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Chapter 9

Fate of micropollutants

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ABSTRACT

Micropollutants (MPs) are biological or chemical compounds resulting from human activities that make their way into water bodies in trace quantities. They cause adverse effects on aquatic environments and their complexity and costly quantification makes them difficult to monitor and, consequently, the implementation of legislation for controlling their disposal. Thus, the aim of this chapter is to describe occurrence, environmental and health impacts, and current regulatory frameworks of MPs. The fate and removal of these contaminants in anaerobic reactors treating domestic wastewater is discussed and strategies for enhancing MP removal are presented. Studies on MP removal in anaerobic systems are still emerging and a great deal of work should be carried out to evaluate whether conventional anaerobic reactors applied to domestic wastewater treatment under usual operating conditions are able to effectively remove contaminants of emerging concern. Transferring the mechanistic understanding of the anaerobic biotransformation of MPs to feasible changes to be implemented in mainstream anaerobic domestic wastewater treatment remains a major challenge. Moreover, the study of new operating strategies and reactor configurations seems to be mandatory to comply with the requirements of removing organic matter, nutrients, and MPs, as well as generating energy (biogas), thus resulting in robust, safe, and sustainable units.

Keywords: anaerobic digestion, domestic sewage, emerging contaminants, legislation, micropollutant, pesticides, pharmaceutical residues, sweeteners.

9.1 MICROPOLLUTANTS IN DOMESTIC WASTEWATER

Micropollutants (MPs) or emerging contaminants include new pollutants that, until recently, were not detected. They are biological or chemical compounds resulting from human activities that make their way into water bodies in trace quantities (at or below μg/L). The complexity of MPs and their costly quantification makes them difficult to monitor and, consequently, the implementation of legislation for controlling their disposal (Aquino *et al.*, 2013). A few examples of common MPs are pharmaceutical residues, endocrine disruptors, plasticizers, pesticides, sweeteners, and personal hygiene products.

Sources of MPs in the environment are diverse. Pharmaceuticals mainly come from domestic wastewater (from excretion), hospital effluents, and surface run-off from concentrated animal feeding

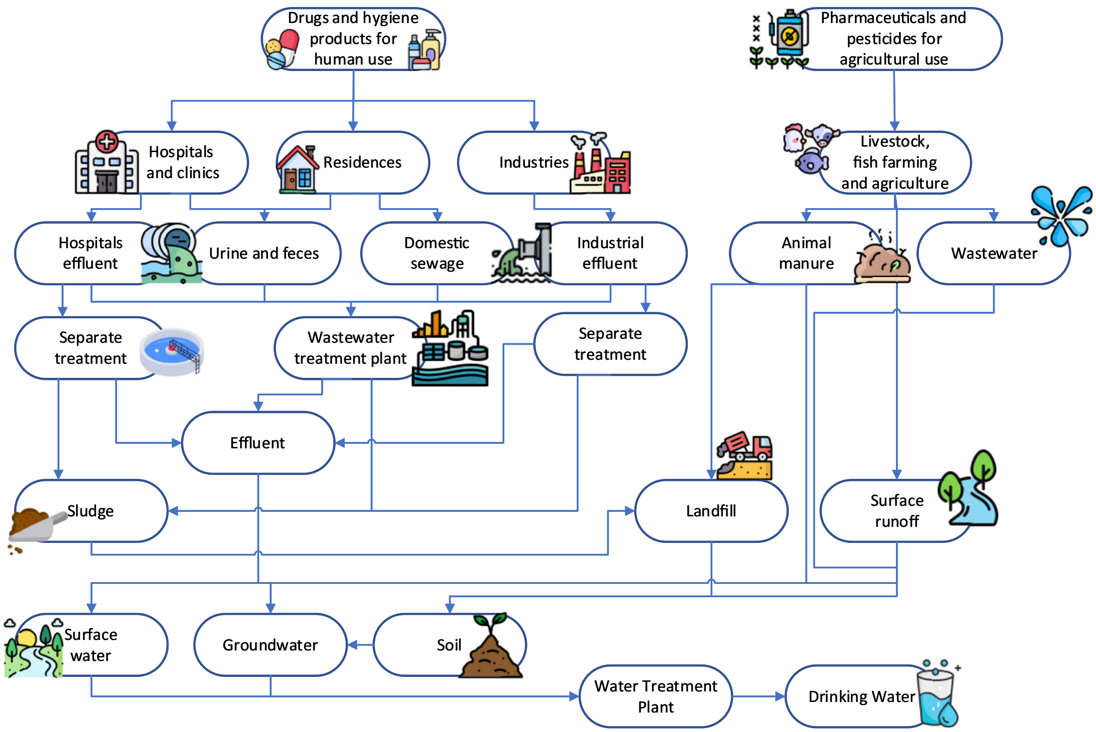

Figure 9.1 Contamination pathway for MPs.

operations and aquaculture. MPs from personal care products, such as fragrances, disinfectants, and insect repellents, mostly come from household sources, such as bathing, shaving, spraying, and swimming. Steroid hormones come from human excretion and livestock farming. Non-ionic surfactants, plasticizers, and fire retardants come from industrial and domestic wastewater (from production and by leaching out of the material, respectively). MPs from pesticides, such as insecticides, herbicides, and fungicides can come from improper cleaning, run-off from gardens, lawns, roadways, and agricultural run-off (Luo *et al.*, 2014). Figure 9.1 shows the contamination pathways for MPs.

Contamination of water and sewage by MPs has adverse effects, such as resistance in pathogenic bacteria and reduced diversity of bacteria and algae in running water (Carey *et al.*, 2016). These substances cause changes in the behavior and morphology of aquatic biota (Chen *et al.*, 2014; Corcoll *et al.*, 2015; Petersen *et al.*, 2014) and interfere with the hormonal system of wildlife and humans. Several negative effects are often associated with short- and long-term toxicity, regardless of concentrations in the order of ng/L. Even with the partial elucidation of the consequences and toxicity of exposure to these MPs, most countries do not have legislation to impose a maximum limit for the concentration of MPs in water bodies.

Therefore, the aim of this chapter is to describe the occurrence, environmental, and health impacts, and current regulatory frameworks for MPs. The fate and removal of MPs in anaerobic reactors treating domestic wastewater is then discussed and strategies for enhancing MP removal are presented.

9.1.1 Occurrence

Data on the presence of MPs in water bodies can be categorized into: (1) occurrence in wastewater treatment plant (WWTP) influents and effluents; (2) occurrence in surface water; (3) occurrence in groundwater; and (4) occurrence in drinking water. Due to the large number of existing MPs and the cost of their analysis, a limited number of compounds is usually monitored in environmental samples. Frequently, the targeted compounds are chosen based on their frequency of occurrence, or as representatives of particular MP classes. The reported concentrations of MPs in WWTPs vary significantly in space and time due to the rate of production of MPs, sales and practices of a given community, water consumption and use, and size and efficiency of WWTPs (Jelic *et al.*, 2011; Luo *et al.*, 2014). Particularly, the excretion rate plays a crucial role in determining the introduction of pharmaceuticals into raw wastewater: drugs such as aspirin and carbamazepine have an excretion rate lower than 5%; medicines such as amoxicillin, ciprofloxacin, and tetracycline excretion rates are over 70% of the ingested mass. However, the massive use of the former drugs usually leads to high concentrations in domestic effluents. Pharmaceuticals found with the highest concentration in WWTP influents, according to a comprehensive review performed by Luo *et al.* (2014), are ibuprofen (0.004–603 μg/L), followed by caffeine (0.22–209 μg/L) and diclofenac (0.001–94.2 μg/L). Insect repellant *N*,*N*-diethyl-meta-toluamide has been tracked in concentrations between 2.56 and 3.19 μg/L and triclosan, an MP found in personal care products, was found in concentrations of 0.03–23.9 μg/L. In contrast, steroid hormones were found in wastewater at much lower levels (below 100 ng/L). However, their occurrence even at low concentrations is a concern because of their high estrogenic effect. The use of pesticides can be seasonal due to the prevalence of pests under different climatic conditions, and rainfall and sunlight affect the flow pattern of these MPs. Herbicides were found in the range of 0.02–28 μg/L, insecticides between 0.0007 and 4.16 μg/L and fungicides below 1.89 μg/L (Kasprzyk-Hordern *et al.*, 2009; Luo *et al.*, 2014).

The release of WWTP effluents into water bodies has been considered a main cause of the presence of MPs in surface water. Following treatment processes in WWTPs, MPs are subjected to dilution in surface water, sorption onto suspended solids and sediments, direct and indirect photolysis, and biodegradation. Due to river water dilution, pharmaceutical compounds may occur at levels at least one order of magnitude lower than effluent levels (Gros *et al.*, 2007; Luo *et al.*, 2014). Non-steroidal anti-inflammatory drugs, carbamazepine, sulfamethoxazole, and triclosan are the most frequently reported compounds in surface water. However, caffeine is an MP reported at the highest concentration in countries such as Costa Rica, Taiwan, and the USA (up to 10^6 ng/L) (Luo *et al.*, 2014).

Groundwater has been found to be less contaminated with MPs than surface water. Better characterization of MPs in groundwater has been only done in some parts of Europe and North America. MP contamination of groundwater mainly results from landfill leachate, groundwater–surface water interaction, infiltration of contaminated water from agricultural land or seepage of septic tanks, and sewer systems. In France, Germany, Spain, and the USA, most MPs were detected at below 100 ng/L (Luo *et al.*, 2014).

Publications reporting the occurrence of MPs in drinking water are scarce. Some recent studies showed that most MPs in tap water were below the limit of quantitation or limit of detection and that drinking water treatment plays a significant role in eliminating MPs from drinking water. The maximum occurrence concentrations of most MPs were reported to be below 100 ng/L in France, Spain, the USA, and Canada except for carbamazepine (1000 ng/L) and caffeine (200 ng/L) (Luo *et al.*, 2014). However, two recent studies conducted in China report the presence of pesticides and flame retardants in the region of Taihu Basin, in which even advanced treatment procedures were inefficient in removing these contaminants (Ren *et al.*, 2020). In the region of northeast China (Heilongjiang, Jilin, and Liaoning provinces), 19 kinds of pesticides, 6 kinds of organophosphates, 2 kinds of phthalates, and 22 kinds of pharmaceutical and personal care product pollutants were found in drinking water samples (Wang *et al.*, 2022).

9.1.2 Environmental and health impacts

So far, little is known about the possible chronic health effects associated with the long-term ingestion of MP mixtures in drinking water. Furthermore, after entering an aquatic environment, MPs are subject to natural attenuation processes, such as microbial degradation, photodegradation, sorption in suspended particulate matter, and deposition in sediments. All these processes influence the fate and toxicity of contaminants in water bodies (Gibs *et al.*, 2013; Yang *et al.*, 2011). One must also consider the predicted no-effect concentrations of these MPs, which represent the concentration of a substance below which an unacceptable effect most likely will not occur. The known environmental and health impacts of a few major MPs are described below.

(1) Ibuprofen: a drug from the group of non-steroidal anti-inflammatory drugs, used to treat pain, fever, and inflammation. It is a popular over-the-counter drug with a high daily therapeutic dose (600–1200 mg/day), of which 70–80% is excreted. Along with diclofenac, it was considered a priority for studies by the *Global Water Research Coalition*. While ibuprofen readily degrades under aerobic conditions, it exhibits resistance to anaerobic degradation. Among the adverse effects caused by its contamination, the induction of vitellogenin (a protein present only in females) in mussels exposed to the drug was observed (Gonzalez-Rey & Bebianno, 2014).
(2) Diclofenac: a popular drug, also belonging to the class of non-steroidal anti-inflammatory drugs, with analgesic, antipyretic, and anti-inflammatory properties. Diclofenac has the highest acute toxicity of this type of drug and has been detected in water and sewage treatment plants due to its high level of consumption and resistance to biodegradation in the aquatic environment. Considered a priority for study, its presence in water bodies causes adverse effects, such as hormonal changes in aquatic beings. It has a significant deleterious effect on the survival and reproduction of fish and zooplanktonic and benthic organisms (an effect also caused by propranolol) (Fent *et al.*, 2006).
(3) Propranolol: an antihypertensive drug used for the treatment and prevention of myocardial infarction, angina pectoris, and cardiac arrhythmias. Although designed for human use, it is equally effective when used in physiological studies in fish and causes growth disorders in invertebrates at concentrations above 0.5 mg/L (Fent *et al.*, 2006).
(4) Triclosan: bactericide used in medicines, cosmetics, and personal hygiene products. In Brazil, the National Sanitary Agency allows a concentration of up to 0.3% of triclosan in personal care products, although it is prohibited in the USA. There are indications that prolonged exposure to products with bactericides can generate bacterial resistance and hormonal changes. It can cause oxidative stress in fish and mollusks, and at 500 ng/L of triclosan, changes were observed in the levels and activities of some enzymes in such organisms (Ku *et al.*, 2014).
(5) Carbamazepine: a medicine that belongs to the group of antiepileptics. Carbamazepine is one of the most persistent drugs of concern in water bodies receiving effluents and is resistant to both conventional and advanced wastewater treatment. In addition to being stable in the environment, studies show that it is captured by plants irrigated with wastewater, as well as its bioaccumulation in aquatic organisms. Furthermore, as a psychoactive drug, carbamazepine has the potential to make fish more vulnerable to predators (Keen *et al.*, 2012).
(6) Atenolol: indicated for cardiac patients, atenolol is mainly used to control arterial hypertension and angina pectoris. Atenolol is part of the group of beta-blocker drugs and is widely prescribed worldwide. Atenolol is a drug regularly found in wastewater, as 90% of it is eliminated in feces and urine and is captured by plants and vegetables (Beltrán *et al.*, 2020).
(7) Ciprofloxacin: fluoroquinolone antibiotic is usually applied to treat bacterial infections. Given the high usage of ciprofloxacin, it can be found in hospital and industrial wastewater at over 31 mg/L. Ciprofloxacin is of particular concern since genotoxic and mutagenic effects have been reported in bacteria (Kümmerer *et al.*, 2000; Richard *et al.*, 2014).
(8) Bisphenol A: a chemical produced in large quantities used primarily in the production of polycarbonate plastics. It is found in various products including shatterproof windows, eyewear, water bottles, and epoxy resins that are used to coat some metal food cans, bottle tops, and water supply pipes. Bisphenol A is a suspected anthropogenic endocrine disruptor. Although it

is less estrogenic toward aquatic organisms than natural hormones, it has been reported to be able to induce feminization phenomena in various species of animals at high concentrations (Metcalfe *et al.*, 2001). Golub *et al.* (2010) concluded that bisphenol A mainly affects offspring viability, sex differentiation, immune hypersensitivity, and gender-differentiated morphology, thus affecting the endocrine system when prenatally exposed (Richard *et al.*, 2014).

(9) Caffeine: in the surface water quality report, caffeine appears as a chemical quality indicator, used as a tracer of the presence of human excreta and some substances from the contaminant group (Bernegossi, 2019). The mutagenic effects of caffeine can cause increased cell death (inactivation of DNA regeneration), and interference with enzymatic reactions and replication mechanisms in cells and microorganisms (Fernandes *et al.*, 2017; Kihlman, 1974).

(10) Cyclamate, aspartame, and sucralose (sweeteners): artificial sweeteners are synthetic chemicals used as a substitute for sugar. These molecules have been found both in surface water and in sewage treatment plants. They are potential indicators of anthropogenic contamination of surface water by sanitary sewage (Zirlewagen *et al.*, 2016). Studies on the consequences arising from the presence of sweeteners in water bodies are scarce, but it has been shown that the presence of sucralose causes changes in behavior and feeding pattern in crustaceans (Li *et al.*, 2018).

(11) Chlorpyrifos: the most widely used pesticide on crops, including corn, soybeans, broccoli, and apples, and it is also widely used in non-agricultural settings such as golf courses. Chlorpyrifos was invented as an alternative to the pesticide dichloro-diphenyl-trichloroethane and has become part of a pattern known as 'regrettable substitution.' Chlorpyrifos works by attacking insects' nervous systems. High doses, for instance, what farmers are exposed to when they spray pesticides, can cause people to experience nausea, dizziness, and confusion. The most disconcerting effect of chronic exposure to chlorpyrifos, however, is its potential to impair children's developing brains (Burke *et al.*, 2017; Hu, 2018).

9.1.3 Current regulatory frameworks

Political awareness of water quality has been growing over the last few decades, especially as WWTPs have been identified as a major source of MP pollution (Rogowska *et al.*, 2020). However, very few countries have implemented legal norms to regulate the maximum concentration of MPs that can be detected in water samples. A lack of bi-directional communication between scientists and policymakers has contributed to fragmentation and inconsistencies in chemical inventories and environmental regulations (Sanganyado, 2022). The identified current regulatory frameworks of major countries are described and summarized in Figure 9.2.

(1) The European Union: Regulations have been adopted for limiting the presence of micro-contaminants in water bodies throughout the territory of the European Union. Environmental quality standards for a few MPs have been regulated by the European Parliament through Directive 2008/105/EC. Annex I of this directive lists the annual average and the maximum allowable concentration of 33 MPs, including chlorpyrifos and a few pesticides. In October 2022, the European Commission reviewed and updated the lists of pollutants in surface water and groundwater, including additional MPs such as carbamazepine, sulfamethoxazole, diclofenac, ibuprofen, erythromycin, triclosan, and others. If the proposal is agreed by the European Union Council and the European Parliament, Member States will be required to take measures to meet the quality standards for additional pollutants, and to make their monitoring data available on a more frequent basis (European Commission, 2023). Currently, the legislation of the European Union is the best worldwide for emerging MPs.

(2) The United States of America: The United States Environmental Protection Agency regulates the pollution of water bodies. Currently, the agency has a strong program for screening and regulating endocrine disruptors in water samples. The National Primary Drinking Water

Figure 9.2 Current regulatory frameworks for MPs in water samples around the world.

Regulation enforces primary standards for a few microorganisms, disinfection by-products, disinfectants, inorganic chemicals, radionuclides, and organic chemicals (MPs listed include majorly pesticides, herbicides, and chemicals from the discharge of industrial chemical factories) (The United States Environmental Protection Agency, 2023).

(3) Canada: Environment and Climate Change Canada and the Environmental Protection Agency have reported that MPs are increasingly and consistently being found in groundwater, surface water, municipal wastewater, drinking water, and food sources. The MPs being tracked are mostly polybrominated diphenyl ethers (fire retardant), acetaminophen, ibuprofen, chlortetracycline, caffeine, bisphenol A, triclosan, and a few others. However, although water quality criteria have been established for a few emerging contaminants, they are not legally enforced. The Guidelines for Canadian Drinking Water Quality regulate the maximum amount of a few pesticides/herbicides, in which chlorpyrifos is among them (Government of Canada, 2023).

(4) China: In 2014, China declared a 'war on pollution.' Since then, air quality has improved significantly, but China's standards for environmental quality and pollutant emissions mainly focus on conventional pollutants, as do its lists of managed chemicals. Most feature on one of the two lists: for air pollutants and for water pollutants. Once listed, chemicals can be controlled under laws on air and water pollution. A first list of 'new pollutants for priority control' is expected to be published in 2023. Substances on those lists will either be banned or subjected to usage and emission restrictions. Meanwhile, regulators are currently revising guidelines on industrial restructuring to gradually phase out some pesticides, veterinary drugs, cosmetics, and industrial chemicals (Zi, 2022).

(5) Southeast Asia: Although research of emerging contaminants in southeast Asia is insignificant in comparison to other regions globally, it has gained substantial momentum in recent years.

Except for Timor-Leste, all southeast Asian countries are part of the Association of Southeast Asian Nations (ASEANs), a collaborative intergovernmental organization that started in 1967. To enhance water quality and better water management practices, the ASEAN working group on Water Resource Management was created to increase regional cooperation and provide frameworks to assist member countries. However, there are no ASEAN-specific water quality guidelines similar to those of the European Union, and only some member countries have developed or adopted a country-specific water quality index to evaluate the quality of their water resources. Even then, the parameters measured were focused on basic indicators and microbial risk (ammoniacal nitrogen, biochemical oxygen demand, total coliform bacteria, pH, etc.), and there are no water quality guidelines created for MPs (Lee *et al.*, 2022).

(6) Latin America: The class of MPs that is most measured in Latin America is pharmaceuticals, followed by personal care products and endocrine disruptors. The lack of information about MPs in countries such as Cuba, El Salvador, Haiti, Honduras, Nicaragua, Panama, Paraguay, Peru, and the Dominican Republic is largely economical, due to the high cost of quantification of these compounds and environmental political interests. Currently, representatives from Argentina, Brazil, Chile, Cuba, Costa Rica, Guatemala, Ecuador, Nicaragua, Panama, Paraguay, and Uruguay have participated in the project RLA/7/019 'Elaboration of indicators to determine the effects of pesticides, heavy metals, and emerging pollutants in continental aquatic ecosystems important for agriculture and agro-industry.' The main objective of this project is to improve quality of life, food security, and agricultural resources in Latin America and the Caribbean through the proper management of water resources. However, legislation in this context in Latin America is almost non-existent (Peña-Guzmán *et al.*, 2019).

9.2 FATE AND REMOVAL OF MPS IN ANAEROBIC REACTORS TREATING DOMESTIC WASTEWATER

9.2.1 Fate of MPs during wastewater treatment

Traditional domestic wastewater treatment systems are typically designed and operated to remove influent solids, organic, and macronutrient loads. Organic MPs present in wastewater, which are not specifically targeted, exhibit varying degrees of removal, due to the combined effect of different biotic and abiotic mechanisms. Broadly speaking, the concentration of MPs in wastewater can be attenuated by abiotic degradation (due to photolysis, chemical oxidation, and hydrolysis reactions), volatilization, a partition to the solid phase (adsorption), and biotransformation reactions. The extent of the contribution of each of these pathways to the overall MP removal is highly dependent on the physicochemical properties of MPs, wastewater treatment technology, environmental conditions at treatment plants, and their operational parameters.

The widespread environmental presence of MPs originating from domestic sewage is indicative of their chemical stability and resistance to abiotic degradation under ambient conditions. As volatilization is only relevant for compounds with high vapor pressures, sorption to the particulate phase and biotransformation are considered the main removal mechanisms of these recalcitrant MPs during secondary (biological) treatment of domestic wastewater.

Adsorption of MPs to the particulate phase may occur due to hydrophobic interactions between aliphatic and aromatic groups of MPs and the lipidic fractions of biomass and sludge; electrostatic interactions between charged functional groups and the superficial charge of solids; as well as the formation of complexes between the MPs and metal ions present in the solid phase (Tran *et al.*, 2018). The properties of MPs that influence their adsorption include molecular size; charge; hydrophobicity; and the presence of specific functional groups in their chemical structure. Naturally, the properties of sorbents (which depend on, among other things, the sludge type and sludge age) and environmental factors such as pH, temperature, and ionic strength of the medium are equally relevant in determining the extent of adsorption, particularly for MPs harboring ionizable moieties. A large number of parameters involved in the characterization of the phenomena makes the theoretical prediction of MP sorption unfeasible. Thus, the combined effect of these parameters is condensed in liquid–solid partitioning coefficients (K_d), which can be experimentally determined for the sorbate–sorbent pair and are often used as predictors of the sorption potential of an MP onto the particulate phase in WWTPs (Berthod *et al*., 2016).

The strength of the sorbate–sorbent interaction determines the reversibility of the adsorption, which in turn influences the MP mobility in the environment once the particulate phase is removed from a WWTP. Reversible adsorption of MPs onto sludge raises concerns of environmental spread in cases where sewage sludge is disposed of on agricultural land, in the form of biosolids. In these situations, MP removal by adsorption would not be a desired mechanism, as the environmental risk would remain unchanged, simply being transferred out of the treatment plant.

The reversibility of the adsorption also affects MPs availability to undergo further biological transformations. As most of the anabolic and catabolic microbiological reactions are mediated by intracellular enzymes, MPs should be in solution and available for uptake by microorganisms (and therefore, not physically adhered to a surface – adsorbed) in order to be biotransformed. This, however, is not a consensus in the literature, as some authors consider the adsorbed MPs to be bioavailable, whether due to biotransformation mediated by extracellular enzymes or the consideration of reversible adsorption as an initial transport step to biodegradation (Gonzalez-Gil *et al*., 2018a).

Finally, the significance of sorption as an MP removal mechanism depends on sludge-wasting practice in WWTPs, as measured by solid retention times (SRTs) in bioreactors. For aerobic reactors based on the activated sludge technology, which are usually operated under short SRTs (3–10 days), there is a considerable removal of MPs adsorbed to wasted sludge. Anaerobic processes, on the contrary, have lower biomass yield in comparison with the aerobic ones, and bioreactors are typically operated under much longer SRTs (hundreds of days) and therefore with minimal sludge wasting. The time necessary for saturation of MPs sorbed onto the anaerobic sludge is insignificant relative to the SRT, and therefore adsorption is negligible as a removal pathway, when compared to biotransformation reactions (Harb *et al*., 2019). This is not to say that adsorption does not play a role in MP removal in anaerobic reactors, as the retention time of some MPs is increased due to adsorption, which could favor the occurrence of biological transformation.

Biotransformation is a broad term that encompasses different types of reactions mediated by microorganisms. Biotransformed MPs can be partially degraded to other organic compounds of lower molecular mass (which is often termed biodegradation); conjugated to form products of higher molecular mass; or completely mineralized to CO_2, H_2O, CH_4, and other inorganic compounds. Conjugation is a biotransformation process in which functional groups are added to an MP, usually rendering it less toxic, more water-soluble, or more amenable to biodegradation. The resulting conjugated products can be reverted back to the parent compound, which is often observed in WWTPs (Verlicchi *et al*., 2012).

The organic products of biotransformation, whether from biodegradation or conjugation, are commonly referred to as transformation products (TPs). TPs of some MPs might exhibit higher toxicity or recalcitrance than the parent compound, posing different environmental risks (Escher & Fenner, 2011). During secondary treatment, TPs might accumulate in the medium as 'dead-end' metabolites, or they might be further transformed by different microbial groups as part of a wider metabolic network (Fischer & Majewsky, 2014). Thus, simply following the disappearance of an MP is not enough to assess the effectivity of treatment systems in reducing potential environmental risks (Stadler *et al*., 2012). Complete mineralization or the formation of innocuous TPs should be the desirable endpoints of MP biotransformation in WWTPs.

Similar to adsorptive removal, the susceptibility of an MP to biotransformation is contingent on a wide range of factors, such as temperature, pH, redox potential, bioavailability, microbial diversity, presence of other substrates, hydraulic retention time (HRTs), and the physicochemical properties of MPs (Falås *et al*., 2016). Particularly for MPs, the concentration level is a key aspect in determining the type of biological transformation the MPs will undergo during secondary treatment, as it will define the metabolic pathways acting on them. MPs might be part of the central metabolic routes of the microorganisms or they might be fortuitously transformed due to low substrate specificity of some enzymes (co-metabolism). Considering that MPs are found in domestic wastewater in the ng/L to μg/L range, it is not expected that their presence alone would be enough to induce the production of enzymes and cofactors necessary for their metabolization. Carbon and energy derived from the degradation of MPs would not be sufficient to support biomass growth. Thus, the biotransformation of MPs is understood to be necessarily dependent on other growth-supporting substrates (Kennes-Veiga *et al.*, 2022).

The complexity of removal mechanisms and their dependence on a multitude of factors explain the wide variation in overall removal efficiency found for similar compounds in similar wastewater treatment technologies (Alvarino *et al.*, 2018). Recognition and characterization of the mechanisms by which MPs are removed from domestic wastewater during mainstream biological treatment are essential to substantiate the proposition of novel treatment technologies constituting more effective barriers in containing the release of MPs to the environment.

9.2.2 MP removal in anaerobic reactors

Most of the investigations on MP removal during secondary treatment of domestic wastewater have focused on aerobic reactors, mainly those based on activated sludge technology. As mainstream anaerobic wastewater treatment is increasingly used for domestic wastewater, the literature on the fate of MPs in these systems is much scarcer. The transformation of MPs in biological reactors revolves around the action of enzymes on functional groups present in the contaminant's molecules. While some of these enzymatic reactions are known to proceed in both aerobic and anaerobic environments, as the enzymes that catalyze these reactions are redox-independent (e.g., hydrolases and transferases; Gonzalez-Gil *et al.*, 2019), some occur exclusively or at least preferentially under anaerobic conditions. This, in turn, results in distinct MP removal capabilities between anaerobic and aerobic reactors.

Several studies have shown that most MPs are biotransformed under anaerobic conditions, albeit to variable extents (Ghattas *et al.*, 2017), as presented in Table 9.1. There is, however, significantly

Table 9.1 Apparent removal of selected MPs during mainstream anaerobic treatment of real domestic wastewater.

Selected MPs	Removal Range (%)	References
Bisphenol A	<0–87	[1–3, 14]
Caffeine	0–98	[4–6]
Carbamazepine	5–96	[5–8]
Ciprofloxacin	84–100	[5, 9]
Diclofenac	<0–78	[1, 2, 4, 5, 7, 9–14]
Ibuprofen	<0–91	[4–7, 9–12, 14]
Propranolol	46–100	[8, 12]
Sulfamethoxazole	<0–100	[1, 2, 5, 8]
Triclosan	18–89	[3, 6, 12, 13]
Trimethoprim	33–100	[1, 2, 5, 9]

[1] Queiroz *et al.* (2012); [2] Brandt *et al.* (2013); [3] Mladenov *et al.* (2022); [4] Arrubla *et al.* (2016); [5] Dutta *et al.* (2014); [6] Reyes-Contreras *et al.* (2011); [7] Chen *et al.* (2019); [8] McCurry *et al.* (2014); [9] Butkovskyi *et al.* (2015); [10] de Graaff *et al.* (2011); [11] Pirete *et al.* (2022); [12] Granatto *et al.* (2021); [13] Butkovskyi *et al.* (2018); [14] Vassalle *et al.* (2020).

little understanding of the fundamental mechanisms that lead to that removal. Obtaining mechanistic insight is difficult owing to the complexity of biological treatment systems. Thus, much of the work has been focused on unraveling the various factors (reactor-related or MP-related) that directly or indirectly influence the underlying microbiological process.

Among the MP-related properties (chemical structure, molecular weight, hydrophobicity, dissociation constants, etc.), the types of functional groups present in the molecule are of particular interest in assessing their removal in anaerobic reactors. It has been proposed, mostly agreeing with experimental data, that MPs containing electron-donating groups (such as amines, methyl, and hydroxyl) are more susceptible to anaerobic biotransformation, whereas MPs with electron-withdrawing groups (such as chloro, sulfonyl, amide, carboxyl, nitrile, and aldehyde) are more recalcitrant to anaerobic treatment (Wijekoon *et al.*, 2015). This, however, is not a universal rule, as structurally similar MPs often exhibit distinct transformation rates in the same bioreactor (Luo *et al.*, 2014). The interaction with other factors must be considered.

Diverse environmental (temperature, pH, ionic strength) and reactor-related properties (HRT, organic loading rate – OLR, SRT, redox potential, presence of growth-supporting matrices, wastewater composition) shape the composition of the microbial consortium present in anaerobic reactors, and thus the metabolic potential for MP biotransformation. It is believed that increased microbial diversity is beneficial to MP removal due to an increased number of functional traits in the community (Falås *et al.*, 2016). In this context, using longer SRTs would be beneficial: not only does it allow for the establishment of slow-growing organisms, but also extends the exposure of adsorbed MPs to the microbial population (Harb *et al.*, 2019). However, the exposure of the non-sorbed fraction remains limited by the HRT.

The putative existence of key microbial populations involved in MP biotransformation, which could be selectively enriched in anaerobic reactors to enhance overall MP removal, has motivated recent research efforts to isolate the contribution of the different stages of an anaerobic process (hydrolysis, acidogenesis, acetogenesis, methanogenesis). Experimental evidence so far has discussed acidogenesis, acetogenesis, and methanogenesis as the main steps involved in MP removal (Carneiro *et al.*, 2020; Gonzalez-Gil *et al.*, 2018b). However, some MPs are removed to similar extents under both acidogenic and methanogenic conditions, which might indicate that either the reactions are carried out by enzymes common to the different microbial groups, or that the biotransformation of MPs is not necessarily linked to the main metabolic pathways in a reactor, but to specific microbial communities common to all anaerobic environments (Kennes-Veiga *et al.*, 2022).

Transferring the mechanistic understanding of anaerobic biotransformation of MPs, which is still in its infancy, to feasible changes to be implemented in mainstream anaerobic domestic wastewater treatment remains a major challenge.

9.2.3 Development of anaerobic reactors for MP removal

Most of the research focusing on the application of anaerobic reactors for MP removal is performed with lab-scale units. The option for such reduced prototypes is a scientific strategy to best control the process and to search for fundamentals for the removal process. Moreover, lab-made (simulated or synthetic) domestic wastewater is frequently applied to avoid interferences of a cocktail of compounds found in real domestic sewage, thus facilitating the mass balance and, consequently, the evaluation of anaerobic removal pathways. However, some studies also use real domestic sewage to prevent extreme simplifications from masking the obtained results.

The studies on MP removal in anaerobic lab-scale reactors can be divided into two categories: reproduction of conventional anaerobic reactors applied to domestic wastewater, that is, upflow anaerobic sludge blanket (UASB) reactors, and proposition of new configurations of reactors to enhance the removal of compounds. The first type aims at searching for the best operating conditions, as mainstream anaerobic WWTPs are designed to remove influent solids, as well as organic and macronutrient loads. Moreover, a combination of conventional anaerobic reactors with biological or physical–chemical processes is addressed in some studies, often using anaerobic technology as the core of the process. The second type of study is focused on design procedures, mainly related to the increment of the SRT over the HRT, and consequently, the achievement of a high concentration of microorganisms, while at the same time trying to maximize the diversity of the cell population. Invariably, these studies are based on immobilized-cell technologies or with advanced techniques of cell retention, such as membrane processes, whose configurations are meant to comply with such requirements. Additionally, some studies in this line have sought to evaluate the influence of the phase separation of anaerobic processes in specific reactors, such as hydrolytic, acidogenic, and predominantly methanogenic ones as further discussed.

The challenge of developing more efficient and reliable bioreactors is subject to exhaustive research that begins on a laboratory scale. At this stage, the main variables that interfere with reaction rates and the stability of the system must be evaluated. These data can lead to the proposal of a model that allows a rational increase of the scale for a pilot unit. This new unit must also be studied to validate the model or modify it with the purpose of a new increase in scale. The progressive increase in scale, based on rational data, ensures security to the configuration of development process; however, it is more time-consuming. For this reason, this approach should be more unpretentious and freer from market pressures for quick results. It is an experimental–mechanistic approach, in which the experiment provides subsidies for models based on fundamental phenomena that will serve for scale-up, design, simulation, and optimization of the units.

Contrary to the experimental–mechanistic approach, there is a more traditional and more common approach in the development of anaerobic reactor configurations. This approach, which can be called purely experimental or empirical, is based on smaller-scale, pilot, or even on real-scale studies, focusing on directly observable and manipulable parameters, such as HRT and OLR. These parameters encompass physical, chemical, and biochemical phenomena and can be the main factors for scale-up or reactor design. This type of approach allows for faster evolution of the development of a given configuration but is generally less secure because it approaches the system as small 'black boxes,' which involve many physical, chemical, microbiological, and biochemical phenomena that are not properly elucidated.

The opposition of these two approaches is presented by Wentzel and Ekama (1997), who call the empirical approach the 'black-box approach,' in which applications are restricted to the experimental conditions that generated the model. According to the authors, the empirical approach only allows interpolation of results, whereas the experimental–mechanistic approach (called only mechanistic by the authors) would allow interpolations and extrapolations.

There would still be a third approach fundamentally based on mathematical modeling. However, the lack of mechanistic models that adequately cover all steps of the anaerobic process, parameters, and historical series of operational data means that this approach still encounters little or no applicability in this field.

It is clear that these three approaches are not completely independent and, even within the same research group, there is a need to balance the approaches well, to allow research to result in real advances in the area of anaerobic reactors. However, the experimental–mechanistic approach, although more complex and more time-consuming to generate practical results, should be the one that can make the greatest contribution to the consolidation of anaerobic treatment processes as a viable and reliable alternative. Furthermore, this approach allows studies on the microbiology and biochemistry of anaerobic digestion to be included in the generated models, allowing such studies to gain practical meaning.

In general, studies on MP removal in anaerobic reactors are based on the experimental–mechanistic approach, mainly because the mechanisms involved in the degradation of different compounds have to be elucidated to better understand the system. A black-box approach in this area may lead not only to sub-optimized units as occurs in the case of organic matter or nutrient removal, but also to unsafe systems incapable of removing MPs in the required levels. In addition, using a scientific method of trial and error, in this case, can be disastrous not only because it releases compounds that are harmful to the environment, but also because it releases degradation products into the environment that can be even more toxic than the original compound.

Conventional anaerobic reactors commonly applied for the treatment of domestic wastewater, such as expanded granular sludge bed (EGSB) and UASB, have been studied on lab scale, mainly focusing on the HRT required to degrade some MPs, as performed by Granatto *et al.* (2021), who evaluated degradation of diclofenac (35–37% removal), ibuprofen (43–44% removal), propranolol (46–51% removal), triclosan (51–72% removal), and linear alkylbenzene sulfonate (63–65% removal). In the same configuration, Gutiérrez *et al.* (2022) evaluated the removal of nonylphenol ethoxylate (48–82% removal) in the co-digestion of domestic sewage and commercial laundry wastewater. In both studies, such a conventional reactor was evaluated under specific operating conditions and not related to the design parameters commonly used for this technology when organic matter removal is the main objective. For UASB reactors, the literature also explores HRT beyond the conventionally applied or conjugated technologies, aiming at MP removal. For example, Mora-Cabrera *et al.* (2021) studied a UASB reactor followed by a membrane electrochemical bioreactor to treat domestic wastewater containing ibuprofen (24% removal), carbamazepine (23% removal), diclofenac (29% removal), and 17α-ethinylestradiol (26% removal), whereas Vassalle *et al.* (2020) combined UASB with high-rate algal ponds to remove ibuprofen (65% removal), diclofenac (65% removal), naproxen (71% removal), paracetamol (65% removal), gemfibrozil (39% removal), estrone (95% removal), 17β-estradiol (91% removal), 17α-ethinylestradiol (92% removal), estriol (89% removal), nonylphenol (70% removal), and bisphenol A (43% removal). In both studies, the HRT applied to UASB reactors was commonly applied in domestic WWTPs, in which the focus of the studies was on combining the systems, searching for reliable post-treatment units.

The proposition of new configurations of anaerobic reactors focusing on MP removal is based on the enhancement of the SRT/HRT ratio and the achievement of a high-diversity microbial population with increased concentration. One way to achieve this goal is to use cells immobilized on an inert support, as obtained in anaerobic filters, or even self-immobilized in the form of granules, as observed in UASB reactors. In addition, the use of adhered or immobilized cell technology allows for obtaining cell concentrations greater than those obtained in systems with non-adhered cells, with obvious benefits for the treatment of wastewater and for MP removal. In these systems, however, the kinetic analysis becomes more complex, as the phenomena of mass transfer from the liquid phase to the biological solid phase effectively influence the global rates of conversion of organic matter.

In the case of anaerobic reactors, in addition to the objective of increasing the cell retention time, the immobilization of the biomass can be used to improve the relationships between the different microorganisms, facilitating the transfer of primary and intermediate substrates between the various groups that participate in the complex process of anaerobic digestion. In addition, resistance to mass transfer in systems containing immobilized cells may represent protection for organisms when potentially toxic compounds or inhibitors are present.

More than an alternative, Speece (1996) considers the retention of biomass essential for the maintenance of methanogenic organisms, which have a low growth rate. The classic way of treating reactors containing immobilized biomass derives from the way of treating heterogeneous reactors containing immobilized enzymes. Two resistances to mass transfer are considered in this approach: transfer in the liquid phase, in the stagnant liquid film around a bioparticle, and transfer in the solid or intraparticle phase as classically presented by Bailey and Ollis (1986).

Uncertainty regarding granulation (self-immobilization) in UASB or EGSB reactors and the empiricism involved in the design of conventional anaerobic filters were some of the main motivators for proposing new reactor configurations containing cells immobilized on different and varied support materials, which allow adhesion and growth of diverse or specific biomass, depending on the application. Support material can be used as a selection or enrichment factor for some desirable organisms and the elimination of undesirable ones.

Immobilized-cell anaerobic bioreactors have been proposed in different configurations for MP removal from domestic wastewater. Carneiro *et al.* (2019) compared two ways of packing the support material in a fixed-bed reactor. An anaerobic packed-bed reactor was compared to a structured-bed one for sulfamethoxazole and ciprofloxacin removal from domestic sewage. In this study, a structured bed showed to be potentially more viable as it presented the same performance for a quantity of support material 50% lower than that in a packed bed. Moreover, the structure of the bed, thus providing high bed porosity, may prevent hydrodynamic misbehavior, common in fixed-bed reactors, such as channeling and dead zones. Besides the fixed-bed configuration, immobilized cell reactors can be configured as expanded or even fluidized-bed, leading to the improvement of mass transfer fluxes, leading to benefits in the overall reaction rate although with higher energy demands.

Another way of achieving high SRT/HRT ratios is to separate suspended biomass and recirculate it to the reactor, thus decoupling the SRT from the HRT. Using efficient separation systems, such as processes using membranes, allows not only high HRT/SRT ratios but also the possibility of obtaining higher concentrations of microorganisms in a reactor. This alternative has been studied in some research groups as presented by Sawaya *et al.* (2022) and Arcanjo *et al.* (2022).

As mentioned earlier, adopting combined acidogenic–methanogenic reactors can be a feasible strategy to enhance MP removal. Carneiro *et al.* (2020) observed that the acidogenic phase is crucial in the biotransformation of some MPs, whereas the hydrolysis of carbohydrates does not significantly contribute to the metabolic transformation of such compounds. The removal of some compounds, such as galaxolide, celestolide, tonalide, erythromycin, and roxithromycin was favored under acidogenic conditions compared to acetogenesis/methanogenesis whereas the removal of other compounds, such as triclosan, fluoxetine, bisphenol A, and carbamazepine depends on acetogenesis/methanogenesis. Macêdo *et al.* (2021) evaluated tetrabromobisphenol A removal in two anaerobic structured-bed reactors under acidogenic and methanogenic conditions and observed that the biodegradation occurred during acidogenesis via co-metabolism. Pirete *et al.* (2022) found that acidogenic bacteria were responsible for diclofenac and ibuprofen biodegradation in an anaerobic fluidized-bed reactor.

A combination of anaerobic and aerobic processes may be relevant for MP removal from domestic wastewater. This approach is known as a hybrid anaerobic–aerobic process. In a hybrid process, the anaerobic step is used to convert complex organic compounds into simpler compounds, such as volatile fatty acids, which are then fed to an aerobic bioreactor for further degradation. An aerobic step can be used to remove residual organic matter and to provide additional treatment of MPs that are not effectively removed by the anaerobic process. This combination of anaerobic and aerobic processes can result in a more efficient removal of MPs compared to using either process alone. Anaerobic processes can remove MPs that are biodegradable and have low solubility, whereas aerobic processes can remove MPs that are more recalcitrant and have higher solubility.

9.2.4 Strategies for enhancing MPs removal in anaerobic reactors

The development of anaerobic reactors for MP removal from wastewater faces several challenges, including: (1) the selection of suitable microorganisms: it is important to select microorganisms that can efficiently degrade the MPs present in wastewater without generating toxic by-products; (2) organic load control: the quantity and quality of organic matter in wastewater can affect the performance of anaerobic reactors. The organic load needs to be controlled to avoid system overload; (3) MP monitoring: MPs in wastewater can be difficult to detect and quantify. It is important to monitor them to assess the reactor's efficiency and identify possible issues; (4) reactor scaling-up: reactor sizing should consider various factors, such as the type of MPs present in wastewater, the organic load, and the treatment system's characteristics; (5) cost–benefit: the development of anaerobic reactors for MP removal must be economically viable, considering the cost of materials, energy required for system operation, and the reactor's lifespan; and (6) legislation: environmental legislation may impose limits on the amount of MPs allowed in treated wastewater. It is essential to develop treatment systems that meet these legal requirements.

Different approaches have been considered to enhance MP removal in anaerobic reactors. In addition to manipulating traditional operational variables known to be crucial to the performance of anaerobic reactors (such as pH, OLRs, solids, and HRTs), other more structurally demanding alternatives have also shown promise in enhancing the removal of MPs or enabling the removal of certain MPs. Recent studies have highlighted the potential of two-phase anaerobic reactors; a combination of anaerobic–aerobic or anaerobic–physicochemical processes; the use of membrane separation; and the addition of external substrates to domestic wastewater, which would serve as additional electron donors.

The utilization of two-phase anaerobic reactors, which consist of separate hydrolytic–acidogenic and acetogenic–methanogenic stages, has been demonstrated to be advantageous for the treatment of domestic wastewater over traditional single-phase reactors. Initially developed to treat high-strength waste, this approach has been shown to lead to a more stable process, increased methane production rates and yields, and greater microbial diversity than that of single-phase reactors (Carneiro *et al*., 2022; Rajagopal *et al*., 2019; Smith *et al*., 2017). The improved performance is a result of providing optimal environmental conditions for the spatially separated microbial groups active in an anaerobic process. Current research suggests that these modifications can have positive effects on MP removal (Carneiro *et al*., 2020), although further investigation is needed to fully assess this potential benefit.

Treatment systems incorporating biological processes that occur under different redox conditions have been proposed to enhance MP removal. As aerobic and anaerobic bioreactors mainly target different moieties of MPs, a combination of the two environments would broaden the range of compounds removed during biological treatment. Theoretically, the aerobic environment can remove MPs that are recalcitrant to anaerobic degradation and vice versa. In the context of domestic wastewater treatment, this combination of redox conditions can be achieved in biological nutrient removal setups consisting of alternating anaerobic, aerobic and anoxic tanks, or through direct microaeration of anaerobic reactors. Falås *et al*. (2016) investigated the removal of 31 organic MPs in 15 biological reactors incorporating different redox conditions and found that although different redox conditions led to an increased removal of a few compounds (venlafaxine, diatrizoate, tramadol, codeine, and trimethoprim), a large number of MPs persisted in the treated wastewater, regardless of the operational conditions. Similar results were found by Wolff *et al*. (2018), who evaluated reactor cascades combining aerobic and strictly anaerobic treatments and observed a significant improvement in the removal of selected MPs (diatrizoate (20–70 percentage points increase), venlafaxine (90–98 percentage points increase), and diclofenac (10–70 percentage points increase)), but only a slight improvement in the overall MP removal. do Nascimento *et al*. (2021) investigated the effects of the injection of small amounts of oxygen directly into a UASB reactor treating domestic wastewater on the removal of seven MPs (estrone, 17β-estradiol, 17α-ethinylestradiol, bisphenol A, diclofenac, sulfamethoxazole, and trimethoprim). The authors found significant enhancements of MP removals for all evaluated MPs (67–81 percentage points increase) and no significant deterioration in reactor performance. The microaeration prompted a gradual alteration of the microbial community inside the reactor, without compromising the archaeal community and therefore, the methanogenesis. Thus, microaeration presents a practical and promising alternative for retrofitting existing treatment plants to reduce MP emissions.

Due to the typical concentration range of MPs in domestic wastewater, their removal is often reliant on the presence of other growth-supporting organic substrates. Therefore, for low-strength wastewater such as domestic sewage, the presence of sufficient degradable organic matter might be a limiting factor for MP removal. Studies have shown that the addition of external electron donors can significantly enhance MP degradation (Oliveira *et al*., 2016). This is also why dosing external electron donors in post-denitrifying reactors for residual nitrogen removal can increase MP degradation (Torresi *et al*., 2017). Thus, it can be hypothesized that co-treating domestic sewage with other wastewaters could favor the overall removal of MPs. However, this approach is still in its early stages, and it is necessary to evaluate the impacts of the subsequent increase in organic load on the treatment system's efficiency. Additionally, practical applicability must be considered, including aspects such as the availability and transportation costs of appropriate co-substrates.

The previously discussed emerging strategies for enhancing MP removal rely on the biological degradation route, which might still be insufficient for acutely recalcitrant MPs. In these cases, oxidative physicochemical post-treatments constitute compelling alternatives. There are numerous established and innovative oxidative physicochemical processes capable of removing MPs, such as ozonation, ultraviolet-peroxide, chlorination, hydrodynamic cavitation, sonolysis, Fenton-based processes, electrochemical oxidation, and ferrate oxidation. These processes are non-selective and generally capable of high-MP transformation rates. Some processes, such as chlorination and ozonation, are already found in domestic WWTPs containing tertiary stages for effluent polishing. While it is not within our current scope to provide an in-depth review of the performance of each of these technologies in MP removal, it is important to discuss the applicability of upgrading existing treatment plants aiming at MP oxidation. Oxidative chemical post-treatments typically entail elevated operating costs associated with high-energy requirements and costly inputs. While complete mineralization of some MPs is achievable for some of the processes, in some cases this might demand unfeasible reaction times, resulting in incomplete transformation of MPs. In some cases, TPs (deriving from MPs or from the wastewater matrix) can be more resistant or even more toxic than the initial target compounds (Ribeiro *et al.*, 2015). Furthermore, the efficacy of oxidative chemical treatments is dependent upon the overall quality of the preceding wastewater treatment, as residual organic matter and common inorganic ions (sulfide, carbonate, bicarbonate, and nitrate) act as scavengers for the oxidant species, increasing the process cost. Nevertheless, cost-effective MP removal through ozonation has been implemented on full scale in Germany and Switzerland (Rizzo *et al.*, 2019).

The strategies discussed to enhance MP removal from domestic wastewater involve adding a subsequent unit process to an anaerobic reactor. Naturally, these alternatives should achieve superior MP removal compared to relying solely on traditional anaerobic treatment. However, these options involve a significant degree of modification to WWTPs, and their implementation solely to reduce MP discharges may prove impractical in most cases. Adopting these systems is more likely to be successful when integrated with further polishing of other water quality parameters. This allows for more valued uses for the treated wastewater, such as water reuse and controlled groundwater recharge. It is important to keep in mind that any increase in effluent quality is accompanied by an increase in treatment cost and in the overall impacts associated with producing the necessary inputs for these post-treatments. In other words, the abatement of MP discharge might create environmental burdens beyond the walls of the treatment plant. Therefore, the endpoints for effluent discharge must be carefully assessed, aiming for an overall environmental optimum rather than the lowest achievable. A comprehensive benefit analysis is necessary.

9.3 CONCLUDING REMARKS

Sources of MPs in the environment are diverse. They can come from domestic wastewater, hospitals, commercial and industry effluents, farms, and several run-offs. This ample origin makes them diverse, complex, and difficult to monitor. Contamination of water and domestic sewage by MPs has adverse effects, such as resistance in pathogenic bacteria and reduced diversity of bacteria and algae in aquatic environments. These substances cause changes in the behavior and morphology of aquatic biota and interfere with the hormonal system of wildlife and humans. Even with the partial elucidation of the consequences and toxicity of exposure to MPs, most countries do not have legislation to impose a maximum limit for their concentration in water bodies. Currently, regulations have been adopted for a few micro-contaminants in some countries and regions only in the European Union.

Advanced physical–chemical treatment technologies, such as adsorption and membrane processes, have been demonstrated to be promising choices for MP removal; however, they imply high operation costs and formation of by-products. A biological anaerobic process of conversion of organic matter has, therefore, received attention from several research groups trying to assess if it is a viable option to convert MPs in domestic sewage. The development of anaerobic reactors for the removal of MPs from wastewater faces several challenges, including a selection of suitable microorganisms, organic load control, MP monitoring, reactor scaling-up, and cost–benefit. Studies on MP removal in anaerobic systems are emerging and a great deal of work should be carried out to evaluate whether conventional anaerobic reactors applied to domestic wastewater treatment under usual operating conditions are able to effectively remove contaminants of emerging concern. Moreover, in order to comply with the requirements of removing organic matter, nutrients, and MPs, beyond generating energy (biogas) in a robust, safe, and sustainable way, the study of new operating strategies and reactors configurations are required.

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