in Zawiercie, Poland. Hum Ecol Risk Assess 26:757–781. https://doi.org/10.1080/10807039.2018.1536520

Jarosiewicz P, Zagibajło K, Rudziński K, et al (2018) The occurrence of plant protection agents in Pilica basin according to crop characteristics in river catchment (in polish). Wroclaw

Kamagata Y, Fulthorpe RR, Tamura K et al (1997) Pristine environments harbor a new group of oligotrophic 2,4- dichlorophenoxyacetic acid-degrading bacteria. Appl Environ Microbiol 63:2266–2272

Kamrin MA (1997) Phenoxy and benzoic acid herbicides. In: Kamrin MA (ed) Pesticide Profiles. CRC Press, New York, pp 299–224

Kitagawa W, Takami S, Miyauchi K et al (2002) Novel 2,4-Dichlorophenoxyacetic acid degradation genes from oligotrophic. Society 184:509–518. https://doi.org/10.1128/JB.184.2.509

Kubrak OI, Atamaniuk TM, Storey KB, Lushchak VI (2013) Goldfish can recover after short-term exposure to 2,4-dichlorophenoxyacetate: use of blood parameters as vital biomarkers. Comp Biochem Physiol C-TOXICOLOGY Pharmacol 157:259–265. https://doi.org/10.1016/j.cbpc.2012.12.005

Li K, Wu JQ, Jiang LL et al (2017) Developmental toxicity of 2,4-dichlorophenoxyacetic acid in zebrafish embryos. Chemosphere 171:40–48. https://doi.org/10.1016/j.chemosphere.2016.12.032

Lindsay S, Chasse J, Butler RA et al (2010) Impacts of stage-specific acute pesticide exposure on predicted population structure of the soft-shell clam, Mya arenaria. Aquat Toxicol 98:265–274. https://doi.org/10.1016/j.aquatox.2010.02.012

Liu Y-J, Liu S, Drake HL, Horn MA (2013) Consumers of 4-chloro-2-methylphenoxyacetic acid from agricultural soil and drilosphere harbor cadA , r/sdpA , and tfdA -like gene encoding oxygenases. FEMS Microbiol Ecol 86:114–129. https://doi.org/10.1111/1574-6941.12144

Loganathan BG, Ahuja S, Subedi B (2020) Synthetic organic chemical pollutants in water: origin, distribution, and implications for human exposure and health. In: Ahuja S, Loganathan BG (eds) Contaminants in our water: identification and remediation methods. American Chemical Society, pp 13–39

López-Roldán R, Jubany I, Martí V et al (2013) Ecological screening indicators of stress and risk for the Llobregat river water. J Hazard Mater 263:239–247. https://doi.org/10.1016/j.jhazmat.2013.07.008

Lozano VL, Vinocur A, y Garcia CA, et al (2018) Effects of glyphosate and 2,4-D mixture on freshwater phytoplankton and periphyton communities: a microcosms approach. Ecotoxicol Environ Saf 148:1010–1019. https://doi.org/10.1016/j.ecoenv.2017.12.006

Machado F, Anderson C, Meenken E et al (2018) Soil & tillage research the importance of plants to development and maintenance of soil structure , microbial communities and ecosystem functions. Soil Tillage Res 175:139–149. https://doi.org/10.1016/j.still.2017.09.002

Martinez S, Delgado M, Jarvis P (2016) Removal of herbicide Mecoprop from surface water using advanced oxidation processes (AOPS). Int J Environ Res 10:291–296. https://doi.org/10.22059/ijer.2016.57723

Martínez-Ruiz EB, Martínez-Jerónimo F (2018) Exposure to the herbicide 2,4-D produces different toxic effects in two different phytoplankters: a green microalga (Ankistrodesmus falcatus) and a toxigenic cyanobacterium (Microcystis aeruginosa). Sci Total Environ 619–620:1566–1578. https://doi.org/10.1016/j.scitotenv.2017.10.145

Matamoros V, Arias CA, Nguyen LX et al (2012a) Occurrence and behavior of emerging contaminants in surface water and a restored wetland. Chemosphere 88:1083–1089. https://doi.org/10.1016/j.chemosphere.2012.04.048

Matamoros V, Nguyen LX, Arias CA et al (2012b) Evaluation of aquatic plants for removing polar microcontaminants: a microcosm experiment. Chemosphere 88:1257–1264. https://doi.org/10.1016/j.chemosphere.2012.04.004

Mcgowan C, Fulthorpe R, Wright A, Tiedje JM (1998) Evidence for interspecies gene transfer in the evolution of 2,4- dichlorophenoxyacetic acid degraders. Appl Environ Microbiol 64:4089–4092

Metcalfe CD, Helm P, Paterson G et al (2019) Pesticides related to land use in watersheds of the Great Lakes basin. Sci Total Environ 648:681–692. https://doi.org/10.1016/j.scitotenv.2018.08.169

Mierzejewska E, Baran A, Urbaniak M (2018) The influence of MCPA on soil phytotoxicity and the presence of genes involved in its biodegradation. Arch Environ Prot 44:58–64. https://doi.org/10.24425/122303

Mierzejewska E, Baran A, Tankiewicz M, Urbaniak M (2019a) Removal and Ecotoxicity of 2,4-D and MCPA in microbial cultures enriched with structurally-similar plant secondary metabolites. Water 11:1451. https://doi.org/10.3390/w11071451

Mierzejewska E, Baran A, Urbaniak M (2019b) Biodegradation potential and Ecotoxicity assessment in soil extracts amended with Phenoxy acid herbicide (2,4-D) and a structurally-similar plant secondary metabolite (Ferulic acid). Bull Environ Contam Toxicol 104:200–205. https://doi.org/10.1007/s00128-019-02760-5

Ministry of Health in New Zealand (2017) Datasheets – Chemical and physical determinands. Part 2.3: Pesticides. In: Guidelines for Drinking-water Quality Management for New Zealand (3rd edn). Wellington

Musilova L, Ridl J, Polivkova M et al (2016) Effects of secondary plant metabolites on microbial populations: changes in community structure and metabolic activity in contaminated environments. Int J Mol Sci 17:1205. https://doi.org/10.3390/ijms17081205

Nielsen L, Dahllof I (2007) Direct and indirect effects of the herbicides Glyphosate, Bentazone and MCPA on eelgrass (Zostera marina). Aquat Toxicol 82:47–54. https://doi.org/10.1016/j.aquatox.2007.01.004

Nojiri H, Fukuda M, Tsuda M, Kamagata Y (2014) Biodegradative bacteria: how bacteria degrade, survive, adapt, and evolve. Biodegrad Bact How Bact Degrad Surviv Adapt Evolve:1–358. https://doi.org/10.1007/978-4-431-54520-0

Nykiel-Szymańska J, Stolarek P, Bernat P (2018) Elimination and detoxification of 2,4-D by Umbelopsis isabellina with the involvement of cytochrome P450. Environ Sci Pollut Res 25:2738–2743. https://doi.org/10.1007/s11356-017-0571-4

Palma P, Matos C, Alvarenga P et al (2018) Ecological and ecotoxicological responses in the assessment of the ecological status of freshwater systems: a case-study of the temporary stream Brejo of Cagarrão (South of Portugal). Sci Total Environ 634:394–406. https://doi.org/10.1016/j.scitotenv.2018.03.281

Paszko T (2011) Adsorption and desorption processes of MCPA in Polish mineral soils. J Environ Sci Heal Part B 46:569–580. https://doi.org/10.1080/03601234.2011.586593

Paszko T, Muszynski P, Materska M et al (2016) Adsorption and degradation of phenoxyalkanoic acid herbicides in soils: a review. Environ Toxicol Chem 35:271–286. https://doi.org/10.1002/etc.3212

Pereira T, Cerejeira MJ (2000) Use of microbiotests to compare the toxicity of water samples fortified with active ingredients and formulated pesticides. 15:401–405

Perez DJ, Okada E, De Geronimo E et al (2017) Spatial and temporal trends and flow dynamics of glyphosate and other pesticides within an agricultural watershed in Argentina. Environ Toxicol Chem 36:3206–3216. https://doi.org/10.1002/etc.3897

Petrie AJ, Melvin MAL, Plane NH, Littlejohn JW (1993) The effectiveness of water treatment processes for removal of herbicides. Sci Total Environ 135:161–169. https://doi.org/10.1016/0048-9697(93)90287-G

Plimmer JR (2001) Chemistry of pesticides. In: Handbook of pesticide toxicology. Elsevier, pp 95–107

Polish Ministry of Environment (2012) Regulation of the minister of the environment of November 27, 2002 on requirements to be met by surface water used to supply people with drinking water. Poland

Polish Ministry of Health (2017) Regulation of the minister of health of December 7th 2017 on the quality of water intended for human consumption

Poll C, Pagel H, Devers-Lamrani M et al (2010a) Regulation of bacterial and fungal MCPA degradation at the soil–litter interface. Soil Biol Biochem 42:1879–1887. https://doi.org/10.1016/j.soilbio.2010.07.013

Poll C, Pagel H, Devers-Lamrani M et al (2010b) Regulation of bacterial and fungal MCPA degradation at the soil-litter interface. Soil Biol Biochem 42:1879–1887. https://doi.org/10.1016/j.soilbio.2010.07.013

Posmyk K, Urbaniak M (2014) Fitoremediacja jako alternatywna metoda oczyszczania środowiska. Aura 7:10–12

Ramborger BP, Ortis Gularte CA, Rodrigues DT et al (2017) The phytoremediation potential of Plectranthus neochilus on 2,4-dichlorophenoxyacetic acid and the role of antioxidant capacity in herbicide tolerance. Chemosphere 188:231–240. https://doi.org/10.1016/j.chemosphere.2017.08.164

Reshma AC, Krishna RR (2012) Plant species identification for phytoremediation of mixed contaminated soils. J Hazardous, Toxic 19:218–229. https://doi.org/10.1061/(ASCE)HZ

Rheinheimer dos Santos D, Monteiro de Castro Lima JA, Paranhos Rosa de Vargas J et al (2020) Pesticide bioaccumulation in epilithic biofilms as a biomarker of agricultural activities in a representative watershed. Environ Monit Assess 192:381. https://doi.org/10.1007/s10661-020-08264-8

Rippy MA, Deletic A, Black J et al (2017) Pesticide occurrence and spatio-temporal variability in urban run-off across Australia. Water Res 115:245–255. https://doi.org/10.1016/j.watres.2017.03.010

Rodríguez-Espinosa PF, Mendoza-Pérez JA, Tabla-Hernandez J et al (2018) Biodegradation and kinetics of organic compounds and heavy metals in an artificial wetland system (AWS) by using water hyacinths as a biological filter. Int J Phytoremediation 20:35–43. https://doi.org/10.1080/15226514.2017.1328397

Ruiz de Arcaute C, Soloneski S, Larramendy ML (2016) Toxic and genotoxic effects of the 2,4-dichlorophenoxyacetic acid (2,4-D)-based herbicide on the Neotropical fish Cnesterodon decemmaculatus. Ecotoxicol Environ Saf 128:222–229. https://doi.org/10.1016/j.ecoenv.2016.02.027

Sarikaya R, Yilmaz M (2003) Investigation of acute toxicity and the effect of 2,4-D (2,4-dichlorophenoxyacetic acid) herbicide on the behavior of the common carp (Cyprinus carpio L., 1758; Pisces, Cyprinidae). Chemosphere 52:195–201. https://doi.org/10.1016/S0045-6535(03)00106-1

Scalon M, Rechenmacher C, Siebel A et al (2010) Evaluation of Sinos River water genotoxicity using the comet assay in fish. Brazilian J Biol 70:1217–1222. https://doi.org/10.1590/S1519-69842010000600011

Scrimshaw MD, Lester JN (1996) The occurrence and effects of organic micropollutants in salt marsh sediments with reference to the UK Essex coast: a review. Environ Technol 17:951–964. https://doi.org/10.1080/09593331708616464

Singer AC, Crowley DE, Thompson IP (2003) Secondary plant metabolites in phytoremediation and biotransformation. Trends Biotechnol 21:123–130. https://doi.org/10.1016/S0167-7799(02)00041-0

Siwek M (2008) Biologiczne sposoby oczyszczania srodowiska – fitoremediacja. Wiadomości Bot 52:23–28

Skiba E, Wolf WM (2017) Commercial phenoxyacetic herbicides control heavy metal uptake by wheat in a divergent way than pure active substances alone. Environ Sci Eur 29:26. https://doi.org/10.1186/s12302-017-0124-y

Statistics Poland (2018) Statistical yearbook of agriculture. Warsaw

Sun Y, Cao M, Wan Y et al (2020) Spatial variation of 2,4-D and MCPA in tap water and groundwater from China and their fate in source, treated, and tap water from Wuhan, Central China. Sci Total Environ 727. https://doi.org/10.1016/j.scitotenv.2020.138691

The Council of the European Union (1998) Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption

U.S. EPA (2012) Edition of the drinking water standards and health advisories. EPA 822-S-12-001

U.S. EPA (2020) Pesticide products and label system. https://iaspub.epa.gov/apex/pesticides/f?p=PPLS:1. Accessed 8 Jul 2020

Urbaniak M, Mierzejewska E (2019) Biological remediation of Phenoxy herbicide-contaminated environments. In: Environmental chemistry and recent pollution control approaches. IntechOpen

Urbaniak M, Mierzejewska E, Tankiewicz M (2019) The stimulating role of syringic acid, a plant secondary metabolite, in the microbial degradation of structurally-related herbicide, MCPA. Peer J 7:e6745. https://doi.org/10.7717/peerj.6745

Veeh RH, Inskeep WP, Camper AK (1996) Soil depth and temperature effects on microbial degradation of 2,4-D. J Environ Qual 25:5–12. https://doi.org/10.2134/jeq1996.00472425002500010002x

Vroumsia T, Steiman R, Seigle-Murandi F et al (2005) Fungal bioconversion of 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4-dichlorophenol (2,4-DCP). Chemosphere 60:1471–1480. https://doi.org/10.1016/j.chemosphere.2004.11.102

World Health Organization (2017) Guidelines for drinking-water quality: fourth edition incorporating the first addendum. Geneva

World Health Organization (2019) The WHO recommended classification of pesticides by hazard and guidelines to classification

Ye Y, Bruning H, Li X et al (2018) Significant enhancement of micropollutant photocatalytic degradation using a TiO2 nanotube array photoanode based photocatalytic fuel cell. Chem Eng J 354:553–562. https://doi.org/10.1016/j.cej.2018.08.064

Zabaloy MC, Gómez MA (2014) Isolation and characterization of indigenous 2,4-D herbicide degrading bacteria from an agricultural soil in proximity of sauce Grande River, Argentina. Ann Microbiol 64:969–974. https://doi.org/10.1007/s13213-013-0731-9

Zagibajło K, Sikorski P, Miszczak A (2017) Control of plants protection agents residuals in surface waters (in polish). http://www.inhort.pl/files/aktualnosci/2017/nauka_praktyce/materialy/2.5_Poster_Kontrola_woda.pdf. Accessed 21 Jul 2020

A Review on Distribution and Removal Techniques for Perfluoroalkyl and Polyfluoroalkyl Substances (PFASs) in Water and Wastewater

Pavithra K, Avanti Roy-Basu, Girija K. Bharat, and Paromita Chakraborty

Abstract Perfluoroalkyl and polyfluoroalkyl substances (PFASs) are refractory anthropogenic contaminants which are of high concern for environmental regulators because they are widespread, persistent, and bioaccumulative. In this chapter, we are presenting an overview of research papers on global distribution of PFASs in water and wastewater, and the associated remediation techniques. A brief discussion of novel remediation technologies developed for the elimination of PFASs from the environment, and regulatory actions on PFASs of global concern is provided. PFASs were widely used as surfactants in many industrial applications such as in paints, firefighting foams, cookware, etc., due to their unique oleophobic and hydrophobic property. A large group of 4700 PFASs are in use on the global market. Some of the studies revealed that effluents of wastewater treatment plants are considered as significant point sources of PFASs. It is difficult to eliminate them from the environment because of their stable C-F bond. Conventional treatment technologies are found ineffective for PFASs. Chitosan with amino groups is recommended as a good adsorbent with adsorption capacity of 5.5 mmol/g for PFOS. USEPA classified PFASs as a potential human carcinogen. Perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) are considered as persistent organic pollutants by the Stockholm Convention.

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1 Introduction

Perfluoroalkyl and polyfluoroalkyl substances (PFASs) are man-made chemicals. They have been in use since the 1950s, and have various applications in industries like water repellent on clothing, cookware, and surface tension lowering agents in fire-fighting foam (Wang et al. 2020a; Dauchy 2019). PFASs are aliphatic substances in which all the hydrogen atoms attached to the carbon atoms have been replaced by fluorine atoms. PFASs differed from other fluorinated compounds with perfluoroalkyl moiety C_nF_2n PLUS_SPI 1– (Buck et al. 2011). $F(CF_2)_n$-R is the general chemical formula of PFASs, where R is the functional group which is hydrophilic. PFASs are a family of compounds, each with several individual homologous members and isomers (Buck et al. 2011). PFASs with carbon numbers 6–8 such as perfluorinated carboxylic acids (PFCAs) and perfluorosulfonic acids (PFSAs) are considered as long-chain PFASs, which are chemically more inert. The short-chain PFASs are the ones with carbon number less than 6, such as perfluorobutanoic acid (PFBA), having greater mobility in the environment because of their high solubility with lower sorption tendency (Buck et al. 2011; Ji et al. 2020). PFASs were widely used in industrial and household applications because of their unique physicochemical properties, such as thermal stability and oxidative resistance (Arvaniti and Stasinakis 2015).

The bioconcentration and bioaccumulation potential of PFASs with longer half-lives made them persistent in humans (Prevedouros et al. 2006; Ahrens et al. 2010; Krafft and Riess 2015). The most widely used water treatment processes such as sedimentation, filtration, chlorination, biofiltration, and low-pressure membranes are not able to remove PFASs effectively (Arvaniti and Stasinakis 2015). The biodegradation of PFASs during wastewater treatment does not seem possible. The transformation of precursor compounds to PFASs during biological wastewater treatment is possible (Rahman et al. 2014).

PFASs are very stable, because of their strong C-F bond (Buck et al. 2011). PFASs are found to be effective surfactants or surface protectors because of the hydrophobic and oleophobic nature of the perfluorocarbon moiety (Kissa 2001; Glüge et al. 2020). Fluorinated surfactants are used as processing aids in electrochemical fluorination, telomerization, and oligomerization of tetrafluoroethylene (Kissa 2001; Prevedouros et al. 2006). Because of their excellent surface activity, globally PFASs were used in a wide range of products such as fluoropolymers, liquid repellents for paper, leather, carpet goods, electronics manufacturing, metal plating, lubricants, nonstick cookware, water- and greaseproof textiles, food packaging materials, protective coatings, and firefighting foams (Clara et al. 2008; Wang et al. 2019; Dauchy 2019; Buck et al. 2011; Kissa 2001).

Perfluorooctanesulfonic acid (PFOS) and Perfluorooctanoic acid (PFOA) are persistent, bioaccumulative, and toxic (Clara et al. 2008), and in humans, they are possible carcinogens (Cooke 2017). Both PFOA and PFOS are identified as endocrine disruptors; in steroidogenic ovarian cells, they possibly affect the dependent functions of sexual steroids. In the endocrine glands, the functions and hormone-dependent processes could get altered (Chaparro-Ortega et al. 2018). Seven US States have developed their own health-based guideline levels from 13 to 1000 ng/L for PFOA and/or PFOS in drinking water (Cordner et al. 2019). The risk of female infertility due to endometriosis may be increased by exposure to perfluorobutane sulfonic acid (PFBS) (Wang et al. 2017). The fate, transport, and remediation technologies of many well-known PFASs (PFOA, PFOS, PFBA, etc.) in different environmental matrices have been studied worldwide (Prevedouros et al. 2006; Kim et al. 2016; Chen et al. 2016).

In the present study, we aim to review the distribution of the categorized PFASs, and the remediation techniques in water and wastewater. The objectives of this study are:

1. To provide information about the chemistry and usage of PFASs.
2. To review the classification and sources of PFASs.
3. To analyze the sampling and analytical techniques used for determination of PFASs in different water matrices (surface water, groundwater, tap water) and wastewater.
4. To review the available removal technologies for PFASs in water and wastewater (for those considered as persistent organic pollutants (POPs) – PFOA and PFOS).

2 Review of Sampling and Analytical Techniques of PFASs

2.1 Sampling Technique

An automated composite sampler was used to collect the sample for 24 hours from wastewater treatment plants (WWTPs) of five major industrial sectors in South Korea (Kim et al. 2016). Polypropylene (PP) bottles for sampling were pre-rinsed using Milli-Q water and methanol and were used to collect surface water samples from six major South Korean rivers and lakes, and then stored in ice at 4 °C (Lam et al. 2014). Samples were collected using two ice bag composite samplers from the effluent and influent of WWTPs, and were stored in PP bottles (Kwon et al. 2017). From the effluents of the municipal WWTPs, composite samples were collected daily. Grab samples were collected from industrial facilities. Samples were stored in a freezer at 20 °C (Clara et al. 2008). In India, river water and groundwater samples near the riverbank were collected from the Ganges for the assessment of PFASs. For river water and groundwater, the sampling was concurrent. Precleaned high-density polyethylene (HDPE) bottles were used to collect grab bulk water samples. The groundwater samples located within 5 km of the riverbank were obtained using hand pumps. Before the samples were collected, the bottles were pre-rinsed with the same water at least twice and placed in an icebox at 4°C (Sharma et al. 2016).

2.2 Materials Used

Two ^{13}C8-labeled recovery standards were used (Kim et al. 2016), a mixture of nine surrogate standards was purchased with PFAC-MXB (Lam et al. 2014), native and mass-labeled linear PFAS isomers, and T-PFOA mixture for branched isomers (Shi et al. 2015), and a mixture of six PFCAs and three PFSAs (Gao et al. 2014) were purchased from Wellington Laboratories. Reagents such as ammonium acetate, acetonitrile, MTBE, Milli-Q water, and methanol of high-performance liquid chromatography (HPLC) grade were used.

2.3 Extraction and Cleanup

Wastewater samples were filtered and spiked with internal standards before extraction. Solid-phase extraction (SPE) was carried out using methanol-preconditioned cartridges and Milli-Q water. The dried cartridge was methanol-eluted. TurboVap II was used to concentrate up to 500 μL of the extract (Kim et al. 2016; Kwon et al. 2017). A 2 ng of mass-labeled internal standards was spiked to the filtered sample. A Sep-Pak concentrator was used for SPE. Methanol was used for the elution of the analyte (Chen et al. 2016).

2.4 Analysis of PFASs

PFASs were identified using an Agilent 1200 HPLC system coupled with an electrospray triple quadruple mass spectrometer (ESI-MS-MS). Identification and quantification were done using multiple reaction monitoring (MRM) (Kim et al. 2016; Lam et al. 2014). PFASs from the complex matrices were separated using a guard column and a C18 HPLC column (Kim et al. 2016). Liquid chromatograph coupled with a tandem mass spectrometer (LC-MS/MS) was used in negative ionization mode for analysis of PFASs (Zhang et al. 2012).

Table 1 Methods for analyzing PFASs

Methods	Matrix tested	No. of analytes	Sample preparation procedure	References
EPA 533	Drinking water	25	Solid-phase extraction	Rosenblum and Wendelken (2019)
EPA 537.1	Drinking water	18	Solid-phase extraction	Shoemaker et al. (2008)
EPA 8327	Drinking water	24	Dilute and shoot	Winchell et al. (2021)
ASTM 7979	Surface water, groundwater, wastewater influent and effluent	21	Dilute and shoot	Winchell et al. (2021)
ISO/DIS 21675	Drinking water, sea water, fresh water, wastewater	30	Solid-phase extraction	Winchell et al. (2021)

2.5 General Methods of Analysis of PFASs in Different Water Matrices

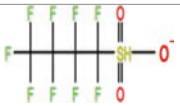
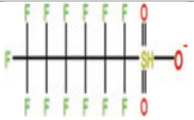
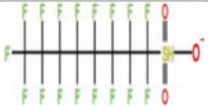
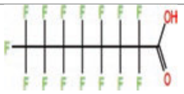
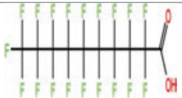
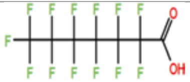
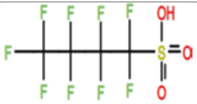
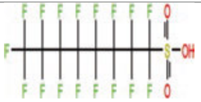
For the determination of PFASs from the environment, there are various analytical methods, as given in Table 1.

3 Result and Discussion

3.1 Classification of PFASs

PFASs are a family of compounds, each with several individual homologous members and isomers (Buck et al. 2011). They are categorized as ionic PFASs (i-PFASs) and neutral PFASs (n-PFASs), because of their distinct physiochemical properties and functional group. The fate of i-PFASs and n-PFASs into the environment depends on their functional group (Wang et al. 2020a; Trier et al. 2011). The use and development of PFCAs is known as a direct source of PFASs. The indirect sources are chemical reaction impurities and degradation of fluorinated polymers such as polytetrafluoroethylene (PTFE, e.g., Teflon), which may lead to the formation of PFASs (Begley et al. 2005; Prevedouros et al. 2006). While the use of PFASs was relatively limited in Class B firefighting foams, they are considered to be a significant source of PFCAs (Glüge et al. 2020). PFCAs were released directly into the soil and water surrounding the training areas for firefighting (Prevedouros et al. 2006). This section provides information about the chemical properties of majorly studied PFASs.

Table 2 Majorly studied PFAAs with their properties

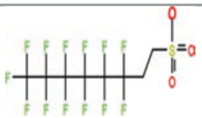
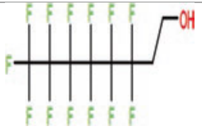
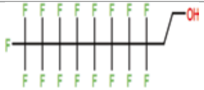
S.N.	Compound and abbreviation	CAS No.	Mol. weight (g/mol)	Structural formula	Structure	Uses
Perfluoroalkane sulfonates						
1	Perfluorobutyl sulfonate [PFBS$^-$]	29,420–49-3	299.21	$C_4F_9SO^-$		Surfactant
2	Perfluorohexyl sulfonate [PFHxS$^-$]	No CAS	399.22	$C_6F_{13}SO^-{}_3$		Surfactant and surface protection products
3	Perfluorooctyl sulfonate [PFOS$^-$]	45,298–90-6	499.23	$C_8F_{17}SO^-{}_3$		Surfactant
Perfluoroalkyl carboxylic acids						
1	Perfluorooctanoic acid [PFOA]	335–67-1	414.07	$C_8HF_{15}O_2$		Surfactant
2	Perfluorononanoic acid [PFNA]	375–95-1	464.08	$C_9HF_{17}O_2$		Intermediaten products
3	Perfluoroundecanoic acid [PFUdA]	2058-94-8	564.09	$C_{11}HF_{21}O_2$		Intermediate products
4	Perfluoroheptanoic acid [PFHpA]	375–85-9	364.06	$C_7HF_{13}O_2$		Surfactant
Perfluoroalkane sulfonic acids						
5	Perfluorobutane sulfonic acid [PFBS]	375–73-5	300.09	$C_4HF_9O_3S$		Surfactant
6	Perfluorooctanesulfonic acid [PFOS]	1763-23-1	500.13	$C_8HF_{17}O_3S$		Surfactant

(de Voogt and Sáez 2006; Buck et al. 2011; Kissa 2001; Rahman et al. 2014)

3.1.1 Perfluoroalkyl Acids

A number of compounds, such as carboxylic acids, sulfonic and sulfinic acids, and phosphonic and phosphinic acids, are incorporated into perfluoroalkyl acids (PFAAs) (Buck et al. 2011). Among those, the two main compounds are PFSAs and

Table 3 Majorly studied fluorotelomer substances with their properties

S.N.	Compound and abbreviation	CAS no.	Mol. weight (g/mol)	Structural formula	Structure	Uses
1	6:2 fluorotelomer sulfonate [6:2 FTS]	425,670–75-3	428.16	$C_8H_4F_{13}S^{-}{}_3$		Surfactant
2	6:2 fluorotelomer alcohol [6:2 FTOH]	647–42-7	364.11	$C_8H_5F_{13}O$		Surfactant and surface Protection products
3	8:2 fluorotelomer alcohol [8:2 FTOH]	678–39-7	464.12	$C_{10}H_5F_1O$		Intermediate products

(de Voogt and Sáez 2006; Buck et al. 2011; Kissa 2001; Rahman et al. 2014)

PFCAs (Ji et al. 2020). Some of the majorly studied PFAAs and their chemical properties are given in Table 2.

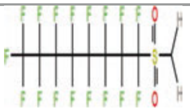
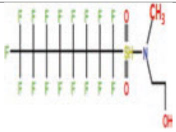
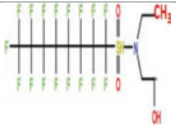
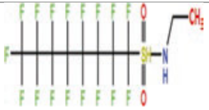
3.1.2 Fluorotelomer Substances

The two key methods of fluorotelomer alcohol (FTOH) processing are sulfation/hydrolysis and solvolysis (Prevedouros et al. 2006). Fluorotelomer alcohol is the main raw material used for the manufacture of n:2 fluorotelomer acrylate. Substances of fluorotelomer were primarily used as surfactants and in defense products, and were also formed as intermediate products (Buck et al. 2011). Some of the majorly studied fluorotelomers and their chemical properties are given in Table 3.

3.1.3 Perfluoroalkane Sulfonamides

Perfluoroalkane sulfonamide substances are mainly produced by electrochemical fluorination and are mainly used as surfactants and products for surface defense (Buck et al. 2011). Some of the majorly studied sulfonamide substances and their chemical properties are given in Table 4.

Table 4 Sulfonamide substances with their properties

S.N.	Compound and abbreviation	CAS No.	Mol. weight (g/mol)	Structural formula	Structure	Uses
1	Perfluorooctane sulfonamide [PFOSA]	754–91-6	499.14	$C_8H_2F_{17}O_2NS$		Surface Protection products
2	N-methyl perfluorooctane sulfonamidoethanol [N-MeFOSE]	24,448–09-7	557.23	$C_{11}H_8F_{17}NO_3S$		Surfactant and surface protection products
3	N-ethyl perfluorooctane sulfonamidoethanol [N-EtFOSE]	1691-99-2	571.26	$C_{12}H_{10}F_{17}NO_3S$		Surfactant and surface Protection products
4	N-ethyl perfluorooctane sulfonamido ethylacrylate [N-EtFOSA]	4151-50-2	527.2	$C_{10}H_6F_{17}NO_2S$		Surfactant and surface protection products

(de Voogt and Sáez 2006; Buck et al. 2011; Kissa 2001; Rahman et al. 2014)

3.2 Sources and Distribution of PFASs

PFOA never breaks down; it is carcinogenic and has been found in the blood of Arctic indigenous peoples and wildlife (IPEN 2019b). The adverse effects of PFOA were discovered during a leak from landfills receiving PFAS-related industrial waste. The contamination of water and soil surrounding the firefighting training areas and airports was due to the usage of PFASs in aqueous film-forming foams (ITRC 2020). Different studies and the concentration range of PFOA and PFOS in surface water, groundwater, tap water, and wastewater reported are listed in Tables 5 and 6. Various methods were used from the sampling until the compound analysis, so the concentrations presented in these studies are not comparable.

3.2.1 Water Resources

3.2.1.1 Groundwater and Tap Water

There are a few studies that illustrate the concentration of PFASs in groundwater and tap water. The highest concentration in the groundwater sample from South Korea was up to 5200 ng/L (Hepburn et al. 2019). Various studies on monitoring of PFASs in groundwater and tap water in different countries are given in Table 5.

Table 5 Concentration range of PFASs in groundwater and tap water

S.N.	Place/country	Type of compound	Range (low to high) (ng/L)	Mean ± std/ median	References
1	South Korea/ groundwater	$\sum_{14}$PFAS	26 – 5200	-	Hepburn et al. (2019)
2	Tap water/Shanghai	PFCs	-	130	Mak et al. (2009)
3	Australia/ groundwater	PFASs	ND – 36.9	-	Yong et al. (2021)
4	Ganges river basin/ groundwater/India	PFBA PFBS	<MQL – 9.2 <MQL – 4.9	-	Sharma et al. (2016)
5	Tap water/ Bangkok, Thailand	PFASs	0.58 – 1.15	-	Tabtong et al. (2015)
6	Tap water/Goa, Coimbatore, and Chennai	PFHxS	-	81	IPEN (2019a, b)

Table 6 Concentration range of PFASs in surface water

S.N.	Place/country	Type of compound	Range (low to high) (ng/L)	References
1	Velachery/India	PFOA PFOS	4 – 93 3 – 29	Sunantha and Vasudevan (2016)
2	River Elbe/Europe	ΣPFCs	7.6 – 26.4	Ahrens et al. (2009)
3	Baiyangdian Lake/ China	ΣPFCs	1.70 – 73.5	Shi et al. (2012)
4	Bohai Sea/China	ΣPFASs	5.3 – 41,700	Chen et al. (2017)
5	South China Sea/China East China Sea/China	ΣPFASs	0.062 – 0.494 0.181 – 2.68	Chen et al. (2017)
6	Xiamen Bay/China	ΣPFASs	13 – 98	Wang et al. (2020b)
7	Pearl River/China	ΣPFASs	2.24 – 99.34	So et al. (2007)
8	Rhine River/Europe	ΣPFASs	4.1– 39	Möller et al. (2010)
11	Japan	PFOS	0.2 – 157	Saito et al. (2003)
9	River Ganges/India	PFHxA PFBS	0.4 – 4.7 <MQL – 10.2	Sharma et al. (2016)

3.2.1.2 Surface Water

A few studies on the concentration of PFASs in surface water are available. The concentration in the Bohai Sea, China, of PFASs ranges up to 41,700 ng/L (Chen et al. 2017). With a concentration range of 3.41–35.44 ng/L, PFOA is the dominant contaminant found in Dianchi Lake, China (Zhang et al. 2012). In a separate study, about 15 PFASs in varied locations were detected along River Ganges, India (ranging from 1.3 to 15.9 ng/L), due to industrial effluents being dumped directly into the river (Sharma et al. 2016). Various studies on monitoring of PFASs in surface water in different countries are given in Table 6.

Table 7 Concentration range of PFASs in wastewater

S.N.	Place/country	Type of compound	Range (ng/L)	References
1	Taiwan	PFOS PFHxA	ND – 293 ND – 406	Lin et al. (2010)
2	Austria	PFOS PFOA PFHxA	ND – 340 ND – 220 ND – 280	Clara et al. (2008)
3	China (influent)	ΣPFASs	0.04 – 91	Zhang et al. (2012)
	China (effluent)		0.01 – 107	
4	China	PFASs	103 – 443	Chen et al. (2016)
5	USA/Kentucky	PFOS PFOA	7 – 149 22 – 334	Loganathan et al. (2007)
	USA/Georgia	PFOS PFOA	1.8 – 22 1 – 227	

3.2.2 Wastewater

The effluents from industrial WWTPs and municipal WWTPs have been examined in Austria. The higher concentration detected in the metal industry was PFOS, and the dominant PFOA emission was found in the paper industry (Clara et al. 2008). The concentration range of PFCAs and PFASs in WWTPs of Kentucky and Georgia in the USA was studied. PFOA was dominant in both plants followed by PFOS (Loganathan et al. 2007). Various studies on monitoring of PFASs in wastewater of different countries are given in Table 7.

3.3 PFASs Removal Technologies

A study has shown that activated sludge recirculation performs better with PFASs compared to the biological filtration system. The production and life of aquatic species may be influenced by the concentration of PFASs in the effluent that enters the water bodies after treatment (Kibambe et al. 2020). In this review, we are discussing some treatment technologies that were adopted to remove PFASs from water and wastewater. The technologies developed for the treatment of PFASs by various studies are given in Table 8.

3.3.1 Adsorption

Some traditional adsorbents such as activated carbon, resin, and zeolite have been tested, and high sorption potential for PFOS was shown by the powder activated carbon and anion-exchange resin. Chitosan has been widely used as a cheap biosorbent to extract heavy metals and dyes from wastewater, and among the recorded adsorbents, it has also shown the highest sorption potential of up to 5.5 mmol/g for

Table 8 Treatment technologies for PFASs

S.N.	Removal adopted	Treatment concentration	Degradation achieved	References
1	Cross-linked GAC beads	PFO Srange 0.093 – 0.744 mmol/L	5.5 mmol/g of PFOS	Zhang et al. (2011)
2	Molecularly imprinted polymers	10 μg/L	700 mg/g for carbon nanotubes and 170 mg/g for maize ash	Chen et al. (2011)
3	RO	500 to 150,000 μg/L	Individual PFC removal = 99%	Tang et al. (2006)
4	Nanofiltration with RO	10,000 μg/L	PFOS removal = 99% and PFOA removal = 90–99%	Tang et al. (2007)
5	Ozone and ozone/peroxide	PFOS and PFOA – 50 μg/L–5 mg/l in wastewater	Percentage removal = 85–100%	Lin et al. (2012)
6	Ozone, ozone/UV, ozone/peroxide	10 g/L of mixed PFCs	No degradation of PFOS	Schröder and Meesters (2005)
7	UV/TiO2 photocatalysis	0.330 μg/L PFOS	PFOS removal = 10%	Benotti et al. (2009)
8	Sono-chemical treatment	65 μg/L to 13,100 μg/L of PFOS	PFOS removal = 73%	Vecitis et al. (2008)
10	Ferrate-based reduction of PFOS and PFOA	0.779 – 1.252 mg/L PFOS and 4.515–7.022 mg/L PFOA	PFOS removal = 34% and 23%	Yates et al. (2014)
12	Heat-activated persulfate	155 mg/L	PFAS removal =77.5%	Hori et al. (2008)
13	Mild heat-activated persulfate	241.5 mM PFOA	PFOA removal = 80.5%	Lee et al. (2012)
14	Hydrogen peroxide and heat	100 mg/L	PFOS removal = 97.5%	Hawley et al. (2012)
15	Superoxide and hydroperoxide	100 μg/L	PFOA removal = 68%	Mitchell et al. (2014)
16	Fungal degradation	PFOA – 0.01 mg/L – 10 mg/L	PFOA removal = 30%	Huang (2013)

PFOS. The amino groups can be protonated in an acidic solution in the chitosan polymer and adsorb anionic PFOS. PFOS tends to accumulate in blood plasma and kidney to concentrate in fat in the animal body, unlike other POPs, and adsorption can be the responsibility of the protein-containing amine groups. Although the cross-linked chitosan beads are more costly than activated carbon, they are cheaper than resins, demonstrating a possible use for PFOS removal in wastewater treatment (Zhang et al. 2011). The potential for treating 17 PFASs using 44 inorganic and organic sorbents was established. Compared to sand, magnesium chloride-fortified biochar, *Moringa* crop, and pyrolytic carbon waste showed a 17 to 25 times greater sorption potential for PFASs. An increase in sorption capability was seen by increasing the chain length. Principal component analysis (PCA) showed that hydrophobic sorption dominated for shorter-chained PFASs, for electrostatic sorption dominated, and for longer-chained PFASs (Sörengård et al. 2020). Activated carbon (AC) has a high adsorption potential for PFOS/PFOA among the various adsorbents, but the associated issue is regeneration. In wastewater treatment, adsorption and degradation of perfluorinated compounds (PFCs) can be accomplished simultaneously by coating efficient catalysts on ACs (Du et al. 2014). Adsorption demonstrated strong PFOS and PFOA remediation followed by reverse osmosis (Zhang et al. 2011; Tang et al. 2006; Tang et al. 2007).

3.3.2 Membrane Filtration

The removal of PFOA and PFOS using a micro-filtration membrane with a nominal size of 100 nm is ineffective, but removal is improved when a DC electrical field is present (Tsai et al. 2010). For the removal of PFAAs using nanofiltration, a thin-film composite membrane NF270 composed of polyamide was tested. Some studies have found rejection of many PFAAs decreased by organic matter fouling. Greater than 93% removal of all PFAAs was achieved by virgin and fouled NF270. The NF270 membrane rejected all PFAAs, including the shorter-chain PFCAs (Appleman et al. 2013).

3.3.3 Advanced Oxidation Process (AOP)

Sono-chemical effects are caused by interactions of ultrasonic irradiation with aqueous solutions. Cavitation occurred during the process generated a temperature of 4000–10,000 K inside bubbles and 1000–1500 K near the interface of the bubble. Pyrolytic degradation of PFASs occurred by sono-chemical treatment (Gole et al. 2018). Advanced electrochemical oxidation using lead peroxide (PbO_2) from lead-acid battery to breakdown has been used for the removal of PFASs, where >99% of PFASs was removed with defluorination of 60% (Fang et al. 2018). High-valent iron-based oxidants were used to treat PFOS and PFOA. The highest removal efficiency of 34% for PFOS and 23% for PFOA was achieved with Fe (IV). Alkaline pH showed a greater tendency toward oxidation than at neutral conditions (Yates et al. 2014). Complete mineralization of microcontaminants to CO_2, H_2O, and mineral salts can be achieved using AOPs at full scale, while the most important factor affecting the application is the high operating costs, especially those associated with the cost of reagents (Miralles-Cuevas et al. 2017).

Compared to a high temperature of 150 °C, the removal of C5–C9 PFCAs and perfluoroether carboxylic acids using $S_2O_8^{2-}$ in hot water at a low temperature of 80 °C showed high performance. After 6 hours at a temperature of 80 °C, the decomposition of PFOA effectively produced 77.5% and 70.2% of F-ions and CO_2. With perfluoroether carboxylic acids, the F-ion yield was 82.9–88.9%, and the CO_2 yield was 87.7–100% (87.7–100%) (Hori et al. 2008).

The degradation of PFOA and PFOS using ozone and peroxide at an environmentally relevant concentration of 50 μg/L to 5 mg/L in wastewater from electronics and semiconductor industries under alkaline conditions achieved 85–100% removal efficiency. Half-life values of 0.5–2 h were produced for ozonation in alkaline conditions, and it was 10 min–0.5 h with peroxone. Therefore, the treatment of peroxone has shown a more energy-efficient procedure compared to ozonation (Lin et al. 2012). Two low-pressure mercury lamps with a wavelength of 254 nm and 185 nm were used along with persulfate ($K_2S_2O_8$) as an oxidant. The decomposition of PFOA with 185 nm light irradiation was significantly higher than 254 nm. The by-products produced were similar such as F^-, SO_4^{2-}, and CO_2 along with shorter-chain PFCAs. The maximum recovery ratios of 97.89% were achieved for carbon and 96.7% for sulfur and 96.94% for fluorine, respectively.

The mechanism for PFOA degradation is given below.

$$\mathrm{S2O8}^{2-} + h\nu \rightarrow 2\mathrm{SO}_4^{\bullet-}$$

$$\mathrm{SO}_4^{\bullet-} + \mathrm{PFO} \rightarrow \mathrm{SO}_4^{2-} + \mathrm{PFOA}\bullet$$

Two anionic radicals SO_4^{2-} are formed by photolysis of potassium persulphate. These radicals contribute to oxidation, produced a reactive radical of PFOA and lead to the cleavage of the C-F bond adjacent to the COOH functional group (Chen and Zhang 2006)

3.3.4 Biodegradation

The biodegradation potential of fluorinated sulfonates using different model compounds was studied. Among these, in a well-defined mineral medium, difluoromethane sulfonate (DFMS) was defluorinated entirely under aerobic sulfur-limiting conditions by strain D2. With a pH of 6.9–7.0, the medium was preserved. DFMS was effectively used by the strain as a sulfur source and not as a carbon source or for energy production (Huang 2013). Biodegradable and natural surfactants were synthesized to treat waters having PFASs and heavy-metal ions. PFOA removal from the water was carried using cysteine-based surfactant. The co-surfactant readily removed 72% of PFOA. The foam fractionation technique was found valuable for the removal of PFASs because 1- octanoylcysteine surfactant is biodegradable and having consistent foaming properties. Biodegradable surfactant synthesis is simple and has tremendous potential to resolve the risk associated with the presence of dangerous contaminants for global concern in drinking water (Ziaee et al. 2021)

4 Regulatory Framework – National and International

4.1 PFASs and the Stockholm Convention

Since 2009, PFOS and associated derivatives have been included in the Stockholm Convention (SC). The SC on POPs is an international environmental treaty (signed in 2001 and effective from May 2004) that aims to eliminate or restrict the production and use of POPs. During the fourth meeting of the Conference of the Parties (COP-4) held in 2009, PFOS, its salts, and PFOSF were included under Annex B of the SC (for restriction). The COP adopted a work program and formulated an evaluation of the need for these chemicals for "acceptable purposes and specific exemptions." During SC COP-9 held in 2019, PFOA, its salts, and PFOA-related compounds were included to Annex A of the Convention (for elimination). Prohibition of manufacturing and use of these compounds was announced with specific exemptions with a limited timeframe and expiry at a specified time (5 years). The specific exemptions for the different use categories (METI. 2019) included photolithography, photographic coating, oil- or water-repellent fiber products, medical equipment, foam-type fire extinguishing agent, etc. Also, the exemption of the use of perfluorooctane iodide (PFOI) (for manufacturing pharmaceuticals) would expire in 2036, by which the member countries would need to evaluate and decide on the necessary steps for complete elimination of these chemicals. Perfluorohexane sulfonic acid, its salts, and Perfluorohexane sulfonic acid-related compounds are being considered for inclusion in the SC and consequent global elimination.

4.2 PFASs Regulations in Other Regions/Countries

Some PFASs have been regulated in Europe and have been restricted in the European Union (EU) for more than a decade, under the EU's POPs Regulation. The manufacture and use of some PFASs is being restricted under REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals). There is an ongoing restriction proposal by Germany and Sweden for certain perfluorinated carboxylic acids (C9–14 PFCAs) including their salts and precursors. Norway has proposed a restriction on PFHxS, its salts, and related substances. Germany has also submitted a further restriction proposal for undecafluorohexanoic acid (PFHxA), its salts, and related substances. The Netherlands and Germany, along with Norway, Denmark, and Sweden, will develop a restriction proposal on the uses of a wide range of PFASs. In June 2019 and January 2020, two groups of PFASs were identified as SVHCs (REACH List of "substances of very high concern") that were identified based on their persistence, mobility, and toxicity and having environmental and health implications (including through drinking water).

The United States Environmental Protection Agency (USEPA) has taken certain regulatory actions for the management of PFASs. The PFAS Action Plan was introduced in February 2019 (and revised in 2020) to identify and address current PFASs contamination, prevent future contamination, and communicate about PFASs to the public effectively (USEPA. 2019). The USEPA has issued a health advisory for providing a margin of protection from a lifetime of exposure (of people, especially sensitive groups) to PFOA and PFOS from drinking water, at 70 parts per trillion, which essentially implies non-regulatory concentrations at or below which adverse health effects are not anticipated to occur over specific exposure durations. In 2021, PFOA and PFOS have been mandated to be designated as 'hazardous substances' to improve the knowledge and understanding on the releases of PFOA and PFOS within communities. There are currently no "Maximum Contaminant Levels" for PFASs in the USA. The USEPA's oral non-cancer reference doses (RfDs) for both PFOS and PFOA are 0.00002 mg/kg/day, where RfDs are known to be an approximation of the amount of daily exposure that is unlikely to have any lifetime adverse effects (Cooke 2017). In 2021, the USEPA introduced the 'PFAS Strategic Roadmap' with a detailed time-bound action plan for 2021–2024 aiming at protecting public health from PFASs contamination. Also, the USEPA's Unregulated Contaminant Monitoring Rule has mandated a Nationwide Monitoring for 29 PFASs and lithium in drinking water to be conducted between 2023 and 2025. Further, a national PFASs testing strategy is being developed to use its Toxic Substances Control Act (TSCA) authorities 'to require PFASs manufacturers to provide information on PFASs'.

In Asia, PFOS has been restricted in line with the SC, but most other PFASs remain unregulated in countries like Indonesia, Thailand, and Vietnam. PFASs are not regulated in Bangladesh. In Japan, most PFASs are unregulated but have few partial regulations on PFOA, PFHxA, PFHxS, and PFOS (IPEN 2019a, b).

4.3 PFASs Regulations in India

At present, PFASs and its compounds are not adequately regulated in India. In 2006, India became a member country of the SC. However, India had not accepted the restriction on these substances, and it is still reported to be unregulated, along with other PFASs.

There is a lack of adequate knowledge and information on the production, use, storage, trade, and waste management for PFASs in India. Results from scientific research and analysis of regulatory status of PFASs in India indicate its harmful effects on human and animal health, and underline the urgent need for stringent regulatory measures. Tao et al. (2008) found PFCs in breast milk samples of women from seven Asian countries including India (Chidambaram, Kolkata, and Chennai), with PFOS being the key pollutant followed by PFHxS (perfluorohexane sulfonate) and PFOA. A study found a link between Teflon (PFOA-containing) cookware and hair loss in humans. About 80% of the people (aged between 18 and 44 years, irrespective of gender) using non-stick Teflon cookware and suffering from hair loss were found to be PFOA-positive (in blood levels) as compared to others who were using other forms of cookware (earthen, steel, or aluminum) (HIRTC. 2015-2016).

PFOS was the key perfluorochemical found in biological samples (fish, shrimp, river dolphin) from River Ganges along with perfluoroundecanoic acid (PFUnDA) and perfluorodecanoic acid (PFDA) (Yeung et al. 2009). In terms of transboundary pollution, Indian monsoons contributed to 70% of PFASs in the snow in China, PFOA on Mt. Zuoqiupu in Tibet, and PFBA in the snowpack of Lake Namco (Wang et al. 2019; Wang et al. 2019). PFOA was also found in the Sundarban mangrove area (UNESCO World Heritage Site and Ramsar Wetland of International Importance) with an average level of 11.61 parts per billion (ppb) dry weight (Corsolini et al. 2012). Shallow, intermediate, and deep groundwater sources in Varanasi, India, were polluted with PFOS levels ranging from 0.0001 to 0.033 $\mu g\ L^{-1}$ (Lapworth et al. 2018). Higher hepatic concentrations of PFOS were found in all the samples from female pigs living on an open waste dumping site in Perungudi in Chennai, India (Watanabe et al. 2010).

A 2019 study by Toxics Link provided pertinent recommendations for controlling PFASs in India (IPEN 2019a, b). It was suggested that a detailed inventory of PFASs needs to be developed to compensate for the dearth of information on its sectoral use, control, and management. Export and import data of PFASs is required to help identify trade flows. Regular monitoring of PFASs is essential to identify industrial hotspots. India must replace PFAS-containing foams (used in firefighting) with fluorine-free foams. PFAS needs to be banned through passing specific regulations for prohibition of its production, use, import, and export. Further scientific research on the health impacts of PFASs in different environmental matrices must be taken up.

In conclusion, it may be stated that the elimination of PFASs in India will not just help deliver the requirements of the Stockholm Convention, but might contribute to achieve the national achievement of targets related to the United Nations Sustainable Development Goals (UN-SDGs). Efforts to control and phase out PFASs as a class may contribute to the achievement of several key SDGs, such as SDG 3 (Health), 6 (Water), 9 (Industry, Innovation, and Infrastructure), 12 (Responsible Consumption and Production), 14 (Life below water), 15 (Life on land), and 16 (Peace, Justice and Strong Institutions). Research and policy interventions to manage PFASs will have positive impacts on public health and environment, and contribute towards pollution control of drinking water, surface water, and groundwater resources.

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References

Ahrens L, Plassmann M, Xie Z, Ebinghaus R (2009) Determination of polyfluoroalkyl compounds in water and suspended particulate matter in the river Elbe and North Sea, Germany. Front Environ Sci Eng China 3(2):152–170

Ahrens L, Taniyasu S, Yeung LW, Yamashita N, Lam PK, Ebinghaus R (2010) Distribution of polyfluoroalkyl compounds in water, suspended particulate matter and sediment from Tokyo Bay, Japan. Chemosphere 79(3):266–272

Appleman TD, Dickenson ER, Bellona C, Higgins CP (2013) Nanofiltration and granular activated carbon treatment of perfluoroalkyl acids. J Hazard Mater 260:740–746

Arvaniti OS, Stasinakis AS (2015) Review on the occurrence, fate and removal of perfluorinated compounds during wastewater treatment. Sci Total Environ 524:81–92

Begley T, White K, Honigfort P, Twaroski M, Neches R, Walker R (2005) Perfluorochemicals: potential sources of and migration from food packaging. Food Addit Contam 22(10):1023–1031

Benotti MJ, Stanford BD, Wert EC, Snyder SA (2009) Evaluation of a photocatalytic reactor membrane pilot system for the removal of pharmaceuticals and endocrine disrupting compounds from water. Water Res 43(6):1513–1522

Buck RC et al (2011) Perfluoroalkyl and polyfluoroalkyl substances in the environment: terminology, classification, and origins. Integr Environ Assess Manag 7(4):513–541

Chaparro-Ortega A et al (2018) Endocrine disruptor effect of perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) on porcine ovarian cell steroidogenesis. Toxicol In Vitro 46:86–93

Chen J, Zhang P (2006) Photodegradation of perfluorooctanoic acid in water under irradiation of 254 nm and 185 nm light by use of persulfate. Water Sci Technol 54(11–12):317–325

Chen X, Xia X, Wang X, Qiao J, Chen H (2011) A comparative study on sorption of perfluorooctane sulfonate (PFOS) by chars, ash and carbon nanotubes. Chemosphere 83(10):1313–1319

Chen H et al (2016) Occurrence, spatial and temporal distributions of perfluoroalkyl substances in wastewater, seawater and sediment from Bohai Sea, China. Environ Pollut 219:389–398

Chen H et al (2017) Occurrence and seasonal variations of per-and polyfluoroalkyl substances (PFASs) including fluorinated alternatives in rivers, drain outlets and the receiving Bohai Sea of China. Environ Pollut 231:1223–1231

Clara M, Scharf S, Weiss S, Gans O, Scheffknecht C (2008) Emissions of perfluorinated alkylated substances (PFAS) from point sources—identification of relevant branches. Water Sci Technol 58(1):59–66

Cooke M (2017) Technical fact sheet–Perfluorooctane sulfonate (PFOS) and Perfluorooctanoic acid (PFOA). Emergency, O o L a, ed, United States Environmental Protection Agency

Cordner A, Vanessa Y, Schaider LA, Rudel RA, Richter L, Brown P (2019) Guideline levels for PFOA and PFOS in drinking water: the role of scientific uncertainty, risk assessment decisions, and social factors. J Expo Sci Environ Epidemiol 29(2):157–171

Corsolini S et al (2012) Perfluorinated compounds in surficial sediments of the Ganges River and adjacent Sundarban mangrove wetland, India. Mar Pollut Bull 64(12):2829–2833

Dauchy X (2019) Per-and polyfluoroalkyl substances (PFASs) in drinking water: current state of the science. Curr Opin Environ Sci Health 7:8–12

de Voogt P, Sáez M (2006) Analytical chemistry of perfluoroalkylated substances. TrAC Trends Anal Chem 25(4):326–342

Du Z et al (2014) Adsorption behavior and mechanism of perfluorinated compounds on various adsorbents—a review. J Hazard Mater 274:443–454

Fang X et al (2018) Distribution and dry deposition of alternative and legacy perfluoroalkyl and polyfluoroalkyl substances in the air above the Bohai and Yellow Seas, China. Atmos Environ 192:128–135

Gao Y et al (2014) Occurrence and fate of perfluoroalkyl substances in marine sediments from the Chinese Bohai Sea, Yellow Sea, and East China Sea. Environ Pollut 194:60–68

Glüge J et al (2020) An overview of the uses of per-and polyfluoroalkyl substances (PFAS). Environ Sci: Processes Impacts 22(12):2345–2373

Gole VL, Sierra-Alvarez R, Peng H, Giesy JP, Deymier P, Keswani M (2018) Sono-chemical treatment of per-and poly-fluoroalkyl compounds in aqueous film-forming foams by use of a large-scale multi-transducer dual-frequency based acoustic reactor. Ultrason Sonochem 45:213–222

Hawley E, Pancras T, Burdick J (2012) Remediation technologies for perfluorinated compounds (PFCs), including perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA). Pollut Eng 44(5):20–23

Hepburn E, Madden C, Szabo D, Coggan TL, Clarke B, Currell M (2019) Contamination of groundwater with per-and polyfluoroalkyl substances (PFAS) from legacy landfills in an urban re-development precinct. Environ Pollut 248:101–113

HIRTC (2015-2016) Hairline international research and treatment center (HIRTC), effect of Perfluorooctanoic acid in the blood and its correlation to hair loss and health. PFOA 1 final 15 ver (hairline.in). In. Retrieved from PFOA 1 final 15 ver (hairline.in)

Hori H, Nagaoka Y, Murayama M, Kutsuna S (2008) Efficient decomposition of perfluorocarboxylic acids and alternative fluorochemical surfactants in hot water. Environ Sci Technol 42(19):7438–7443

Huang Q (2013) Remediation of Perfluoroalkyl contaminated aquifers using an in-situ two-layer barrier: laboratory batch and column study. GEORGIA UNIV ATHENS

IPEN (2019a) IPEN and toxic link. India PFAS Situation Report. . In. Retrieved from https://ipen.org/conferences/cop9 last Accessed February 9, 2021

IPEN (2019b) PFAS pollution across the Middle East and Asia,. In. Retrieved from https://ipen.org/sites/default/files/documents/pfas_pollution_across_the_middle_east_and_asia.pd last Accessed 9 Feb 2021

ITRC (2020) PFAS technical and regulatory guidance documents and factsheets PFAS-1. Washington D.C.: Interstate Technology & Regulatory Council PFAS Team. In. Retrieved from https://pfas-1.itrcweb.org/

Ji B, Kang P, Wei T, Zhao Y (2020) Challenges of aqueous per-and polyfluoroalkyl substances (PFASs) and their foreseeable removal strategies. Chemosphere 250:126316

Kibambe M, Momba M, Daso A, Coetzee M (2020) Evaluation of the efficiency of selected wastewater treatment processes in removing selected perfluoroalkyl substances (PFASs). J Environ Manag 255:109945

Kim H-Y, Seok H-W, Kwon H-O, Choi S-D, Seok K-S, Oh JE (2016) A national discharge load of perfluoroalkyl acids derived from industrial wastewater treatment plants in Korea. Sci Total Environ 563:530–537

Kissa E (2001) Fluorinated surfactants and repellents, vol 97. CRC Press

Krafft MP, Riess JG (2015) Per- and polyfluorinated substances (PFASs): environmental challenges. Curr Opin Colloid Interface Sci 20(3):192–212

Kwon H-O, Kim H-Y, Park Y-M, Seok K-S, Oh J-E, Choi S-D (2017) Updated national emission of perfluoroalkyl substances (PFASs) from wastewater treatment plants in South Korea. Environ Pollut 220:298–306

Lam N-H et al (2014) Perfluorinated alkyl substances in water, sediment, plankton and fish from Korean rivers and lakes: a nationwide survey. Sci Total Environ 491:154–162

Lapworth D et al (2018) Deep urban groundwater vulnerability in India revealed through the use of emerging organic contaminants and residence time tracers. Environ Pollut 240:938–949

Lee Y-C, Lo S-L, Kuo J, Lin Y-L (2012) Persulfate oxidation of perfluorooctanoic acid under the temperatures of 20–40 C. Chem Eng J 198:27–32

Lin AY-C, Panchangam SC, Ciou P-S (2010) High levels of perfluorochemicals in Taiwan's wastewater treatment plants and downstream rivers pose great risk to local aquatic ecosystems. Chemosphere 80(10):1167–1174

Lin AY-C, Panchangam SC, Chang C-Y, Hong PA, Hsueh H-F (2012) Removal of perfluorooctanoic acid and perfluorooctane sulfonate via ozonation under alkaline condition. J Hazard Mater 243:272–277

Loganathan BG, Sajwan KS, Sinclair E, Kumar KS, Kannan K (2007) Perfluoroalkyl sulfonates and perfluorocarboxylates in two wastewater treatment facilities in Kentucky and Georgia. Water Res 41(20):4611–4620

Mak YL et al (2009) Perfluorinated compounds in tap water from China and several other countries. Environ Sci Technol 43(13):4824–4829

METI (2019) Ninth meeting of the conference of the parties to the Stockholm convention (COP9) held. Joint press release with the Ministry of the Environment. Ministry of Economy, Trade & Industry (METI), Japan. In. Retrieved from https://www.meti.go.jp/english/press/2019/0514_001.html last Accessed 9 Feb 2021

Miralles-Cuevas S, Darowna D, Wanag A, Mozia S, Malato S, Oller I (2017) Comparison of UV/H2O2, UV/S2O82−, solar/Fe (II)/H2O2 and solar/Fe (II)/S2O82− at pilot plant scale for the elimination of micro-contaminants in natural water: an economic assessment. Chem Eng J 310:514–524

Mitchell SM, Ahmad M, Teel AL, Watts RJ (2014) Degradation of perfluorooctanoic acid by reactive species generated through catalyzed H2O2 propagation reactions. Environ Sci Technol Lett 1(1):117–121

Möller A et al (2010) Distribution and sources of polyfluoroalkyl substances (PFAS) in the River Rhine watershed. Environ Pollut 158(10):3243–3250

Prevedouros K, Cousins IT, Buck RC, Korzeniowski SH (2006) Sources, fate and transport of perfluorocarboxylates. Environ Sci Technol 40(1):32–44

Rahman MF, Peldszus S, Anderson WB (2014) Behaviour and fate of perfluoroalkyl and polyfluoroalkyl substances (PFASs) in drinking water treatment: a review. Water Res 50:318–340

Rosenblum L, Wendelken S (2019) Method 533: determination of per-and polyfluoroalkyl substances in drinking water by isotope dilution anion exchange solid phase extraction and liquid chromatography/tandem mass spectrometry. US Environmental Protection Agency Washington DC

Saito N, Sasaki K, Nakatome K, Harada K, Yoshinaga T, Koizumi A (2003) Perfluorooctane sulfonate concentrations in surface water in Japan. Arch Environ Contam Toxicol 45(2):149–158

Schröder HF, Meesters RJ (2005) Stability of fluorinated surfactants in advanced oxidation processes—a follow up of degradation products using flow injection–mass spectrometry, liquid chromatography–mass spectrometry and liquid chromatography–multiple stage mass spectrometry. J Chromatogr A 1082(1):110–119

Sharma BM et al (2016) Perfluoroalkyl substances (PFAS) in river and ground/drinking water of the Ganges River basin: emissions and implications for human exposure. Environ Pollut 208:704–713

Shi Y, Pan Y, Wang J, Cai Y (2012) Distribution of perfluorinated compounds in water, sediment, biota and floating plants in Baiyangdian Lake, China. J Environ Monit 14(2):636–642

Shi Y et al (2015) Characterizing direct emissions of perfluoroalkyl substances from ongoing fluoropolymer production sources: a spatial trend study of Xiaoqing River, China. Environ Pollut 206:104–112

Shoemaker J, Grimmett P, Boutin B (2008) Determination of selected perfluorinated alkyl acids in drinking water by solid phase extraction and liquid chromatography/tandem mass spectrometry (LC/MS/MS). US Environmental Protection Agency, Washington, DC

So M et al (2007) Perfluorinated compounds in the Pearl river and Yangtze river of China. Chemosphere 68(11):2085–2095

Sörengård M, Östblom E, Köhler S, Ahrens L (2020) Adsorption behavior of per- and polyfluoralkyl substances (PFASs) to 44 inorganic and organic sorbents and use of dyes as proxies for PFAS sorption. J Environ Chem Eng 8(3):103744

Sunantha G, Vasudevan N (2016) Assessment of perfluorooctanoic acid and perfluorooctane sulfonate in surface water-Tamil Nadu, India. Mar Pollut Bull 109(1):612–618

Tabtong W, Boontanon SK, Boontanon N (2015) Fate and risk assessment of perfluoroalkyl substances (PFASs) in water treatment plants and tap water in Bangkok, Thailand. Procedia Environ Sci 28:750–757

Tang CY, Fu QS, Robertson A, Criddle CS, Leckie JO (2006) Use of reverse osmosis membranes to remove perfluorooctane sulfonate (PFOS) from semiconductor wastewater. Environ Sci Technol 40(23):7343–7349

Tang CY, Fu QS, Criddle CS, Leckie JO (2007) Effect of flux (transmembrane pressure) and membrane properties on fouling and rejection of reverse osmosis and nanofiltration membranes treating perfluorooctane sulfonate containing wastewater. Environ Sci Technol 41(6):2008–2014

Tao L, Ma J, Kunisue T, Libelo EL, Tanabe S, Kannan K (2008) Perfluorinated compounds in human breast milk from several Asian countries, and in infant formula and dairy milk from the United States. Environ Sci Technol 42(22):8597–8602

Trier X, Granby K, Christensen JH (2011) Tools to discover anionic and nonionic polyfluorinated alkyl surfactants by liquid chromatography electrospray ionisation mass spectrometry. J Chromatogr A 1218(40):7094–7104

Tsai Y-T, Yu-Chen Lin A, Weng Y-H, Li K-C (2010) Treatment of perfluorinated chemicals by electro-microfiltration. Environ Sci Technol 44(20):7914–7920

USEPA (2019) EPA's Per- and Polyfluoroalkyl substances (PFAS) action plan. In. Retrieved from https://www.epa.gov/sites/production/files/2019-02/documents/pfas_action_plan_021319_508compliant_1.pdf last Accessed 9 Feb 2021

Vecitis C, Park H, Cheng J, Mader B, Hoffmann M (2008) Enhancement of perfluorooctanoate and perfluorooctanesulfonate activity at acoustic cavitation bubble interfaces. J Phys Chem C 112(43):16850–16857

Wang B et al (2017) Perfluoroalkyl substances and endometriosis-related infertility in Chinese women. Environ Int 102:207–212

Wang X, Chen M, Gong P, Wang C (2019) Perfluorinated alkyl substances in snow as an atmospheric tracer for tracking the interactions between westerly winds and the Indian monsoon over western China. Environ Int 124:294–301

Wang Q, Ruan Y, Lin H, Lam PK (2020a) Review on perfluoroalkyl and polyfluoroalkyl substances (PFASs) in the Chinese atmospheric environment. Science of the Total Environment:139804

Wang S et al (2020b) Occurrence and partitioning behavior of per-and polyfluoroalkyl substances (PFASs) in water and sediment from the Jiulong Estuary-Xiamen Bay, China. Chemosphere 238:124578

Watanabe MX et al (2010) Dioxin-like and perfluorinated compounds in pigs in an Indian open waste dumping site: toxicokinetics and effects on hepatic cytochrome P450 and blood plasma hormones. Environ Toxicol Chem 29(7):1551–1560

Winchell LJ, et al. (2021) Analyses of per-and Polyfluoroalkyl substances (PFAS) through the urban water cycle: toward achieving an integrated analytical workflow across aqueous, solid, and gaseous matrices in water and wastewater treatment. Science of The Total Environment:145257

Yates BJ, Darlington R, Zboril R, Sharma VK (2014) High-valent iron-based oxidants to treat perfluorooctanesulfonate and perfluorooctanoic acid in water. Environ Chem Lett 12(3):413–417

Yeung LW et al (2009) A survey of perfluorinated compounds in surface water and biota including dolphins from the Ganges River and in other waterbodies in India. Chemosphere 76(1):55–62

Yong ZY, Kim KY, Oh J-E (2021) The occurrence and distributions of per-and polyfluoroalkyl substances (PFAS) in groundwater after a PFAS leakage incident in 2018. Environ Pollut 268:115395

Zhang Q, Deng S, Yu G, Huang J (2011) Removal of perfluorooctane sulfonate from aqueous solution by crosslinked chitosan beads: sorption kinetics and uptake mechanism. Bioresour Technol 102(3):2265–2271

Zhang Y et al (2012) Determination and partitioning behavior of perfluoroalkyl carboxylic acids and perfluorooctanesulfonate in water and sediment from Dianchi Lake, China. Chemosphere 88(11):1292–1299

Ziaee F, Ziaee M, Taseidifar M (2021) Synthesis and application of a green surfactant for the treatment of water containing PFAS/hazardous metal ions. J Hazard Mater 407:124800

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