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Remediation of Emerging Contaminants

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Abstract Water pollution by emerging contaminants has become a major source of concern and a priority for society and public authorities. Emerging contaminants are a group of natural and synthetic chemicals and biological agents that are not routinely monitored or regulated in the environment and may have known or suspected

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adverse effects on the environment and human health. The list of these substances is particularly long and includes pharmaceuticals, personal care products and cosmetics, pesticides, surfactants, industrial products and additives, nanoparticles and nanomaterials, and pathogens. Many emerging contaminants are released continuously into the environment and can cause chronic toxicity even at low concentra-

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tions, endocrine disruption in humans and aquatic life, and the development of antibiotic resistant bacteria. It is therefore necessary to mobilize efforts to protect human health and biodiversity.

Two of the main sources of emerging contaminants are wastewater treatment discharges and agricultural practices. However, conventional wastewater treatment plants have not been designed to remove such contaminants. It is therefore important to develop effective treatment methods capable of eliminating the parent emerging molecules and their metabolites. This is a difficult and challenging task because most of emerging contaminants are recalcitrant substances. The methods must also target not only water chemicals but also water microbiols in order to reduce and eliminate the toxicity and impact of the treated wastewater.

During the past two decades, several physical, chemical and biological technologies have been proposed for emerging contaminant removal. Each technology has its own advantages and constraints not only in terms of cost, but also in terms of efficiency, feasibility, and environmental impact. However, among the various treatment processes currently cited for wastewater treatment, only few are commonly employed by the industrial sector for technological and economic reasons. Extensive research on this topic highlights the growing interest of scientists in developing treatment systems that are increasingly effective in removing mixtures of trace pollutants, simple to implement from a technological point of view, economically viable and environmentally friendly, with little or no impact on the environment.

The objective of this chapter is to present the recent state of knowledge on the advanced treatments proposed for the removal of emerging contaminants in wastewater when they are present in trace amounts in wastewater. After general considerations on wastewater treatment plant, the first part is focused on adsorption-oriented processes using conventional (activated carbon, clays) or non-conventional (cyclodextrin polymers, metal-organic frameworks, molecularly imprinted polymers, chitosan, nanocellulose) adsorbents. Biosorbents such as cyclodextrin bead polymers have great potential in environmental applications although they are still at the laboratory study stage. The second part presents examples of biological-based technologies for the degradation and elimination of emerging contaminants. Selected biological approaches include constructed wetlands, biomembrane reactors, strategies based on the use of algae, fungi and bacteria, and enzymatic degradation. The third part briefly presents the membrane filtration strategy that is already used as a tertiary treatment. The final part is focused on advanced oxidation processes that also represent one of the most promising strategies because of their simplicity and efficiency.

Keywords Emerging contaminants · Substances of global concern · Pharmaceuticals · Personal care products · Pesticides · Water pollution · Aquatic compartments · Wastewater treatment plants · Remediation · Bioremediation · Conventional removal technologies · Advanced treatments · Adsorption · Biosorption · Cyclodextrin polymers · Constructed wetlands · Membrane bioreactor technology · Membrane filtration · Disinfection · Ozonation · Advanced oxidation processes · Catalytic ozonation · Non-thermal plasma

1.1 Introduction

Emerging contaminants such as pharmaceuticals and personal care products represent a new global water quality challenge, with potentially serious threats to human health and the environment, including water resources. Indeed, the presence of emerging contaminants and biological agents in treated and untreated water has received increasing attention because the risk they pose to human health, ecosystems and water resources is not yet fully understood. For example, antibiotics and endocrine disruptors are among the best examples of “new” contaminants that are known to the public and are of concern. Traces of these substances are being found in water resources, including drinking water, throughout the world. Numerous studies on the presence and behavior of pharmaceuticals in the environment have demonstrated negative effects to aquatic ecosystems and wildlife in general. Another worrying phenomenon is the emergence of antibiotic resistance. Overuse of antibiotics has encouraged the development of antibiotic-resistant strains. Antibiotic resistant bacteria and antibiotic resistance genes pose a public health concern when they transfer antibiotic resistance to human pathogens. All these topics are of great interest to the scientific community and concern to our societies.

The term emerging contaminants includes chemical or biological contaminants without a clearly defined regulatory status. They are often substances, not necessarily of new use, but newly identified, for which data concerning their presence, their fate in the environment and their potential impacts on health or the environment are patchy. Among the emerging pollutants are, in particular, pharmaceuticals subject or not to medical prescription (antibiotics, hormones, illicit drugs, etc.) for human or veterinary use, products for daily use (personal care products, cosmetics, detergents, disinfectants, antioxidants, etc.), products of industrial origin (surfactants, additives, solvents, flame retardants, nanoparticles, etc.), pesticides, and pathogens. The number of molecules concerned is constantly changing both in terms of parent substances and their degradation products (metabolites, for example resulting from biological treatment). In general, these synthetic or naturally occurring chemicals are not commonly monitored in the environment and they are consistently being found not only in wastewaters but also in water resources (groundwater, surface water), and even in drinking water.

Conventional domestic wastewater treatment plants (often stabilization ponds, activated sludge systems) were not designed to treat recalcitrant organic pollutants including emerging substances (Bolong et al. 2009; Teijón et al. 2010; Jelic et al. 2011; Verlicchi et al. 2012; Petrie et al. 2015; Machado et al. 2016; Priac et al. 2017; Botero-Coy et al. 2018; Gogoi et al. 2018; Tolboom et al. 2019; Patel et al. 2019). It is also important to point out that the elimination of microorganisms is not an objective of wastewater treatment plants either (Morin-Crini and Crini 2017). Botero-Coy et al. (2018) reported that the concentrations of some pharmaceuticals (e.g. erythromycin, metronidazole, sulfamethoxazole) in the effluent from a municipal wastewater treatment plant (Bogotá, Colombia) were even higher than in influent, suggesting negative removal efficiencies. Jelic et al. (2011) and Verlicchi et al. (2012) previously reported similar results within European effluents, suggesting

that the wastewater treatment plants act as a concentrator of contaminants. This incomplete removal evidences the need of alternative or complementary treatment technologies (Jelic et al. 2011; Verlicchi et al. 2012; Botero-Coy et al. 2018; Serna-Galvis et al. 2019). Conventional water treatments often involve a combination of methods such as sand filtration coupled with a coagulation pre-treatment, + adsorption + disinfection step, which are usually not effective to remove emerging pollutants. It is therefore important to develop effective treatment methods capable of eliminating not only the parent emerging molecules but also their metabolite and transformation products. These methods must also meet not only water chemistry objectives (particularly in terms of chemical abatement of the residual pollutant load and quality standards) but also water microbiology objectives, in order to reduce and eliminate the toxicity and environmental impact of the treated wastewater. These are two research topics that have been mobilizing the scientific community.

After general considerations on wastewater treatment plants, this chapter presents and discusses advanced treatment methods such as adsorption-oriented processes, biological-based technologies, membrane filtration and advanced oxidation processes. In each of the sections, a state of the art was first conducted and then the authors' research is presented to illustrate each water treatment technology.

1.2 Municipal Wastewater Treatment Plants

Human use of chemicals such as metals began to affect the environment during the “Industrial Revolution” of the second half of the eighteenth century. Since the end of the Second World War, the use of chemical, pharmaceuticals and agrochemical products has greatly increased over the years to meet the growing needs of consumers, who are also rising in number. However, economic development has been accompanied by environmental problems including water pollution. In response to this pollution problem, the first wastewater treatment plants were set up in the 1960s in France, for example. The first European regulations on aqueous discharges appeared a decade later. Today, we are in the “Emerging Pollutant Removal Age” (Crini and Lichtfouse 2018a, b) and, it is, therefore, not surprising that there have been considerable efforts to develop technologies to reduce contaminant emissions. Indeed, the presence of pesticides, pharmaceuticals and personal care products in water challenges the scientific community and water treatment stakeholders to find simple, practical, inexpensive, effective and environmentally friendly disposal solutions.

An important question arises: how do rivers receive emerging contaminants? It is now recognized that the presence in aquatic environments is mainly correlated with the discharge of effluents from municipal wastewater treatment plants (Fig. 1.1), with a higher incidence in wastewater treatment plants in highly industrialized and urban areas (Sole et al. 2000; Gómez et al. 2006; Stackelberg et al. 2007; Kasprzyk-Hordern et al. 2008; Watkinson et al. 2009; Basile et al. 2011; Gonzalez et al. 2012; Meffe and Bustamante 2014; Machado et al. 2016; Morin-Crini and Crini 2017;



Fig. 1.1 Over-consumption of pharmaceuticals and personal care products and contamination of rivers by the same substances present in wastewater from sewage treatment plants. (Region: Sinaloa, Mexico; source: Lorenzo A. Picos-Corrales, Sinaloa, Mexico)

Priac et al. 2017; Gilabert-Alarcón et al. 2018; Mezzelani et al. 2018; Picos-Corrales et al. 2020). However, environmental contamination/pollution originates not only from domestic activity but also from the industrial and agricultural sectors, and other activities such as transport (Morin-Crini and Crini 2017). Indeed, even if all discharges comply with regulations, industrial and urban wastes can still contain a mixture of substances, known or unknown (metabolites, degradation products), and their concentration varies from a few ng/L to a few mg/L. All the substances we use in our daily lives, such as pharmaceuticals or personal care products, can enter the environment through excretion in human and animal urine and feces, through the flushing of unused medicines, or through our domestic uses (cooking, bathing), and results in nanogram per liter to microgram per liter, even after adequate treatment.

For example, Watkinson et al. (2009) investigated the presence of 28 antibiotics in several Australian water matrices, including six rivers and drinking water. The results showed that four substances, i.e., monensin, erythromycin, sulfamethoxazole and norfloxacin, were more frequently detected in surface water, at

concentrations ranging from low ng/L to 2.0 µg/L. The authors demonstrated that in one river that did not receive discharges from municipal wastewater treatment plants, the total concentration of the investigated antibiotics was significantly lower than those in the other five rivers, suggesting that municipal wastewater treatment plants were an important source of antibiotics to the streams. Meffe and Bustamante (2014), Machado et al. (2016) and Gilabert-Alarcón et al. (2018) reported similar conclusions in Italian, Brazilian and Mexican water resources, respectively.

When wastewater is contaminated and remediation becomes necessary, the best purification approach should be chosen to reach the decontamination objectives as established by legislation (Crini and Badot 2007, 2010; Morin-Crini and Crini 2017). A purification process generally consists of five successive steps: (1) preliminary treatment or pre-treatment (physical & mechanical); (2) primary treatment (physicochemical & chemical); (3) secondary treatment or purification (chemical & biological); (4) tertiary or final treatment (physical & chemical); and (5) treatment of the sludge formed (gravity or mechanical thickening and dewatering, drying or incineration). In general, the first two steps are gathered under the notion of pre-treatment or preliminary step, depending on the situation. Pre-treatment removes debris and large solids, while primary treatment focuses on the removal of an appreciable load of organic matter and suspended solids from the influent. This pre-treatment stages, which can be carried out using mechanical or physical means, is indispensable before envisaging secondary treatment because particulate pollution (e.g. suspended solids, colloids, fats, etc.) hinders the posterior treatment, making it less efficient or damaging the decontamination equipment. Primary chemical treatment such as pH adjustment or pre-reduction of a high organic load may also be required. Before its discharge into the environment or its reuse, the pre-treated effluent must undergo secondary purification treatment using in most cases biological processes to produce a satisfactory final effluent. In certain cases, a final or tertiary treatment (including disinfection) can also be required to remove the remaining pollutants or the molecules produced during the secondary purification.

Around the world, almost the same wastewater treatment scheme is used by following the same steps above listed. From a water engineering point of view, the only difference is the type of matrix to be treated (domestic, industrial or drinking). In general, for municipal/domestic wastewaters treatment, the removal of pollutants from the raw wastewater is primarily achieved by biological means (often activated sludge systems). Indeed, biodegradation is one of the main treatment applied to decontaminate wastewater. For industrial wastewaters, e.g. from textile, pulp and paper or surface-treatment industry, pollutant removal is achieved by physical (sand filtration, adsorption onto carbons, membrane filtration, evaporation, extraction), chemical (precipitation, oxidation, electrocoagulation, electrochemical treatment, ion-exchange using organic resins) and biological (lagoon, membrane bioreactors) means, with research focusing on more efficient and less expensive systems combinations or new alternatives such as biosorption, biomass, advanced oxidation processes. In general, precipitation is – together with adsorption – one of the two main treatments applied at industrial scale (Crini and Badot 2007, 2010; Crini 2010). For the production of drinking water, filtration (sand, carbon) and adsorption (activated

carbon) steps are used, coupled with coagulation/flocculation and disinfection (ozonation or chlorination) steps.

The main objective of a conventional municipal wastewater treatment plant, receiving raw wastewater from domestic and industrial discharges, is to remove organic matter and nutrients, e.g. nitrogen and phosphorus. A technological process widely used in the world is the so-called activated sludge, due to its competitive cost and high efficiency. Currently, under optimized conditions, more than 95% of organic and mineral substances can be eliminated by biological-based methods used in municipal wastewater treatment plants. In general, these performance levels make possible to meet the regulatory requirements for the list of substances and water parameters analyzed. However, the efficiency of a conventional system varies depending on the wastewater characteristics and the treatment process used, e.g. activated sludge, membrane biological reactor, with a possible combination with a chemical treatment.

As already mentioned, existing conventional wastewater treatment plants and drinking water treatment plants were not designed to remove pharmaceuticals or nanoparticles, which are difficult to biodegrade or filter, respectively. For example, substances such as acetylsalicylic acid, diclofenac, carbamazepine, atenolol or propranolol are difficult to degrade by conventional biological treatment: performance is estimated to be less than 10% (Patel et al. 2019). Several studies have nevertheless showed that certain substances such as endocrine disruptor compounds can be reduced (Priac et al. 2017; Gogoi et al. 2018; Patel et al. 2019).

In a wastewater treatment plant, besides biodegradation, adsorption to sludge is the most effective process to eliminate substances. Numerous substances are poorly soluble hydrophobic compounds, poorly biodegradable and present a strong affinity for sludge. A typical example is the anti-inflammatory diclofenac that can be partially adsorbed on sludge (Barbosa et al. 2016). In Europe, treated sludge after stabilization is often disposed in the soil or reused for agricultural purposes and composting. A previous study by Johnson and Sumpter (2001) revealed that the essential sewage treatment can rapidly convert organics into biomass that is then separated from the effluent phase by settlement. However, not all compounds were completely broken down or converted into biomass in that study. For example, the steroid estrogens found in effluent corresponded to the products of incomplete breakdown of their respective parent molecules. Liu et al. (2009) also reported that endocrine disruptor compounds were not completely removed by municipal wastewater treatment plants and remained at fluctuating concentrations in the effluent. Thus, the discharge of such water may be the main reason for the wide distribution and occurrence of emerging contaminants in surface waters.

The lists of substances monitored by the treatment plants are beginning to evolve, which will eventually force the plants to upgrade their operations to better treat wastewater. There are two main policies for water pollution control: the first is to focus on reducing pollutant emissions at source, e.g. France, and the second is to focus on downstream reduction at treatment plants, e.g. in Switzerland and Germany (Morin-Crini and Crini 2017). In the latter case, tertiary treatment is required. This final treatment is necessary to remove the remaining pollutants such as

pharmaceuticals and their metabolites. However, the use of tertiary treatment worldwide, including in Europe, is still limited due to significant economic costs. However, it may be necessary in the future if further restrictions are applied (Crini and Lichtfouse 2018a, b).

1.3 Methods for the Removal of Emerging Contaminants

Removing emerging contaminants from wastewater is a difficult and challenging task because most emerging contaminants are recalcitrant substances, often present at trace amounts in complex mixtures. Indeed, a major factor complicating the cleanup of many sites is the coexistence of organic molecules and mineral substances such as metals and metalloids, the so-called mixed wastes. Another complicating factor is the wide range of properties of contaminants, with different chemical structures and functionalities. This diversity of water pollutants requires a wide range of treatment methods that must not only be effective, but also technologically and economically feasible.

To treat emerging contaminants, a multitude of techniques classified as physicochemical treatments, biological treatments, membrane filtration, advanced oxidation technologies, adsorption/biosorption have been proposed in the literature (Fig. 1.2) (Crini and Badot 2007, 2010; Acero et al. 2013; Charles et al. 2014; Secondes et al. 2014; Serna-Galvis et al. 2016, 2019; Bedoya-Ríos and Lara-Borrero 2018; Botero-Coy et al. 2018; Crini and Lichtfouse 2018a, b; Kim et al. 2018).

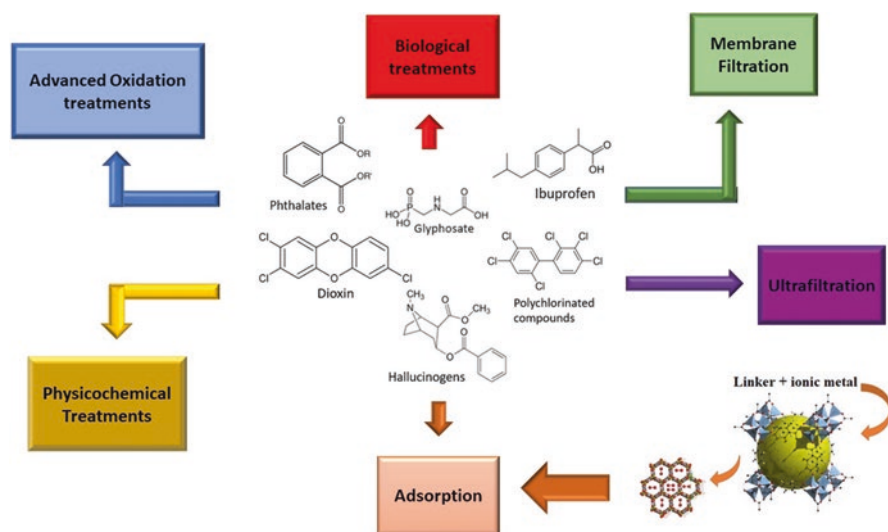


Fig. 1.2 Methods used to remove emerging compounds. (Source: Juan Carlos Moreno-Piraján, Bogotá, Colombia)

Advanced treatments such as biosorption onto non-conventional materials (Wang and Wang 2016; Li et al. 2019a; Fenyvesi et al. 2020; Rojas and Horcajada 2020), filtration membrane coupled with a biological step, algal-based technologies, and oxidation processes combined with an adsorption pretreatment (Serna-Galvis et al. 2016, 2019; Rodriguez-Narvaez et al. 2017) have been proposed to treat domestic water. Recent studies showed that the latter techniques could be a promising way, especially advanced oxidation processes such as ozonation, electrochemistry, photocatalysis, solar-driven processes or solar photo-assisted H₂O₂ treatment (Polo-López et al. 2014; Secondes et al. 2014; Serna-Galvis et al. 2016, 2019). Indeed, advanced oxidation processes have been demonstrated to be very efficient in decreasing not only organic substances but also the pathogen load in contaminated water (Moreira et al. 2016). This is of special interest because of properly treated wastewater could be an alternative renewable water resource, for example for agriculture as an end-use point. All these techniques can also be considered for treating industrial water (Wang and Wang 2016; Crini et al. 2019).

1.4 Adsorption-Oriented Processes for the Removal of Emerging Contaminants

1.4.1 Adsorption of Emerging Contaminants on Activated Carbons

Liquid-solid adsorption/sorption is a key method for removing contaminants, particularly organics, from wastewaters (industrial effluents) or drinking water sources. Indeed, this technique of contaminant removal can produce high quality water, while also being a process that is both technologically simple and economically feasible (Liu and Liptak 2000; Yang 2003; Crini 2010).

Liquid-solid adsorption/sorption involves the accumulation of adsorbate substances from an effluent onto the external and internal surfaces of a material/adsorbent used as a mass separating agent (Crini and Badot 2007, 2010; Fomina and Gadd 2014; Crini and Lichtfouse 2018a, b; Crini et al. 2019; de Andrade et al. 2018; Jeirani et al. 2017). This surface phenomenon is a result of complicated interactions among the three components involved, i.e. the adsorbent, the adsorbate and the effluent (water or wastewater). The data from the literature and also from the industry show that the control of adsorption performances of a solid material in liquid-phase adsorption depends on the following factors: (i) the origin and nature of the solid such as its physical structure, chemical nature and functional groups; (ii) the activation conditions of the raw solid (physical treatment, chemical modifications); (iii) the influence of process variables such as contact time, initial pollutant concentration, solid dosage and dynamic conditions; (iv) the chemistry of the contaminant (as example for an organic molecule, its pKa, polarity, size and functional groups); and finally, (v) the effluent conditions, referring to its pH, ionic strength, temperature and the presence of multi-contaminants and impurities.

Carbon-based materials are one of the oldest and most widely used adsorbents/sorbents, employed since the beginning of the 1900s in the treatment of drinking water (Liu and Liptak 2000; Dąbrowski et al. 2005; Crini and Badot 2007, 2010; Khalaf 2016). These adsorbents have excellent textural properties (high porosity, high specific surface area, large range of particle sizes) and physicochemical properties (surface chemistry) which together account for their excellent adsorption capacity. The process that uses carbons at industrial scale is often carried out by feeding the effluent continuously through a packed bed of carbon (Fig. 1.3). These fixed-bed systems have an important advantage because adsorption depends on the concentration of the substance(s) in the solution being treated. The adsorbent is continuously in contact with fresh effluent; hence, the concentration in the water in contact with a given layer of adsorbent in a column is relatively constant. The process is efficient and economical from the point of view of implementation and operation, which is relatively simple (Geankoplis 1993) and does not generate water by-products as in the case of chemical oxidation or advanced oxidation processes (Rossner et al. 2009; Ahmed et al. 2015; de Andrade et al. 2020), which activities and toxicities still require further studies (Zhang et al. 2016a).

Activated carbons are used as very good adsorbents of a wide range of contaminants and contamination, e.g. to adsorb organic matter in order to reduce the organic load in secondary and tertiary treatment in a municipal wastewater treatment plant, to treat organics such as pesticides, aromatic and phenolic derivatives, volatile aromatics, hydrocarbons and surfactants, to decrease chemical oxygen demand and biological oxygen demand, to discolor water (dye removal) or to treat substances

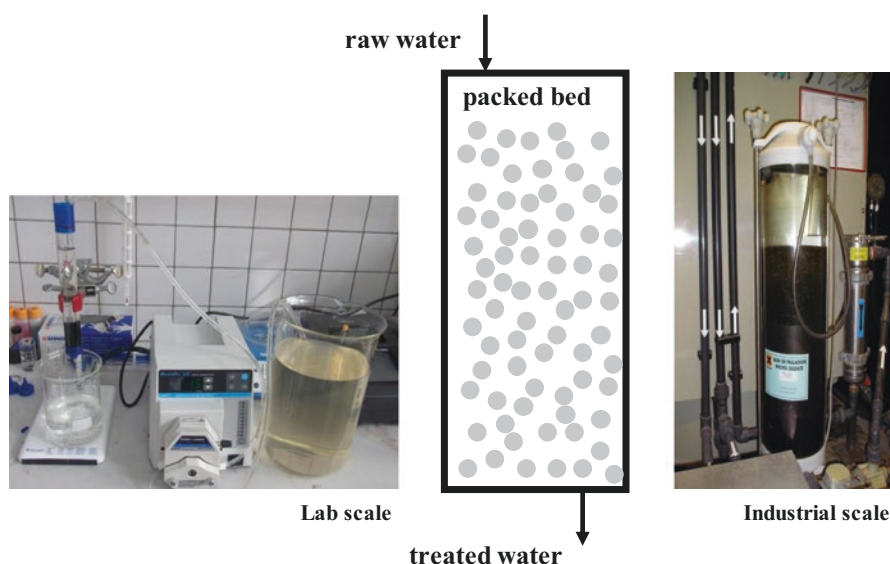


Fig. 1.3 Fixed-bed type process used for adsorption of contaminants from water or wastewater, e.g. for the post-treatment of a pharmaceutical effluent treated by chemical oxidation. (Source: Grégorio Crini, Besançon, France)

that cause specific taste or smell (Crini and Badot 2007, 2010; Couto et al. 2015; Ferreira et al. 2015; Crini et al. 2019; Khan et al. 2020). The adsorption efficiency depends on the type of carbon used, the properties of the adsorbate, as well as the composition of the effluent being treated (Crini and Badot 2010; Ahmed et al. 2015).

Over the past three decades, activated carbons, in granular (GAC) or powder (PAC) form, have been widely used in conjunction with microorganisms for treating wastewater. Macroporous activated carbons can be used as supports for bacteria: the bacteria then degrade part of the adsorbed organic matter (biological elimination) and thus participate in the *in situ* regeneration of the adsorbent. Two combined processes are principally used. Powder activated carbon treatment is obtained by adding carbon to activated sludge. Biological activated carbon (BAC) is a filter made of biofilm-covered granular activated carbon. Commercial activated carbon materials have been employed to remove organic pollutants such as pesticides from wastewater and water. In the purification of drinking water, granular activated carbon filters have commonly been used as a polishing step to remove potentially harmful trace organics. This type of treatment is, in general, coupled to an ozonation stage, further improving the performance of the process. Carbon biological filters are, for instance, used for the detoxification of organic effluent loaded with inorganic ions (removal of iron, manganese, and nitrate). To obtain cost-effective technology (especially in the field of water recycling), carbon powder is used in conjunction with an ultrafiltration membrane or with other techniques, such as oxidation. In Europe, active carbon competes favorably with nanofiltration and begins to replace oxidation with ozone, in particular to remove pesticides (Crini and Badot 2010).

The major advantage of carbon adsorption is that the solid adsorbent can be easily separated from the treated liquid. This allows easy and flexible process operation. However, as it is non-selective, common innocuous organics may interfere with the removal of hazardous compounds. Active carbon technology presents other disadvantages. Active carbons are quite expensive (the higher the quality, the greater the cost). Different qualities of carbon are strongly related to the raw material used, as well as it depends on the carbonization conditions and the way in which activation is performed (physical or chemical). And yet, even though the high absorbing power of active carbons is widely recognized, there are some drawbacks, namely the need of disposal of spent carbons, their rapid saturation, and their regeneration. This regeneration step of saturated carbon is also expensive, not straightforward, and results in loss of the sorbent. Finally, the carbon-adsorption process can be limited in cases of ultra-low concentrations of contaminants (Putra et al. 2009; Lian et al. 2014; Ahmed et al. 2015; Khan et al. 2020).

Various removal efficiencies of emerging contaminants by commercial activated carbons have been published, due to the intrinsic physical and chemical properties of carbons, and the different experimental conditions (pH, contact time, type of water) used (Adams et al. 2002; Westerhoff et al. 2005; Snyder et al. 2007; Foo and Hameed 2010; Rivera-Utrilla et al. 2013; Nam et al. 2014). Interestingly, some hydrophilic pharmaceuticals and personal care products were successfully trapped *via* adsorption, despite of their low hydrophobicities. In fact, the mechanisms of adsorption are not yet fully elucidated (Rivera-Utrilla et al. 2013; Nam et al. 2014; Jeirani et al. 2017).

For example, Adams et al. (2002) showed that pharmaceuticals such as sulfamethazine, trimethoprim, and carbatox were effectively removed (81–98%) from water using powdered activated carbon. In contrast, Westerhoff et al. (2005) reported the wide ranges of removals (20–69%) for the pollutants such as acetaminophen, caffeine, diclofenac, naproxen, sulfamethoxazole, and atrazine by applying powdered activated carbon. Snyder et al. (2007) also demonstrated that 30–78% of pharmaceuticals were removed from river water samples using powdered activated carbon.

Yu et al. (2009) reported a comprehensive study regarding the adsorption of two pharmaceuticals (naproxen and carbamazepine) and an endocrine disrupting (nonylphenol) compound from a full-scale drinking water treatment plant by activated carbon in granular or powder form. The results showed that activated carbon form affected pollutant adsorption to carbon. Powder carbon would be most appropriate for achieving 90% of pharmaceuticals removal at a concentration of 500 ng/L, whereas granular carbon would be more suitable for nonylphenol. The authors explained this result by the fact that nonylphenol was much less impacted by fouling than the other two molecules.

Mailler et al. (2016) tested the use of micro-grain activated carbon (CarboPlus® technology) in a fluidized bed to remove pharmaceuticals, hormones and personal care products contained in treated wastewater from a municipal wastewater treatment plant (Seine Centre Paris, Colombes, France; 240,000 m³/day corresponding to 9000,000 population equivalent). Large-scale experiments using a 5 m high reactor with a surface of 4 m² (10 g or 20 g of carbon per m³, flow rate 1400 m³/day, contact time between 10 and 20 min) have shown that a carbon-based configuration as tertiary treatment substantially improved the overall quality of the discharge waters. Indeed, micro-grain activated carbons can further reduce the residual pollution still present in biologically treated waters: reduction of biological oxygen demand (38–45%), chemical oxygen demand (21–48%), and dissolved organic carbon (13–44%). Besides, removal of ammonium, nitrite (total elimination) and total suspended solids has also been detected. On the other hand, carbon filters were most effective in removing pharmaceutical compounds (52 molecules) and hormones (10 molecules) and other emerging substances (57 molecules) such as alkylphenols, bisphenol A, parabens, pesticides (23 molecules) and sweeteners (50 to >90%). Thirteen campaigns of analytical monitoring have been realized. Pharmaceuticals had a good affinity for micro-grain activated carbon and high (>60%) or very high (>80%) removals were observed for most of the quantified compounds (22 substances of the 32 quantified): for example, atenolol (concentration 448 ± 400 ng/L; reduction of 92–97%), carbamazepine (74 ± 65 ng/L; 80–94%), ciprofloxacin (184 ± 95 ng/L; 75–95%), diclofenac (1120 ± 1400 ng/L; 71–97%), oxazepam (239 ± 110 ng/L; 74–91%) and sulfamethoxazole (1430 ± 1450 ng/L; 56–83%). The ten remaining substances that were less eliminated (25–75%) include for example acetaminophen, ibuprofen and iothalamic acid. Personal care products, alkylphenols, artificial sweeteners, benzotriazole, bisphenol A, pesticides and perfluorinated acids have also a good affinity for micro-grain activated carbon, while phthalates are not or poorly eliminated. Micro-grain activated carbon allowed obtaining performances comparable to conventional powdered activated carbon at a same fresh

activated carbon dose, even if slightly higher removals are observed with powdered activated carbon for several compounds. The differences are explained by the nature of micro-grain activated carbon, which is reactivated, and more likely by the injection of FeCl_3 with powdered activated carbon. However, micro-grain activated carbon removes nitrites and total suspended solids, contrarily to powdered activated carbon. In addition, the micro-grain activated carbon configuration leads to several significant operational advantages over powdered activated carbon for a similar cost (≈ 1000 – 1200 €/ton), such as the ease of operation, the non-necessity to use FeCl_3 and polymer and the reactivability of the adsorbent (no waste to handle). Mailler et al. (2016) concluded that micro-grain activated carbon was more suited than powdered activated carbon for wastewater treatment at large-scale applications.

Nam et al. (2014), studying the adsorption of pharmaceuticals, pesticides and endocrine disruptors, also reported that in addition to carbon form, carbon dose and contact time affected the performance. Increased dosage of activated carbon and increased contact time allowed greater opportunity for the adsorbent to interact with target emerging contaminants, and enhanced adsorption removal was attained. Modifying the adsorbent dosage and contact time can maximize the removal of micropollutants. However, a cost-effectiveness analysis is necessary before implementing these solutions in field facilities. In addition, the adsorption of hydrophilic contaminants, such as caffeine, acetaminophen, sulfamethoxazole, and sulfamethazine, was significantly affected by the pH, whereas low temperature decreased the adsorption of hydrophobic pollutants such as naproxen, diclofenac, 2,4-dichlorophenoxyacetic acid, triclocarban, and atrazine. For example, removal of acetaminophen and sulfamethoxazole changed significantly due to electrostatic interactions between the adsorbent surface and the ionic species of these substances. The charge state of ionizable pollutants can affect micropollutants at certain pH levels. Low temperature can decrease the diffusion of lipophilic pollutants during the hydrophobic interaction with the adsorbent. A decrease in adsorption removal in surface water samples was observed and this decrease was more significant for hydrophobic than hydrophilic compounds. The decline in the adsorption capacity in surface water samples was caused by the competitive inhibition of dissolved organic matter with pollutants onto activated carbon. Nam et al. (2014) pointed out the fact that it was important to consider the effects of dissolved organic matter when treating pollutants in a water treatment plant.

Katsigiannis et al. (2015), studying the removal of emerging contaminants from water by granular activated carbon columns, demonstrated that the process removed endocrine disruptors (bisphenol A, triclosan) more efficiently than pharmaceuticals (ibuprofen, naproxen, ketoprofen) at concentrations up to $2 \mu\text{g/L}$. In all experiments, the performance was enhanced by increasing the depth of the carbon bed. Among the target compounds, triclosan had the highest removal efficiency while ibuprofen was the least effectively removed. At a surface velocity of 3.1 m/h , removal rates after 5 days of continuous operation were 74.7% for bisphenol A, 86.7% for triclosan, 57.4% for ibuprofen, 65.6% for naproxen and 61.4% for ketoprofen for a bed depth of 8 cm, while virtually complete removal was achieved for all target compounds at a bed depth of 16 cm. The authors explained their results by

correlating with the pK_a and the log K_{ow} values of the target substances. During the experiments, microbiological activity was also observed, which stabilized the breakthrough curves that significantly extended the column's service life. Katsigiannis et al. (2015) concluded that activated carbon in the form of granular activated carbon columns can provide for the effective removal of target compounds in a municipal wastewater treatment plant.

Patiño et al. (2015) proposed the adsorption of emerging pollutants (1,8-dichlorooctane, nalidixic acid and 2-(4-methylphenoxy)ethanol) on functionalized multiwall carbon nanotubes. Recently, the use of carbon nanotubes has gained interest for the removal of different pollutants in the aqueous streams. These materials are a new member in the carbon family, including single walled and multi-walled nanotubes distinguished by their number of layers. They had exceptional mechanical properties, excellent electronic properties, large surface specific area, and their structure can be further tuned locally by oxidation treatment or surfactant treatment. Indeed, carbon nanotubes allow the surface modification in order to maximize the selectivity of adsorption through families of compounds, helping to improve the desorption behavior. When combined with membrane filtration, these innovative adsorbents demonstrated excellent removal of pharmaceuticals and personal care products with removals up to 95% (Kurwadkar et al. 2019). Other examples of results obtained using carbon nanotubes are described in the review published by Khan et al. (2020). Carbon nanotubes are considered to be promising adsorbents for water and wastewater treatment, although their high price is an important parameter to consider and their adsorption capacity depends strongly on both the hydrophobicity of the adsorbates and the morphology of the materials used. The materials can also be used in photocatalytic degradation processes in combination with a filtration step for the removal of endocrine disruptors (Patiño et al. 2015; Kurwadkar et al. 2019; Khan et al. 2020).

How to reduce the cost of adsorbents and improve their adsorption performance, while at the same time seeking environmentally friendly materials, has been a pre-occupation of the research community since the 2000s. The development of cheaper, effective and novel materials for pollutant removal is currently an active field of research, as shown by the numerous studies published every year. Research is divided into two directions: the use of natural, cheap and abundant non-conventional materials in raw or modified forms and the development of conventional/commercial and new (synthetic) materials.

Several various studies have been carried out to replace active carbon by other adsorbent/biosorbent materials (Aksu 2005; Crini 2005, 2006, 2010, 2015; Ahmaruzzaman 2008; Vijayaraghavan and Yun 2008; Crini and Badot 2010; Ali 2012; Fomina and Gadd 2014; Kyzas and Kostoglou 2014; Couto et al. 2015; Ferreira et al. 2015). Commercial materials adopted at industrial scale for potable water treatment, effluent treatment and decolorizing applications include zeolites, activated alumina, and silica gels (Crini and Lichtfouse 2018a, b; Crini et al. 2019). Other conventional materials are commercial ion-exchange resins and synthetic organic resins. Non-conventional adsorbents/sorbents include clays (e.g. bentonite), siliceous materials (e.g. perlite, alunite), waste materials from agriculture (e.g. rice

husk, biochar) or forest industries (e.g. bark, sawdust), by-products from industry (e.g. red mud, sludge), coal derived from non-conventional resources, biosorbents (e.g. peat, chitosan, alginate, cyclodextrin polymers), aquatic macrophytes, and biomass (Adriano et al. 2005; Crini 2005, 2006; Bekçi et al. 2006, 2007; Kang et al. 2010; Braga et al. 2011; Liu et al. 2012a, b; Lian et al. 2014; Xie et al. 2014; Freitas et al. 2017; Stofela et al. 2017; Portinho et al. 2017; Maia et al. 2017, 2019; de Andrade et al. 2018; de Souza et al. 2018, 2019; Osei et al. 2019; Fenyvesi et al. 2020; Macedo et al. 2020).

Which is the best adsorbent to replace activated carbon? There is no direct answer to this question because each adsorbent has advantages and drawbacks (Morin-Crini and Crini 2017; de Andrade et al. 2018). It is important to note that all non-conventional materials are basically at the laboratory stage in spite of unquestionable progress. Nevertheless, they will undoubtedly be at the centre of some extremely profitable commercial activities in the future (Morin-Crini and Crini 2017; de Andrade et al. 2018). Examples of such materials are described below.

1.4.2 Removal of Hazardous Contaminants Using Low-Cost Clay-Based Adsorbents

Clays are natural well-known minerals having layered structures with large surface area, high porosity, and high chemical and mechanical stability (Beall 2003; Crini 2006; Bhattacharyya and Gupta 2008; Crini 2010; Lofrano 2012; Gupta and Bhattacharyya 2014; Zhu et al. 2016). In addition, these materials are low-cost and abundant on most continents and they are studied as alternatives to activated carbons (Mercurio et al. 2019). Low-cost is naturally an important advantage of clays as adsorbents, e.g. the cost of montmorillonite can be up to 20 times cheaper than activated carbons (de Andrade et al. 2018). The performance of a clay material depends mainly on its chemical nature and pore structure. Clays are considered as strong candidates for ion-exchange and as host materials with a strong capacity to adsorb neutral and charged species (Bhattacharyya and Gupta 2008; Crini 2006). In general, pollutant removal efficiencies by clays are comparable or even higher than by commercial carbons. So, their use in adsorption-oriented processes for water purification and wastewater decontamination has become commonplace in industry today. The first recognition of their ability to sorb pesticides such as 2,4-dichlorophenoxyacetic acid (herbicide 2,4-D) from aqueous solutions was established in the 1970s (Beall 2003). Other practical applications of clays include purification of air, separation, sterilization and disinfection.

Currently, there is great interest in the adsorptive processes using clays that are considered promising and effective in the environmental remediation of emerging contaminants. As effective adsorbents, clays interact with recalcitrant dyes used in cosmetics (Almeida et al. 2009; Rehman et al. 2013), pharmaceuticals (Maia et al. 2017) such as antibiotics, antihypertensives, anti-inflammatory drugs, beta-blockers, and other psychoactive substances (caffeine), and pesticides (Grundgeiger et al. 2015).

Trimethoprim is an antibacterial agent commonly used in human and veterinary medicine worldwide, often prescribed to be taken in combination with a sulphonamide. This substance was detected at levels between 0.6 and 7.6 $\mu\text{g/L}$ in hospital sewage water in Sweden (Lindberg et al. 2004), at 0.16 $\mu\text{g/L}$ in wastewater effluents from Holland (Batt and Aga 2005), between 40 and 705 ng/L in municipal wastewater treatment plants in US (Renew and Huang 2004), and ranging from 0.013 to 0.15 $\mu\text{g/L}$ in US streams (Kolpin et al. 2002). Bekçi et al. (2006, 2007), studying trimethoprim adsorption onto montmorillonite, demonstrated that clay minerals were efficient to remove drugs. The performance was pH dependent and the maximum adsorption at the equilibrium was observed at pH 5.04. The modelling of adsorption results showed that the adsorption mechanism was a combination of two main interactions, i.e. physisorption and ion-exchange. Later, similar conclusions were reported by Molu and Yurdakoç (2010).

Clay minerals has been proposed by more authors to sorb antibiotics (Parolo et al. 2008; Putra et al. 2009; Wang et al. 2011; Genç et al. 2013; Roca Jalil et al. 2015; Maia et al. 2017). For example, Roca Jalil et al. (2015) demonstrated that montmorillonite was a suitable adsorbent for ciprofloxacin, an antibiotic used in human and veterinary medicine. Its presence in hospital effluents and in domestic wastewater has been reported by Karthikeyan and Meyer (2006) and by Githinji et al. (2011), respectively. The highest performances were obtained at pH values lower than 10 (Roca Jalil et al. 2015). The adsorption capacities (up to 330 mg/g) were higher than that obtained onto commercial activated carbons (112 mg/g) (Wang et al. 2011; Genç et al. 2013). However, the ciprofloxacin aqueous solubility must be taken into account in adsorption tests. The ciprofloxacin adsorption mechanisms on montmorillonite depend mainly on pH (Roca Jalil et al. 2015). The adsorption studies of antibiotics on clays have showed that the molecular structure of the pharmaceutical had a direct influence on the adsorption capacity. This can be explained by the fact that antibiotics have molecules with protonable groups, dependent of the medium pH, affecting the interactions between the antibiotic species available at each pH and the adsorption sites on the surface clay mineral. Roca Jalil et al. (2015) also showed that the adsorption mechanism was complex, due to a combination of several interactions including ion-exchange, electrostatic interactions, surface adsorption, hydrogen bonding and hydrophobic interactions, ionic interactions being the main interactions.

Different clay-based materials were evaluated by Maia et al. (2017, 2019) for the removal of amoxicillin (antibiotic), propranolol (beta-blocker) and caffeine (stimulant). The authors demonstrated that the removal efficiency depended on the drug and material used and varied between 23 and 98% for amoxicillin, 21 and 89% for caffeine, and 29 and 100% for propranolol. High adsorption capacities were also described by Vieira and collaborators (de Andrade et al. 2018; Oliveira et al. 2018, 2019) for caffeine adsorption onto bentonite. Caffeine is a natural stimulant largely consumed, recalcitrant and persistent to conventional water treatments, and continuously released into the environment. Even when present in water at low concentrations, caffeine can negatively affect the metabolism of fish, amphibians, and reptiles (Santos-Silva et al. 2018). Oliveira et al. (2018, 2019) indicated that caffeine

adsorption onto bentonite was due to a combination of physical and ion-exchange phenomena, with significant changes on the bentonite surface after adsorption. These changes were highlighted using several techniques (scanning electron microscopy, mercury porosimetry, helium pycnometry and nitrogen physisorption).

Diclofenac is a nonsteroidal anti-inflammatory drug and due to its structure, the molecule presents low biodegradability and is recalcitrant to conventional sewage treatment plants. Diclofenac is widely detected in wastewater (Radjenovic et al. 2007) and in European surface waters (Jux et al. 2002; Fernández et al. 2010). In the environment, this drug has toxic effects on bacteria, invertebrates and algae. Maia et al. (2019) studied the adsorption of diclofenac sodium onto a commercial organo-clay (Spectroge[®]) and showed that the interaction between diclofenac and the adsorbent was spontaneous and the process was endothermic. High performances were obtained in terms of abatement. A detailed characterization analysis demonstrated that adsorption takes place on the surface of the clay, without significant modifications. The authors concluded that adsorption onto Spectroge[®] is a promising alternative for the removal of pharmaceuticals (Maia et al. 2019). Other examples of adsorption of pharmaceuticals from water and wastewater using non-conventional low-cost materials can be found in a comprehensive review published by de Andrade et al. (2018).

Clay minerals were proposed to sorb pesticides (Polatti et al. 2006; Roca Jalil et al. 2013; Grundgeiger et al. 2015; de Souza et al. 2019). de Souza et al. (2019) studied adsorption of the herbicide 2,4-D from aqueous solution using an organo-modified bentonite clay. The maximum adsorption capacity for this herbicide obtained experimentally was 50.36 mg/g, found at a temperature of 298 K, being higher than other materials reported in the literature. Using a detailed thermodynamic study, the authors showed that the adsorption of 2,4-D in organophilic clays referred to a spontaneous, exothermal process of physical nature. The adsorbent can be easily regenerated when subjected to eluents such as mixtures containing fractions of ethanol/water (desorption = 95%). Another typical example is atrazine, an herbicide that has been widely used in agriculture around the World for the last 50 years. It is now banned in Europe but is still in use in other countries. The US Environmental Protection Agency has set the maximum contamination limit (MCL) for atrazine at 0.003 µg/L. Grundgeiger et al. (2015) proposed organo-beidellites for atrazine adsorption, with the main mechanism being cation exchange.

Increasing the adsorption capacity of clays is a critical objective in the environmental application of these materials for the removal of negatively charged organic contaminants and persistent non-polar and hydrophobic contaminants. Thus, thermal or chemical modifications (e.g. acid washing using HCl or H₂SO₄) have been proposed to alter the structure of clays and their physicochemical properties (Zhu et al. 2016; de Andrade et al. 2018). In general, modified materials present an enhanced porous structure, higher specific surface area, and higher surface acidity. These modifications may enhance the capacity of minerals in uptaking specific contaminants. Table 1.1 shows values for maximum drug adsorption capacity using clays treated by different methods.

Table 1.1 Maximum drug adsorption capacity by the Langmuir isotherm, Q_m (mg/g), obtained under certain experimental conditions of temperature, pH, agitation, equilibrium time and concentration of clay treated by different methods

Adsorbent	Modification	Drug	Operating conditions	Q_m	References
Commercial montmorillonite	Acid treatment	Trimethoprim	30 °C; pH 3; 150 rpm; 7 h; 4 g/L	129.51	Bekçi et al. (2006)
Commercial montmorillonite K10	Acid treatment	Trimethoprim	25 °C; 150 rpm; 6 h; 4 g/L	75.66	Bekçi et al. (2007)
Bentonite – type Verde Lodo	Calcined	Caffeine	30 °C	40.53	Oliveira et al. (2019)
Commercial montmorillonite Mizulite		Caffeine	25 °C	67.19	Shiono et al. (2017)
Exfoliated vermiculite	Thermal treatment	Gemfibrozil	20 °C; pH 7; without agitation; 72 h; 130 g/L	1.05	Dordio et al. (2016)
Lightweight expanded clay aggregates	Thermal treatment	Gemfibrozil	20 °C; pH 7; without agitation; 144 h; 1000 g/L	0.02	Dordio et al. (2016)
Exfoliated vermiculite	Thermal treatment	Mefenamic acid	20 °C; pH 7; without agitation; 72 h; 130 g/L	2.02	Dordio et al. (2016)
Lightweight expanded clay aggregates	Thermal treatment	Mefenamic acid	20 °C; pH 7; without agitation; 144 h; 1000 g/L	0.02	Dordio et al. (2016)
Exfoliated vermiculite	Thermal treatment	Naproxen	20 °C; pH 7; without agitation; 144 h; 1000 g/L	0.07	Dordio et al. (2016)
Lightweight expanded clay aggregates	Thermal treatment	Naproxen	20 °C; pH 7; without agitation; 144 h; 1000 g/L	0.02	Dordio et al. (2016)
Na-montmorillonite	<i>In natura</i>	Tetracycline	25 °C; pH 5.5; 24 h; 0.133 g/L	341.77	Liu et al. (2012a)
Na-montmorillonite	TMA ^a	Tetracycline	25 °C; pH 5.5; 24 h; 0.133 g/L	555.54	Liu et al. (2012a)
Na-montmorillonite	DDTMA ^b	Tetracycline	25 °C; pH 5.5; 24 h; 0.133 g/L	888.87	Liu et al. (2012a)
Na-montmorillonite	HDTMA ^c	Tetracycline	25 °C; pH 5.5; 24 h; 0.133 g/L	740.43	Liu et al. (2012a)

(continued)

Table 1.1 (continued)

Adsorbent	Modification	Drug	Operating conditions	Q _m	References
Bentonite	HDTMA ^c	Amoxicillin	30 °C, 120 min; pH 7; 250 rpm; 4 g/L	27.85	Zha et al. (2013)
Montmorillonite	BDTMA ^d	Diclofenac	25 °C; pH 6.5	59.8	de Oliveira et al. (2020)
Montmorillonite	HDTMA ^c	Diclofenac	25 °C; pH 6.5	54.4	de Oliveira et al. (2020)
Commercial santonite Spectroge [®] – type C	DDMA ^e	Diclofenac	30 °C; 250 rpm 24 h; 10 g/L	36.58	Maiia et al. (2019)

^aOrganophilized with tetramethylammonium

^bOrganophilized with dodecyltrimethylammonium

^cOrganophilized with hexadecyltrimethylammonium

^dOrganophilized with benzyl decyltrimethylammonium

^eOrganophilized with dialkyl dimethylammonium

To conclude, from an industrial point of view, adsorption using clays is technologically simple and economically feasible, plus this represents a process that produces high quality water. This treatment has proved to be efficient in removing emerging contaminants that are non-biodegradable or chemically stable. Research, both fundamental and applied, is currently very active concerning the development of novel classes of materials, as well as the understanding of the mechanisms of activation, adsorption and regeneration. Nevertheless, studies on the adsorption of emerging contaminants, with a focus on continuous multicomponent systems at pilot scale, as well as in-depth technical-economic feasibility and life-cycle analysis studies are still scarce in the literature, making the applicability of these adsorbents still difficult.

1.4.3 Removal of Pharmaceuticals Using Cyclodextrin Bead Polymer

Over the past two decades, much work has been done on the use of cyclodextrin polymers for the manufacture of complex emerging substances for environmental applications. These commercial polymers are becoming very popular for the tracking and removal of trace emerging substances. Conventional water treatment technologies are not very effective in reducing the concentration of these pollutants to a desirable level, prompting researchers to innovate and to propose complementary methods to conventional treatments.

Inclusion of Emerging Contaminants by Cyclodextrin Most of the pharmaceuticals interact with cyclodextrins. These special carbohydrates, produced from starch and characterized by cyclic structure with hydrophilic surface and moderately

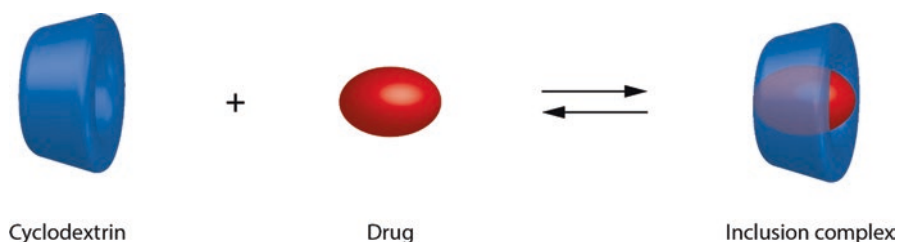


Fig. 1.4 Scheme of inclusion complex formation of cyclodextrin with a drug. (Source: Éva Fenyvesi, Budapest, Hungary; Marc Fourmentin, Dunkerque, France)

hydrophobic inner cavity, are able to include other compounds in their cavity. Since their discovery at the end of the nineteenth century in France, a great body of knowledge has been collected on the effect and mechanism of binding various organics also numerous pharmaceuticals among them (Crini 2014). Within the cavity of cyclodextrins, the water molecules are readily replaced by less hydrophilic guest compounds such as drugs of low water solubility (Fig. 1.4). In this way, inclusion complexes or clathrates are formed without creating or disrupting covalent bonds. The host cyclodextrin and the guest are reversibly connected by hydrophobic interactions, van der Waals forces, etc. therefore the complex can dissociate when the conditions change, e.g. upon dilution, heating or in the presence of other competing guests (Szejtli 1998; Crini et al. 2018). The stability of the inclusion complexes can be enhanced by hydrogen bonds between the hydroxyl groups on outer surface of cyclodextrin and the hydrophilic part of the guest protruding from the cavity. The most important consequences of the inclusion complex formation, such as enhancing the solubility of poorly soluble substances, protecting the included guest molecules against the environmental effects such as oxidation, hydrolysis, decomposition on heat and light, enzymatic degradation, and improving the taste, are utilized broadly by the pharmaceutical industry (Frömming and Szejtli 1994; Loftsson et al. 2005; Szejtli and Szente 2005; Uekama et al. 2006). The number of active ingredients marketed in the form of cyclodextrin complexes is above 80 at the beginning of 2020 and is continuously increasing (CycloLab 2020). Among the three natural cyclodextrins, α -cyclodextrin, β -cyclodextrin and γ -cyclodextrin consisting of 6, 7 and 8 glucopyranose units, respectively, β -cyclodextrin possesses a cavity size with an internal diameter of 0.60–0.65 nm and a depth of 0.78 nm especially suitable for inclusion of a wide range of drug molecules (Szejtli 1998). While the unmodified β -cyclodextrin is used mostly as excipient in pharmaceutical formulations for oral administration, its highly soluble hydroxypropylated and sulfobutylated derivatives have also been approved for parenteral applications (EMA 2017).

Cyclodextrin Bead Polymers While the pharmaceutical industry aims to improve the solubility and consequently the bioavailability of drugs *via* complexation, the objective in wastewater purification is the opposite: to remove the dissolved non-biodegradable pharmaceuticals by sorption/biosorption (both terms are used in the

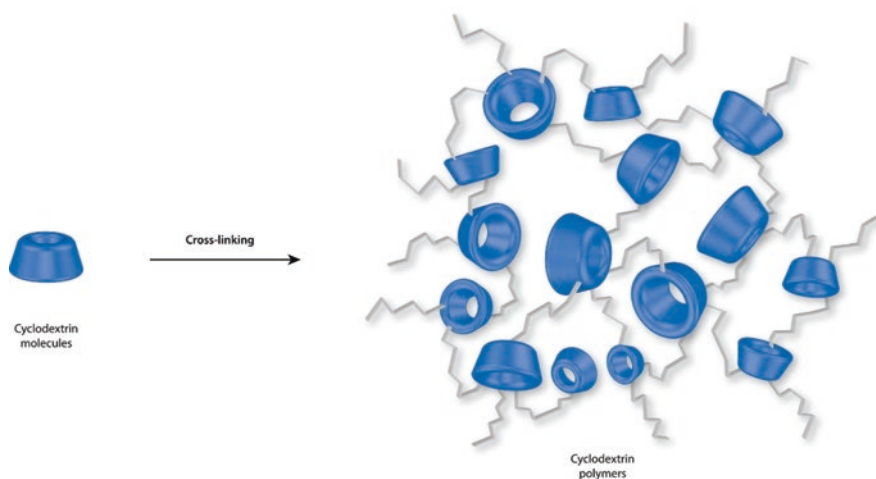


Fig. 1.5 Structure of a cyclodextrin polymer obtained by a cross-linking reaction between cyclodextrin molecules and a cross-linking agent. (Source: Marc Fourmentin, Dunkerque, France; Éva Fenyvesi, Budapest, Hungary; Grégorio Crini, Besançon, France)

literature). As natural cyclodextrins are water-soluble, they must be transformed into water-insoluble sorbents/biosorbents, using three main synthesis routes:

1. by cross-linking with proper bi- or polyfunctional reagents, such as diepoxy compounds, diisocyanates, di- or polycarboxylic acids, fluoroterphthalonitriles, etc. (Wiedenhof et al. 1969; Crini et al. 1998; Yamasaki et al. 2008; Zhao et al. 2009; Alsaiee et al. 2016; Xu et al. 2019; Yang et al. 2020); Fig. 1.5 shows a cyclodextrin polymer obtained by a cross-linking reaction between cyclodextrin molecules and a cross-linking agent;
2. by copolymerization of polymerizable cyclodextrin derivatives with acrylic or vinyl monomers (Wimmer et al. 1992; Janus et al. 1999; He et al. 2012);
3. or by grafting on a macromolecular support such as chitosan, cellulose, alginate and silica (Crini et al. 1995; Sakairi et al. 1999; Aoki et al. 2007; Chung and Chen 2009; Kono et al. 2013; Omtvedt et al. 2019; Yamasaki et al. 2017).

All these gels are preferably prepared in the form of tiny beads by emulsion/suspension polymerization. The spherical shape of the particles has the advantage of high surface area and good accessibility of the cyclodextrin cavities in addition to the technological advantages in scaled up production. Owing to the several hydroxyl groups on cyclodextrins, these gels are highly hydrophilic and swell in water. The degree of swelling depends on the conditions of preparation, e.g. type, concentration and ratio of reactants, temperature, reaction time, etc. (Wiedenhof et al. 1969; Fenyvesi et al. 1979; Romo et al. 2006). The higher the degree of swelling the higher is the accessibility of the inner cyclodextrin cavities but the smaller the mechanical stability against compression. The binding capacity of epichlorohydrin-cross-linked β -cyclodextrin polymer beads is higher in case of

lower degree of cross-linking and reduced temperature (Zhu et al. 1997; Baille et al. 2000). In case of ionic or ionizable pharmaceuticals cyclodextrin polymers modified by ionic groups can be more efficient biosorbents due to the contribution of electrostatic forces to hydrophobic interactions. Depending on the conditions the binding mechanism can be complicated including inclusion and association complex formation, electrostatic interactions, ion exchange, chelation, etc. (Crini et al. 2016; Morin-Crini et al. 2018). Both the π - π interactions with the network and host-guest interactions with the cyclodextrin cavities may contribute to the uptake (Huang et al. 2020).

Removal of Emerging contaminants by Cyclodextrin Bead Polymer Using Biosorption-Oriented Processes Cyclodextrins and their polymers have been found useful for various environmental applications including wastewater treatment (Crini and Morcellet 2002; Gruiz et al. 2011; Landy et al. 2012; Morin-Crini and Crini 2013; Morin-Crini et al. 2018; Fenyvesi et al. 2019). The early sorption/biosorption experiments with cyclodextrin polymer beads aimed at the removal of various organic contaminants such as phenols and dyes. Although these beads usually outperformed activated carbon, it became clear that cyclodextrin polymer beads are too expensive for the removal of compounds present at high concentration. Due to their specific affinity toward drugs (Fenyvesi et al. 1996; Vyas et al. 2008; Mocanu et al. 2009), they found their application for the sorption of non-biodegradable emerging contaminants, such as pharmaceuticals, which survive the traditional wastewater treatment and are usually detected in purified wastewater at very low concentrations.

The epichlorohydrin-cross-linked cyclodextrin polymers successfully removed hormones and other endocrine disrupting chemicals at nanomolar concentrations (Oishi and Moriuchi 2010). High removal rate (70% to >90%) was achieved for 17- β -estradiol, a contraceptive of emerging concern, in the range of 1×10^{-11} to 1×10^{-8} mol/L concentration by using β -cyclodextrin polymer. Similar performance was observed for polymers prepared from γ -cyclodextrin and α -cyclodextrin. The removal ratio was hardly reduced when in addition to 17- β -estradiol the model solution was spiked also with cholesterol in 100-fold molar excess related to the hormone because cholesterol, another steroid typical in wastewaters but with no endocrine disrupting properties, has lower binding affinity to the cyclodextrin cavity. The small scale laboratory batch experiments with real municipal wastewater validated these results. It was recently published that carbonyldiimidazol-cross-linked β -cyclodextrin and γ -cyclodextrin polymer nanosponges efficiently removed the antipsychotic drug pimavanserin from single solutions (93% and 80% removal rates, respectively) and from postreaction raffinates in small scale batch experiments (0.1 g sorbent in 5 mL solution) (Hemine et al. 2020).

The low mechanical strength of the gel beads does not allow the use of column technique in large scale. The higher swelling, e.g. lower degree of cross-linking, results in lower permeability, and thus lower elution rate of water through the gel bed is attained. Therefore fluidization technique was used in up-scaled demonstration of the technology. Another option is applying inorganic core such as silica or

graphene oxide to get beads of high mechanical stability or introduction of rigid structures such as phenyl moieties into the polymer to form pores. For instance, silica coated with β -cyclodextrin using hexamethyl diisocyanate as cross-linking agent was used for the removal of emerging contaminants, also estrogen hormones among them from water (Bhattarai et al. 2012). More than 95% of 17- β -estradiol was removed from single component solution and more than 90% of most of the estrogens in multicomponent system even after 4 regeneration cycles. Also magnetic graphene oxide modified with β -cyclodextrin/poly(L-glutamic acid) showed excellent binding capacity for 17- β -estradiol (Jiang et al. 2016): the sorption capacity was 85 mg/g sorbent at 0.05 g/L sorbent to solution ratio and 25 °C using a model solution of $\sim 7 \times 10^{-7}$ mol 17- β -estradiol concentration. Single component solutions were eluted through a thin layer of β -cyclodextrin polymer with permanent porosity (cross-linked with tetrafluoroterephthalonitrile) to remove around 80% of ethinylestradiol and propranolol as model drugs at 1×10^{-4} mol/L concentration (Aisbaiee et al. 2016). In another study, a solution (8 mL) of 90 pollutants was eluted through the same porous β -cyclodextrin polymer (1 or 5 mg) to achieve nearly complete (over 95%) removal of several drugs including abacavir, amphetamine, cimetidine, codein, diclofenac, estrone, famotidine, fluoxetine, gemfibrozil, ibuprofen, testosterone, triclosan to mention only a few and several pesticides (Ling et al. 2017). Figure 1.6 illustrates the diclofenac biosorption onto a cyclodextrin polymer. More recently, using the same cross-linking agent, the polymer (100 mg) obtained removed over 95% of both ethinylestradiol and estriol ($\sim 1 \times 10^{-7}$ mol/L, 1 L) by filtration from a multicomponent model solution containing other emerging contaminants, too (Xu et al. 2019). A further possibility for preparing filters of good mechanical stability is sintering cyclodextrin polymer gel beads with a thermoplastic polymer such as polyethylene (Jurecska et al. 2014). This process, however, results in reduced binding capacity.

In laboratory experiments modeling post-purification of wastewater by fluidization technology, epichlorohydrin-cross-linked β -cyclodextrin polymer beads (20 g) were used to remove hormones, such as β -estradiol, ethinylestradiol and estriol

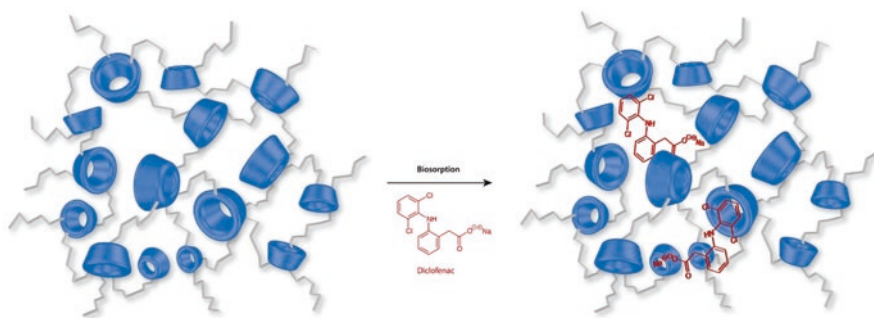


Fig. 1.6 Schematic illustration of the diclofenac sorption onto a cyclodextrin polymer. (Source: Marc Fourmentin, Dunkerque, France; Éva Fenyvesi, Budapest, Hungary; Grégorio Crini, Besançon, France)

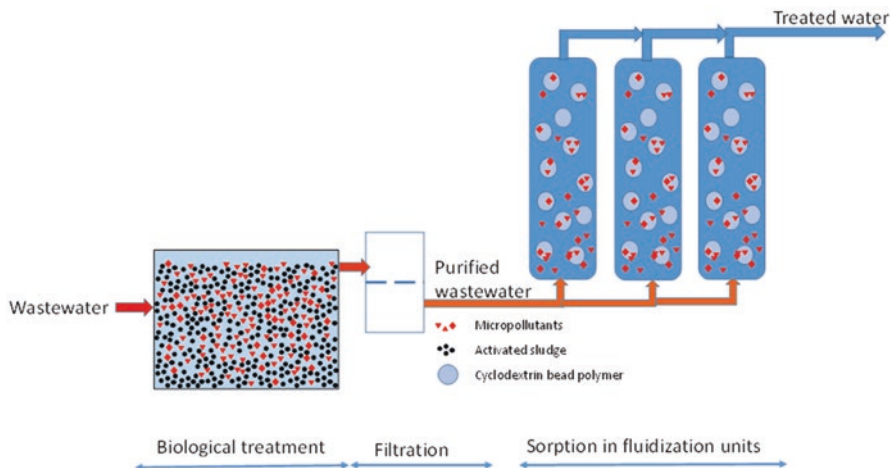


Fig. 1.7 Flow chart of wastewater purification technology applying cyclodextrin polymer beads for sorption of the emerging pollutants and micropollutants such as residual pharmaceuticals. (Source: Éva Fenyvesi, Budapest, Hungary)

(87–99%) from the spiked test solution (800 mL) containing some other emerging contaminants, too. The removal rate for the non-steroidal anti-inflammatory drugs was in the range of 15–70% (Nagy et al. 2014). Based on the positive results of this experiment, a scaled-up fluidization procedure was planned and performed in a pilot-scale wastewater purification plant (Fig. 1.7). β -Cyclodextrin polymer beads (1 kg) were applied to polish 300 L purified municipal wastewater spiked with 9 emerging pollutants at approximately 2×10^{-8} mol/L concentration (among others also drugs, e.g. diclofenac and 17- β -estradiol included in the watch list of substances for Union-wide monitoring in the field of water policy (European Water Framework Directive 2015/495/EU) (Fenyvesi et al. 2020). The hormones such as estradiol (>99.9%), ethinylestradiol (99.9%) and estriol (96.1%) were effectively removed. The removal rate for the non-steroidal anti-inflammatory drugs diclofenac, ibuprofen, ketoprofen and naproxen were 85.5, 86.9, 18.1 and 13.5%, respectively, following roughly the cyclodextrin-drug association constants showing that the main interaction was likely the inclusion complex formation. It should be noted that similarly low removal rate (18%) was obtained by Orprecio and Evans (2003) for naproxen applied at 5×10^{-6} mol/L concentration in single component solution (5 L) using similar epichlorohydrin-cross-linked β -cyclodextrin polymer (10 g) as column packing. The pilot-scale demonstration of the fluidization technology with the β -cyclodextrin polymer beads was successful, most of the pharmaceuticals as emerging contaminants, especially those on the European watch list, were efficiently removed in a short time. The beads are easily regenerated by extracting the sorbed components with methanol or ethanol (Orprecio and Evans 2003; Jurecska et al. 2014; Fenyvesi et al. 2020; Hemine et al. 2020). The recovery of valuable drugs from industrial effluents is also conceivable after regeneration of the cyclodextrin polymer sorbent (Hemine et al. 2020).

For the full scale application of the cyclodextrin-based biosorbents in wastewater treatment the first step is the scaled up production of these polymers. All the examples overviewed in this section used sorbents/biosorbents prepared in laboratory except the epichlorohydrin-cross-linked β -cyclodextrin polymer beads produced on pilot-plant scale. Several research groups are working on development of economic and environmental-friendly technologies for scaling up. The tetrafluoroterephthalonitrile-cross-linked Dextorb[®] adsorbents of Cyclopure Company, which can quickly and safely remove from water hundreds of pollutants including drugs, pesticides and short and long chain polyfluorinated alkyl substances, are probably close to the industrial production (Cyclopure 2020).

All of these studies show that cyclodextrin polymers are a promising alternative in the treatment of wastewater containing a cocktail of emerging trace substances. Industrialists will now have to be convinced to use these materials in their municipal wastewater treatment plants.

1.4.4 Metal-Organic Frameworks for the Removal of Emerging Contaminants

In recent years, metal-organic frameworks have attracted attention as promising materials for the removal of emerging contaminants in effluents by adsorption-oriented and catalytic degradation processes (Dias and Petit 2015; de Andrade et al. 2018; Mon et al. 2018; Bedia et al. 2019; Li et al. 2019b; Dhaka et al. 2019; Rojas and Horcajada 2020). Metal-organic frameworks are a kind of crystalline materials with permanent porosity (more than 50% of their crystal volume) formed by the self-assembly of metal ions or their aggregates/clusters linked together by multi-functional organic ligands. They consist of small organic molecules, usually C6-rings, which are connected by metal clusters as a three-dimensional structure. Like cyclodextrin molecules, metal-organic frameworks have cavities where specific host-guest interactions can take place. These active sites can adsorb and degrade pollutants. In addition to superhigh pore volume, metal-organic frameworks also have values of surface area (1000–10,000 m²/g) superior to those of conventional materials such as carbons. They have also physicochemical properties easily tuned. Reviews by Dias and Petit (2015) and Bedia et al. (2019) describe the different methodologies that can be used for the synthesis of metal-organic frameworks, paying attention to the purification and activation steps.

A typical example of a metal-organic framework is chromium terephthalate MIL-101 (Matériel Institut Lavoisier). It is a polymer built from trimeric chromium (III) triangular cluster complexes, bridged by linear terephthalate linkers. The material has a highly porous three-dimensional structure with large pores (>30 Å), high surface area (>3000 m²/g) and a huge cell volume (702,000 Å³).

Because of their distinctive characteristics, metal-organic frameworks are very useful in chemistry and supramolecular chemistry (gas separation, adsorbent for

carbon capture, hydrogen for energy storage), nanotechnology (electrocatalysis, photocatalysis, biocatalysis), materials science, drug delivery systems, biomedical imaging, sensing, fuel cells, and water and wastewater treatment (adsorption, semiconductor photocatalysis). They have many properties for the removal of pollutants that recommend them in water treatment. Indeed, metallo-organic frames have not only a high pore volume, large surface area and adjustable pore size, but also multiple topologies, hierarchical structure, adjustable surface chemistry (easily functionalized cavities), and high adsorption capacity (de Andrade et al. 2018; Rojas and Horcajada 2020). Their recyclability also gives metal-organic frameworks an advantage over conventional adsorbents. Metallo-organic frames can be synthesized on a large scale and are versatile materials as they can be shaped into monoliths, pellets, membranes or beads for columns, suitable for decontamination devices. An important challenge for using metal-organic frameworks as adsorbents in their stability in contact with water (de Andrade et al. 2018).

Metal-organic frameworks can be used as adsorbent of pollutants or as platform for pollutant degradation through catalytic processes. This research is recent as the first work on metal-organic framework for dye removal and the first metal-organic framework used in the catalytic degradation of phenol were reported in 2010 by Haque et al. (2010) and in 2007 by Alvaro et al. (2007), respectively. In water and wastewater treatment, metal-organic frameworks have proven to be excellent adsorbents for the removal of harmful species such as pharmaceuticals and personal care products, artificial sweeteners and feed additives, agricultural products, organic dyes, BTEX compounds, pesticides, and industrial products such as alkylphenols, products of the photographic industry and plasticizers (Rojas and Horcajada 2020). Their performance is better than that of other adsorbents, especially activated carbons. However, their performance and selectivity with respect to the pollutants targeted for disposal must be regulated by judicious selection of the metal ion and organic linker. Numerous examples of applications in the field of water and wastewater treatment are presented and discussed in the following references: Dias and Petit (2015), de Andrade et al. (2018), Mon et al. (2018), Bedia et al. (2019), Li et al. (2019b), Dhaka et al. (2019), and Rojas and Horcajada (2020).

The extensive data in the literature show that metal-organic frameworks, as a new class of porous materials, have a great potential for water purification by (selective) adsorption and catalytic degradation (photocatalysis) and could also find applications in other advanced oxidation processes (photo-Fenton, electro-Fenton), in soil remediation or in membrane filtration. This is a research topic in full development, particularly in the context of nanotechnologies, but it is still in its early stages and requires a thorough assessment of parameters such as safety, lifetime, reusability and industrial conditions. In addition, the low stability of metal-organic frameworks in water is still a major challenge for their environmental application in industry (Rojas and Horcajada 2020). For a real application and compared to traditional semiconductors such as TiO_2 , two other aspects need to be improved. Firstly, the synthesis conditions must allow larger quantities of material to be obtained in continuous operation. Current processes, such as solvothermal methods, are limited by the slowness of the reactions, and have a relatively high cost (Li et al. 2019b).

Second, research is also needed on their potential toxicity and possible health effects. Indeed, many metal-organic frameworks are constructed from toxic metals, e.g. Cd, Cr, Ag and Co, and some molecules such as the dyes used are also considered as emerging contaminants.

1.4.5 Application of Molecularly Imprinted Polymers for Removal of Emerging Contaminants

Over the past decade, several studies have reported innovative results on molecularly imprinted polymers and non-imprinted polymers for the removal of personal care products, pharmaceuticals, and endocrine disrupting compounds, in industrial effluents, surface waters, and drinking water (Murray and Örmeci 2012; Shen et al. 2013; Huang et al. 2015; Chen et al. 2016a). The molecular imprinting technique is an emerging technology in which the synthesis of a material is performed in the presence of a template molecule. Subsequent removal of the template provides a material with “memory” sites capable of selectively recognizing and re-binding to the original template of a mixture (Alexander et al. 2006; Chen et al. 2016a; Cantarella et al. 2017; BelBruno 2019).

Molecularly imprinted polymers are prepared from cross-linked polymers containing cavities specific to a target analyte. These cavities are created by the copolymerization of cross-linking monomers and functional monomers with an imprinting molecule or template. After polymerization, the template is removed, leaving a cavity specific to the analyte. The molecularly imprinted polymer then selectively re-binds to the compound to be treated (Alexander et al. 2006; BelBruno 2019). The main advantages of the molecularly imprinted polymers are the ease of preparation and the ability to create “tailor-made” binding sites simply by adapting the synthesis procedure for the desired target molecule used as a template during polymerization (Huang et al. 2015; Cantarella et al. 2019). Molecularly imprinted polymers have traditionally been used as solid-phase extraction media for analytical chemistry, e.g. for pre-concentration and selective removal of substances (Chen et al. 2016a; BelBruno 2019).

Non-imprinted polymers are cross-linked polymeric materials that have macropores containing adsorption sites for organic molecules. They are synthesized using the same procedure as molecularly imprinted polymers, but in the absence of a template. They therefore have the same chemical properties as molecularly imprinted polymers but do not contain specific cavities (Murray and Örmeci 2012). Non-imprinted polymers exhibit strong hydrophobic interactions (non-specific binding) between organic pollutants and polymers. The main difference between molecularly imprinted polymers and non-imprinted polymers is their specificity. Molecularly imprinted polymers can selectively remove a target substance such as 17- β -estradiol from biological wastewater, whereas non-imprinted polymers can remove several substances simultaneously. Molecularly imprinted polymers are also generally

more porous, having a greater surface area, which may also explain the higher binding efficiency of molecularly imprinted polymers. However, while the specificity of molecularly imprinted polymers is an advantage for solid-phase extraction application, the same may not be true for complex wastewater (BelBruno 2019).

Molecularly imprinted polymers offer promising applications for water and wastewater treatment. They are advantageous for treatment of trace contaminants as they can be specifically designed to remove one or a group of target compounds (Alexander et al. 2006). This is an advantage over nonspecific technologies such as activated carbon (Pichon and Chapuis-Hugon 2008; Murray and Örmeci 2012). Molecularly imprinted polymers have been studied for their ability to remove, degrade and destroy, in combination with other technologies (advanced oxidation processes), emerging substances such as hormones (Le Noir et al. 2007; Zhongbo and Hu 2008; Chen et al. 2015), pharmaceuticals (Pichon and Chapuis-Hugon 2008; Madikizela et al. 2018; BelBruno 2019; Cantarella et al. 2019), endocrine disruptors (Fernández-Alvarez et al. 2009), personal care products (Alsudir et al. 2012) and pesticides (Murray and Örmeci 2012).

Le Noir et al. (2007), investigating the percolation of wastewater containing 17- β -estradiol through solid-phase extraction columns prepared with molecularly imprinted polymers (flow rate of 50 mL/min), demonstrated that these materials were capable to eliminate the equivalent of 22 ± 4 ng of 17- β -estradiol per L of effluent. The authors also showed that the use of molecularly imprinted polymers allows easy regeneration for subsequent reuse, yielding the same efficiency and reducing overall treatment costs. In another work, the same authors developed a method for regenerating molecularly imprinted polymer with a template of 17- β -estradiol using solvent extraction under ultraviolet light (Fernández-Alvarez et al. 2009). This method was able to regenerate and reuse both the polymeric material and the solvent, as well as the destruction of 17- β -estradiol. For that, acetone was used as a solvent under both ultraviolet-C and ultraviolet-visible light. After a 10-hour cycle, the molecularly imprinted polymer was completely regenerated and the acetone no longer contained residual 17- β -estradiol.

Cantarella et al. (2019) studied the adsorption of diclofenac to molecularly imprinted polymers synthesized by a simple and inexpensive bulk polymerization reaction. The authors also reported that materials can be regenerated and reused by simply washing with a 3 mL methanol/acetic acid solution in 2 min. The performance remained the same after at least four adsorption/regeneration cycles. Molecularly imprinted polymers showed exceptional adsorption capacity for the adsorption of diclofenac and the process was highly selective. In 10 min, 5 mg of molecularly imprinted polymer removed $\sim 90\%$ of diclofenac from an aqueous solution at a concentration of 1×10^{-4} mol/L, while only 8% was removed by the corresponding non-imprinted polymer. The adsorption capacity was 110 $\mu\text{mol/g}$ and 13 $\mu\text{mol/g}$ for the molecularly imprinted polymer and the non-imprinted polymer, respectively. Due to their easy and inexpensive synthesis, high efficiency and selectivity, easy regeneration and reusability, the authors concluded that the technology could be used on a large scale for water treatment.

The use of molecularly imprinted polymers and non-imprinted polymers for the removal of emerging contaminants using adsorption-based or solid-phase extraction processes is a novel approach that has potential in the field of water engineering (BelBruno 2019). Polymers, particularly non-imprinted polymers, are inexpensive to manufacture and can be produced in large quantities (Alexander et al. 2006). After use, the materials can be easily regenerated and reused several times. However, further research is needed to determine how best to integrate this technology into treatment plants. In addition, their potential toxicity and possible health effects are subject to discussion (Murray and Örmeci 2012).

1.4.6 Adsorption of Emerging Contaminants onto Chitosan-Based Materials

Like cyclodextrin polymers, chitosan-based materials have great potential in environmental applications, mainly for metal chelation and dye removal (Crini and Lichtfouse 2018a, b). Chitosan is a biopolymer derived from chitin. This aminopolysaccharide is capable of interacting and adsorbing a wide range of pollutants such as metals, dyes, organics and also emerging substances. In water and wastewater treatment, chitosan represents an alternative as an ecological complexing agent due to its low cost (chitin comes from shellfish wastes), its intrinsic characteristics (renewable, non-toxic and biodegradable resource, hydrophilicity) and its chemical properties (polyelectrolyte at acidic pH, high reactivity, coagulation, flocculation and biosorption properties) resulting from the presence of reactive hydroxyl and especially amine groups in the macromolecular chains. Its use in water treatment is justified by two other important advantages: firstly, its exceptional pollutant binding capacities and excellent selectivity, and secondly, its versatility (Crini and Lichtfouse 2018a, b; Morin-Crini et al. 2019). Chitosan-based materials can be used in solid form for the removal of pollutant from water and wastewater by filtration or adsorption processes or in liquid state, i.e. dissolved in acidic media, for applications in coagulation, flocculation, and membrane filtration technologies (polymer assisted ultrafiltration). Among the proposed materials, cross-linked chitosan hydrogels deserve particular attention (Morin-Crini et al. 2019).

Chitosan-based materials have been investigated for the removal of emerging substances such as perfluorooctane sulfonate (Zhang et al. 2011), bisphenol A (Dehghani et al. 2016; Zhou et al. 2019), amoxicillin (Adriano et al. 2005), sulfamethoxazole (Qin et al. 2015; Zhou et al. 2019), ciprofloxacin (Afzal et al. 2018), diclofenac (Rizzi et al. 2019), ketoprofen (Rizzi et al. 2019), and caffeine (Sanford et al. 2012). For example, Adriano et al. (2005) studied the adsorption of amoxicillin on chitosan beads. Amoxicillin ((2S, 5R, 6R)-6-[[[(2R)-2-amino-2-(4-hydroxyphenyl)acetyl]amino]-3,3-dimethyl-7-oxo-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxylic acid) is an antibiotic that belongs to the beta-lactams groups. It is one of the most important commercial antibiotics due to its high bacterial resistance and

large spectrum against a wide variety of microorganisms. More than 80% of orally administered amoxicillin in humans is excreted in the urine after 2 h of consumption. In conventional wastewater treatment systems, it is a difficult substance to eliminate due to its structure and amphoteric properties resulting from the presence of carboxylic ($pK_a = 2.68$), amine ($pK_a = 7.49$) and hydroxyl ($pK_a = 9.63$) groups (Anastopoulos et al. 2020). Its charge changes gradually with pH, due to the different functional groups. The pH of wastewater affects not only the ionization of the molecules, but also the surface charge of the materials used as adsorbents for their removal. Adsorption results described by Adriano et al. (2005) showed that 0.5 g of cross-linked chitosan were capable of removing amoxicillin from a 2 mL solution at concentrations ranging from 0.2 to 3 mg/L at $pH = 6.5$, with performances being concentration-dependent. The authors reported a maximum adsorption capacity of 8.71 ± 0.6 mg/g (equilibrium time 2 h). The adsorption mechanism was due to strong interactions between the carboxylic, amine and hydroxyl of the amoxicillin molecule and those of chitosan.

From literature data, there is no doubt that chitosan-based hydrogels have high adsorption capacities. However, these materials are at the laboratory stage and pilot studies need to be conducted. Although various laboratories and a few companies can synthesize chitosan-materials to order, it is very difficult to find commercial sources of cross-linked hydrogels with guaranteed reproducible properties. However, the performance can vary depending on the conditions and the method the hydrogels are prepared. Despite an abundance of literature reports on industrial wastewaters, there is still little information available detailing comprehensive comparing various conventional commercial adsorbents under similar conditions. Like other non-conventional materials, further research is needed to determine how best to integrate this technology into treatment plants.

1.4.7 Nanocellulose as a Novel Adsorbent for Environmental Remediation

Nanocelluloses are innovative materials with at least one dimension at the nanoscale that are attracting increasing interest in the field of nanotechnology and materials science. These materials are highly ordered β -(1 \rightarrow 4) glucan chains that are produced naturally or by chemical processes. Nanocelluloses are mainly obtained from naturally occurring cellulose sources. Indeed, they can be obtained from biomass, plants or bacteria, using fairly simple, scalable and effective isolation techniques. Most nanocellulose is produced from lignocellulose. The term “nanocellulose” encompasses a number of cellulose-based materials, whose chemical and physical properties generally vary depending on their source and method of extraction: cellulose nanocrystals, nanofibrillated celluloses, and rigid bacterial nanocellulose (Moon et al. 2011; Lam et al. 2012).

Pure nanocellulose is non-toxic, biodegradable and biocompatible. In addition, it has other advantages such as low cost, abundance, practically renewable, intrinsic properties (large surface area) and high reactivity (easy to modify), making it sustainable material for several applications including electronics, optoelectronics and engineering, paper industry, composites, antibacterial coatings, food packaging, cosmetics and personal hygiene products, medical applications (tissue scaffolds, drug delivery), bio-imaging, biosensors, enzyme immobilization, catalysis and energy storage and production (Putro et al. 2017; Thomas et al. 2018).

Nanocellulose in its various forms (cellulose nanocrystals, cellulose nanofibrils, bacterial cellulose) is also promising material for environmental applications such as water treatment (Lam et al. 2012; Herrera-Morales et al. 2017, 2019; Mahfoudhi and Boufi 2017; Putro et al. 2017; Voisin et al. 2017; Abouzeid et al. 2018; Abujaber et al. 2018; Mohammed et al. 2018; Shak et al. 2018; Wang 2019), air filtration (Nemoto et al. 2015), membrane filtration (Cruz-Tato et al. 2017; Abouzeid et al. 2018; Shak et al. 2018; Mautner 2020), flocculation (Shak et al. 2018) and catalytic degradation (Mahfoudhi and Boufi 2017; Thomas et al. 2018; Shak et al. 2018). Nanocelluloses have been used for the removal of metals, dyes, nitrates, organics and microbes from aqueous solution by filtration-, adsorption- or membrane-oriented processes. However, for industrial applications, native nanocelluloses have a low adsorption capacity due to their hydrophilic crystal structure. Therefore, it is necessary to incorporate functionalities by chemical modification of the cellulose primary hydroxyl groups to have suitable materials and composites suitable for hydrophobic contaminants. This functionalization is also necessary to increase the selectivity and affinity of the substances. Hokkanen et al. (2013) and Yu et al. (2013) reported that modification using succinic anhydride and sodium bicarbonate can increase adsorption to nanocellulose up to tenfold. Shak et al. (2018) reviewed the different strategies for the preparation of nanocellulose for applications in wastewater treatment. An important feature for an application in the water domain is the fact that nanocellulose materials are easily regenerated and reusable.

Numerous studies have shown that nanocellulose-based materials are among the most promising green adsorbents, and comprehensive reviews have recently been published (Mahfoudhi and Boufi 2017; Putro et al. 2017; Voisin et al. 2017; Abouzeid et al. 2018; Mohammed et al. 2018; Shak et al. 2018; Wang 2019; Mautner 2020). Herrera-Morales et al. (2017, 2019) demonstrated that modified nanocelluloses were capable of effectively adsorbing pharmaceuticals such as sulfamethoxazole and acetaminophen (paracetamol). Abujaber et al. (2018) proposed magnetic cellulose nanoparticles electrostatically modified with ionic liquids to adsorb pharmaceuticals (paracetamol, ibuprofen, naproxen and diclofenac) in less than 30 min with extraction recoveries of 86%–16%. Although many studies have been published with promising results, nanocelluloses, and more generally nanomaterials, are still at the laboratory study stage (Shak et al. 2018).

1.5 Biological-Based Technologies for the Degradation and Elimination of Emerging Contaminants

The biological treatment approach, specifically the activated sludge process, is the most commonly used wastewater treatment technology. While it was originally designed to only remove organic carbon, it was subsequently extended to remove nitrogen and phosphorous. Conventional biological-based technologies are not capable of degrading the wide range of organic pollutants present in complex wastewater. These systems have been adapted and different strategies have been studied, including water pre-treatment, the implementation of complementary methods based on potabilization techniques such as ozonation and carbon adsorption, or pilot studies such as membrane filtration. These latter techniques, reserved for very specific water treatment, are already used in industry, but their cost is a brake on their development. Other techniques such as constructed wetlands, algal-based technologies and enzymatic degradation, and bioreactors are being developed.

1.5.1 Constructed Wetlands for the Removal of Emerging Contaminants

Constructed wetlands are engineered systems based on the exploitation of plants for water remediation. These phytodepuration systems can be categorized according to the operational parameters, such as the type of flow (e.g. horizontal vs vertical, free water vs sub-surface), the hydraulic regime and the plant species. In every case, constructed wetlands take advantage of the numerous depuration processes that occur at the interface between the root system and the wastewater under treatment. These physical, chemical and biological processes are the same that may occur in natural wetlands and include adsorption on soil/sediment, volatilization, uptake and degradation (Gorito et al. 2017). Constructed Wetlands are an environmental friendly, low-cost and easy to maintain technology suitable to remove total suspended solids, ammonia, phosphorous, and to reduce the chemical oxygen demand and biological oxygen demand. Thus, they are regarded as an interesting opportunity for wastewater treatment in developing countries (Mahmood et al. 2013) and for decentralized systems treating sewage produced by small communities (Zraunig et al. 2019). An increasing number of studies investigated the possible use of constructed wetlands for the removal of emerging organic contaminants including antibiotics and antibiotic resistance genes (Chen et al. 2016b; Huang et al. 2019), other pharmaceuticals and endocrine disruptors like bisphenol A (Syranidou et al. 2017; Meneghetti Campos et al. 2019) and synthetic dyes (Riva et al. 2019), highlighting the promising potential of phytodepuration also as tertiary treatment downstream conventional wastewater treatment plants that are not specifically designed to remove these types of contaminants, often present in wastewater treatment plant effluents (Castiglioni et al. 2006).

The contaminant removal in constructed wetlands is due to the synergistic effect played by plant roots and their associated microbiome. The plant root system is an environmental niche that offer favorable conditions to microorganisms, which are specifically recruited through the release of root exudates and can help the plants to cope with adverse conditions (Vandenkoornhuyse et al. 2015), like the toxicity of emerging contaminants present in wastewaters (Riva et al. 2020). Moreover, microorganisms can play a direct role in contaminant degradation. Constructed wetlands can be designed using single or mixed plant species, selected among the most applied genera like *Typha*, *Phragmites*, *Iris* and *Juncus*. Interestingly, a constructed wetland co-cultivating the halophytes *Tamarix parviflora*, *Juncus acutus*, *Sarcocornia perrenis*, and *Limoniastrum monopetalum*, proved to efficiently decrease organic matter and pathogen concentration in the effluent (Fountoulakis et al. 2017). This result assumes a relevance for the bioremediation of wastewater produced by aquaculture, an anthropic activity of increasing environmental impact, also due to the intensive use of antibiotics. Constructed wetlands containing *Iris pseudacorus* and *Phragmites australis*, planted as single or mixed, were able to remove antibiotics and antibiotic resistance genes, with different removal efficiencies according to the planting pattern and the target molecule. The tested plants showed the best removal performances in single species constructed wetlands. *I. pseudacorus* removed up to 77.64%, 68.70%, and 58.21% of enrofloxacin, sulfamethoxazole, and total antibiotic resistance genes, while *P. australis* showed removal efficiencies of 81.11%, 64.94%, and 56.26% for the same molecules and antibiotic resistance genes (Huang et al. 2019). Zhang et al. (2016b) setup a laboratory scale study under simplified conditions (i.e. hydroponic culture, artificially spiked wastewater) using different constructed wetland plant genera (i.e. *Typha*, *Phragmites*, *Iris* and *Juncus*) to investigate their remediation capacity towards two pharmaceuticals (ibuprofen and iohexol) characterized by different recalcitrance. Both ibuprofen and iohexol were uptaken by roots and partially translocated in the plant aerial portion, with diverse efficiencies depending upon the plant species and the considered molecule (Zhang et al. 2016b). Moreover, the experiment showed that ibuprofen was almost completely metabolized in the microcosms, and the degradation of iohexol could reach up to 80% of the initial amount using *P. australis*. The removal of ibuprofen and iohexol was due to both plant and microbe metabolisms, and the authors suggested a role of root exudates in the promotion of pharmaceuticals degradation, a well-known mechanism exploited for rhizoremediation of persistent contaminants in soil (Vergani et al. 2017). In a microcosm scale study using also *P. australis* in a vertical subsurface flow constructed wetland, high removal efficiencies were weekly shown for all micropollutants (except for 2-ethylhexyl-4-methoxycinnamate) in both spiked experiments with 36 multi-class pollutants and non-spiked freshwater aquaculture effluents containing atrazine, isoproturon, perfluorooctanesulfonic acid, clarithromycin, erythromycin, fluoxetine, norfluoxetine, and 2-ethylhexyl-4-methoxycinnamate (Gorito et al. 2018). The high removal capacity of *P. australis* was demonstrated also on the antiepileptic carbamazepine in a study that showed how several bacterial species isolated from *P. australis* endosphere (i.e. the internal root tissue) were able to remove and degrade the pharmaceuticals (Sauvêtre and

Schröder 2015). Likewise, bacterial endophytes were isolated from *J. acutus* plants grown in a pilot constructed wetland, treating water contaminated with bisphenol A, and many strains were able to tolerate and use bisphenol A, ciprofloxacin and sulfamethoxazole as sole carbon source (Syranidou et al. 2017).

In the last decade, the role of bacteria dwelling the root system of constructed wetland plants has gained increasing attention, and the importance of microbial metabolism for the degradation of pharmaceuticals and other organic molecules suggested the possibility to exploit bacteria endowed with plant growth promoting capacities, tolerant and able to remove emerging contaminants in the so-called ‘*microbial assisted phytodepuration*’. For example, plant growth promoting bacteria improved the removal of the model azo-dye Reactive Black 5 in constructed wetland microcosms planted using *J. acutus*. Microcosms containing plants inoculated using two different single inocula and a mixed consortium of previously selected root-associated bacteria showed a higher decrease of Reactive Black 5 concentration in the effluent compared to the non-inoculated control ones, suggesting that this approach could be an interesting solution for the remediation of textile industry wastewater (Riva et al. 2019). On the whole, constructed wetlands represent a wastewater treatment technology of interest also for water reclamation, a current world-wide priority in the light of global warming and water crisis, although its benefits and risks should be carefully evaluated according to the final purposes of water reuse (Riva et al. 2020).

1.5.2 Algal-Based Removal Strategies for Emerging Contaminants

One solution could be the use of biological materials such as algae and fungi (Parlade et al. 2018; Silva et al. 2019; Tolboom et al. 2019; Tomasini and León-Santiesteban 2019). Algae are known to be effective in the treatment of water contaminated with organic pollutants through biological processes such as bioremediation (phytoremediation) and biosorption. The use of algae for the removal of emerging contaminants has many advantages such as the use of low-cost materials, low capital investment, simple operation, reduced maintenance and the absence of formation of degradation by-products. Algae are also highly adaptive microorganisms and can grow autotrophically, heterotrophically or mixotrophically. They can grow in very harsh environmental conditions such as low nutrient levels, and extreme pH and temperature. Algae can acclimatize not only to change depending on the temperature and nutrient availability, but also salinity and light. In general, the characteristics of municipal wastewaters and industrial effluents (e.g. textile and pulp and paper industries) are suitable for algae cultivation, since these waters are a source of nutrients. Over the past two decades, extensive research has shown the potential application of advanced algal-based technologies for the removal of pollutants (Silva et al. 2019; Tolboom et al. 2019).

Tolboom et al. (2019) recently reviewed algal-based removal strategies for the removal of emerging contaminants through efficient biological degradation. In laboratory-scale studies, algae-based bioreactors such as open ponds and bubble column photobioreactors are capable of removing pharmaceuticals and endocrine disruptors. Open ponds are artificial ponds of limited depth (around 0.03–0.07 m) used for the cultivation of microalgae without agitation. Their advantages are low investment cost, ease of use and low operating cost. However, a lot of space is required for algae growth. Other problems include poor use of light by the cells, variations in pH and dissolved oxygen, water loss due to evaporation, diffusion of carbon dioxide into the environment, temperature fluctuations, and inefficient agitation. The operational factors that influence algae growth in these open systems are mixing, dilution rate and depth. Open ponds operate with a long hydraulic retention time to consume carbon dioxide during the day (photosynthesis) and provide oxygen for aerobic biodegradation. Closed systems have been designed to overcome most of the problems associated with open systems. Photobioreactors are closed tubular systems, mainly designed in vertical, horizontal and helical form (coil tube, flat plate, bubble column, air column or agitation tank). Each system has its own advantages and drawbacks (Silva et al. 2019). Closed bioreactors provide a tightly controlled environment for the isolation of the microalgal strain, ensuring increased productivity, biomass quality and the ability to explore a wider range of strains. The benefits are an easier pH and temperature control, higher volumetric efficiency, better use of the growing area, higher capture of radiant energy and less water loss. Closed systems also reduce the contamination risk and the loss of carbon dioxide to the atmosphere. This concept is promising, but the costs of such reactors are higher (expensive to install and to maintain) and are an obstacle to its development. Their design must be carefully optimized for each individual strain. A detailed discussion on these systems and their physicochemical characteristics can be found in the following references: de Godos et al. (2012), Singh and Sharma (2012), Slade and Bauen (2013), Meneses-Jácome et al. (2016), Matamoros et al. (2015), Gouveia et al. (2016), Norvill et al. (2017), and Silva et al. (2019).

Tolboom et al. (2019) reported high removal percentages (>90%) for metoprolol, triclosan, and salicylic acid, moderate (50–90%) for carbamazepine and tramadol and very low (<10%) for trimethoprim and ciprofloxacin by inoculation of different microalgae. Similar results were also obtained for metoprolol (Bai and Acharya 2017; Gentili and Fick 2017), tramadol (Ali et al. 2018), salicylic acid (Escapa et al. 2017a, b), and triclosan (Matamoros et al. 2015; Bai and Acharya 2017). However, for ciprofloxacin, a high elimination of >90% was reported by Bai and Acharya (2017). Carbamazepine (Matamoros et al. 2015) and trimethoprim (de Wilt et al. 2016) showed less promising results with elimination rates of 62% and 60%, respectively. In fact, the removal efficiency depended mainly on the algae species used, such as *Chlorella vulgaris*, *Chlorella sorokiniana* and *Nannochloris* sp. For example, Escapa et al. (2017a, b), who evaluated the removal capacity of *Chlorella vulgaris*, *Tetrademus obliquus* and *Chlorella sorokiniana* from wastewater containing

paracetamol and salicylic acid using algae-based bioreactors, demonstrated that *T. obliquus* removed both pharmaceutical contaminants better than *C. vulgaris* in batch culture. The removal efficiency of salicylic acid by *Tetradesmus obliquus* was greater than 93% and that of *Chlorella vulgaris* was higher than 25%. Parameters that play an important role in pollutant degradation processes are not only the consortium of microorganisms present and its efficiency, but also the conditions used during degradation (temperature, seasons, retention time, environmental pH, dissolved oxygen, light periods). Performance also depends on chemical factors related to the pollutants, such as their structure and stereochemistry, concentration, toxicity and the presence of several pollutants.

The mechanisms involved in algae photobioreactors are complex and are being elucidated (de Godos et al. 2012; Matamoros et al. 2015; Xiong et al. 2016; Silva et al. 2019; Tolboom et al. 2019). Nevertheless, the elimination processes often referred to are biodegradation, photodegradation and biosorption (cell sorption and bioaccumulation) to algae. Other mechanisms and interactions are also cited, such as volatilization (stripping), biotransformation, bioprecipitation (biomineralization), and oxidation/reduction reactions. Bioaccumulation of pollutants in algae cells can also induce the generation of reactive oxygen species, free radicals, and non-radical forms such as hydrogen peroxide and single oxygen. For example, de Godos et al. (2012), studying the mechanism of elimination of tetracycline by *Chlorella vulgaris*, reported that photodegradation and biosorption were the main interactions to explain biodegradation. Matamoros et al. (2015) showed that biodegradation and photodegradation were the most relevant removal pathways for 26 contaminants in municipal wastewater in a study conducted in two pilot ponds of “high quality algae”. Volatilization was considered negligible for pharmaceuticals due to their low Henry’s constant values. However, for recalcitrant hydrophobic compounds, volatilization and sorption pathways were predominant. Xiong et al. (2016), studying the removal of carbamazepine by the microalgae *Chlamydomonas mexicana* and *Scenedesmus obliquus*, demonstrated that both species simultaneously promote the biodegradation, adsorption and bioaccumulation of carbamazepine.

All the studies concluded that this technique can open up new opportunities for wastewater treatment and reduce environmental pollution that can have adverse effects on the ecosystem and human health. There are still areas to be explored or improved, such as the testing of other algal species (often the same species are used alone or in combination), the selection of different microorganisms with specific metabolism for different pollutants (currently there is a lot of research on the use of genetically modified microorganisms), the improvement of knowledge on the often slow kinetic and biodegradation mechanisms, and the optimization and better control of the operating parameters (temperature, pH, dissolved oxygen, etc.) as they are difficult to control on a large scale, which is a great challenge for this application. It is also necessary to acquire knowledge on other problems such as the incomplete transformation of certain recalcitrant pollutants.

1.5.3 Use of Fungi for Removal of Emerging Contaminants

Fungi have also been recognized for their ability to transform a wide range of recalcitrant compounds using non-specific intracellular and extracellular oxidizing enzymes (Spina et al. 2012). The use of fungi for the removal of emerging contaminants through biological processes such as mycoremediation and biosorption has the same advantages as those cited for the use of algae (Spina et al. 2012; Zhang et al. 2013; Badia-Fabregat et al. 2015; Asif et al. 2017; Tomasini and León-Santesteban 2019).

Fungi are indeed microorganisms known for their effectiveness in treating water contaminated by pollutants such as pharmaceuticals. Fungal reactors (mycoreactors) can be suspended or immobilized growth systems. They can operate under aerobic or anaerobic conditions. This technology requires specific and controlled conditions in order to maintain a sustainable and efficient process. For example, the oxidative metabolism of fungi can be strongly affected by the presence of nutrients, pH, immobilization on different supports, and agitation or static growth conditions. Recent comprehensive reviews on fungal technologies for the degradation of pharmaceuticals and personal care products have been published (Asif et al. 2017; Rodríguez-Rodríguez et al. 2019; Silva et al. 2019; Tomasini and León-Santesteban 2019).

Cruz-Morató et al. (2013) studied the degradation of pharmaceuticals in non-sterile urban wastewater at the *Universitat Autònoma de Barcelona* (Spain) by *Trametes versicolor* in a fluidized bed reactor. Of the 80 pharmaceuticals analyzed, 13 were detected in the effluent of sterile urban wastewater, the most abundant belonging to the group of analgesic/anti-inflammatory compounds, especially naproxen ($35.58 \pm 4.8 \mu\text{g/L}$) and ibuprofen ($12.61 \pm 1.79 \mu\text{g/L}$). Complete elimination of both analgesics, ibuprofen and naproxen, occurred within 24 h after fungal treatment. A similar conclusion was reported by Marco-Urrea et al. (2009). Other analgesics as acetaminophen and codeine were initially detected at concentrations of $3.87 \pm 0.41 \mu\text{g/L}$ and $0.02 \pm 0.001 \mu\text{g/L}$ and were completely removed after 8 h and 2 days, respectively (Cruz-Morató et al. 2013). The analgesics ketoprofen and salicylic acid were also initially detected in wastewater at concentrations of $0.48 \pm 0.07 \mu\text{g/L}$ and $0.85 \pm 0.11 \mu\text{g/L}$, respectively. Changes in concentrations during treatment showed unexpected behavior with increases and decreases, but after 8 days the concentration were $0.31 \pm 0.04 \mu\text{g/L}$ (ketoprofen) and $1.24 \pm 0.07 \mu\text{g/L}$ (salicylic acid), corresponding to a 35% removal of ketoprofen and a 46% increase in salicylic acid concentration. The possible release of these compounds may be explained by the deconjugation of glucuronides during biological treatment. Complete removal of 7 of the 10 initially detected pharmaceuticals was achieved in non-sterile conditions after 24 h of fungal treatment, while only 2 were partially removed and 1 of the pharmaceuticals tested increased its concentration. Antibiotics such as erythromycin (detected at $0.3 \mu\text{g/L}$) and metronidazole (detected at $0.05 \mu\text{g/L}$) were successfully removed: erythromycin was completely eliminated within 15 min while the elimination of metronidazole was obtained after 2 days.

Carbamazepine, a well-known recalcitrant psychiatric drug in activated sludge treatment was also detected in the wastewater at 0.7 µg/L. Cruz-Morató et al. (2013) showed that carbamazepine and its metabolites were also strongly eliminated by *T. versicolor* during batch treatment in a fluidized bed bioreactor under sterile conditions, in agreement with the results published by Zhang and Geißen (2012). In addition, the *Vibrio fischeri* luminescence test (Microtox® test) showed a significant reduction in wastewater toxicity after treatment. Cruz-Morató et al. (2013) concluded that it was possible to use a fluidized bed bioreactor to remove pharmaceuticals at environmentally relevant concentrations under non-sterile conditions by *T. versicolor*.

In another work, the same authors treated hospital wastewaters (collected in the main sewer of the University Hospital of Girona, Dr. Josep Trueta, Girona, Spain) in a fungal bioreactor with *Trametes versicolor*, under sterile and non-sterile conditions (Cruz-Morató et al. 2014). Preliminary analytical monitoring of hospital wastewater showed that the most frequently detected families of substances were analgesics, antibiotics, psychiatric drugs, endocrine disruptors and X-ray contrast media, at concentrations ranging from ng/L to mg/L. Results showed that 46 of the 51 detected pharmaceuticals were partially degraded and completely eliminated in non-sterile experiments after 8 days. The initial total amount of pharmaceuticals in the bioreactor was 8185 µg in sterile treatment and 8426 µg in non-sterile treatment, and the overall load removal was 83.2% and 53.3% in their respective treatments. In particular, diclofenac (a recalcitrant compound in municipal wastewater treatment plant) and human metabolites of carbamazepine were efficiently removed. The lower removal detected in the non-sterile treatment is explained by the higher concentrations of caffeine (149 µg/L) and iopromide (419.7 µg/L), which are some of the most difficult compounds to be degraded by the fungus (<40% removal). Excluding caffeine and iopromide concentrations, the overall elimination of pharmaceuticals and endocrine disruptors was greater than 94% in both treatments. The treatment time required to achieve complete removal of the targeted pollutants highly depended on the type of pharmaceutical. For instance, almost complete elimination of analgesics was observed within 24 h, whereas similar results were observed for antibiotics within 5 days. Experiments also showed a significant reduction in wastewater toxicity after treatment, confirming the relevance of fungal treatment. The fact that the overall percentage of pollutant removal was similar in sterile and non-sterile treatments indicated that *T. versicolor* played a major role in this process and that the synergistic interaction between native bacteria and fungi did not improve removal efficiency. This result was also relevant as it indicated that sterility was not a mandatory condition for applying *T. versicolor* for this purpose. However, one of the main disadvantages of this process was that after treatment, the pH had to be neutralized since it reached acidic conditions due to the secretion of organic acids by the fungus. Cruz-Morató et al. (2014) concluded that fungi-based technologies were a potential alternative to pretreatment of complex hospital wastewater.

Vasiliadou et al. (2016) studied the biological removal of 13 pharmaceutical compounds using white rot fungi, *Trametes versicolor* and *Ganoderma lucidum*,

with concomitant production of fatty acid methyl esters from the residual biomass. Both strains were used individually or simultaneously for the oxidative removal of pharmaceuticals. *Trametes versicolor* and *Ganoderma lucidum* allowed 100% removal of diclofenac, gemfibrozil, ibuprofen, progesterone and ranitidine by individual or simultaneous strains after 7 days of incubation. Lower removals, ranging from 15 to 41%, were obtained for other less biodegradable substances (4-acetamidoantipyrin, clofibrac acid, atenolol, caffeine, carbamazepine, hydrochlorothiazide, sulfamethoxazole and sulphiride), although the combination of the two strains improved the efficiency of the system. Vasiliadou et al. (2016) also demonstrated efficient production of biodiesel from the residual fungal mass. The white rot fungus *Trametes versicolor* also reduced the estrogenic activity of a mixture of emerging contaminants in wastewater treatment plant effluent (Shreve et al. 2016; Singhal and Perez-Garcia 2016). Cruz del Álamo et al. (2018) also reported on the performance of an advanced bio-oxidation process based on fungi *Trametes versicolor* immobilized in a continuous rotating bioreactor to degrade pharmaceutical compounds in municipal wastewater. Further examples can be found in the review by Asif et al. (2017) and in two books recently edited by Tomasini and León-Santesteban (2019), and by Yadav et al. (2019).

Numerous studies have demonstrated that white rot fungi are capable of degrading a wide range of pharmaceuticals and personal care products, including even xenobiotics and recalcitrant compounds (Yadav et al. 2019). Although the technical feasibility and effectiveness of this technology has been demonstrated, further research is needed before this method can be applied on a large-scale.

1.5.4 Other Biological Strategies for the Biodegradation of Emerging Contaminants

Other biological approaches for the degradation of emerging contaminants and the reduction of their negative impact include enzymatic degradation. Bioremediation using enzymes (transferases, hydrolases, oxidoreductases, etc.) is a cost-effective and environmentally friendly biotechnology. Enzymes are biological catalysts that facilitate the conversion of substrates into products by providing favorable conditions that reduce the activation energy of the reaction. Each enzyme has its own mode of action: transferases catalyze the transfer of a functional group from a donor to an acceptor; hydrolases facilitate the cleavage of C-C, C-O, C-N and other bonds by water; oxidoreductases catalyze the transfer electrons and protons from a donor to an acceptor (Karigar and Rao 2011). The microbial enzyme plays an important role in bioremediation. Laccases are multinuclear copper-containing oxidoreductases and can perform electron oxidation of a broad spectrum of environmental contaminants. They are known for their potential to oxidize a broad spectrum of phenol-based compounds, dyes, inorganic substances and pesticides. This group of versatile enzymes is also known as a green catalyst with significant potential to

tackle emerging substances. These enzymes are an environmentally friendly substitute for conventional chemical reactions. Recent comprehensive reviews published by Iqbal's group are available on these topics (Ahmed and Iqbal 2017; Bilal et al. 2019a, b). Iqbal's group concluded that laccases are one of the most promising enzyme groups with potential uses in bioremediation and treatment of recalcitrant pollutants and xenobiotics. However, knowledge about this enzyme capable of degrading these substances is still limited, partly due to the lack of rapid screening methods (Stadlmair et al. 2018). Nevertheless, this is an area of research in full development and significant advances are expected in the future.

1.5.5 Membrane Bioreactor Technology for Emerging Contaminant Removal

Membrane bioreactor technology has been known since the 1970s, but its development took off in the 2000s. Its market value is currently continuing to increase as environmental regulations are becoming increasingly strict. The technology is becoming more and more profitable as the costs of membranes and the related membrane processes continue to fall. Indeed, among industrial water treatment techniques, membrane water treatment is now considered to be competitive with other techniques both from a chemical efficiency and an economic point of view. However, it has not yet overwhelmed the market due to some serious drawbacks such as membrane fouling.

Full-scale membrane bioreactor technology is a coupling of two wastewater treatment methods, biological treatment and membrane separation (Domańska et al. 2007; Judd 2008; Huang et al. 2010). Conventional treatment of municipal wastewater generally involves three-stages: sedimentation of solids in the feed water (primary treatment), coupled with a coagulation stage when it rains for example, followed by treatment of organic matter by aerobic degradation (e.g. activated sludge, secondary treatment), and finally a second sedimentation process to remove biomass. Tertiary treatment is also possible, either to remove residual pollution and/or to disinfect the treated wastewater.

Membrane bioreactor technology can replace both physical separation processes by filtering the biomass through a membrane. As a result, the quality of water produced is much higher than that generated by conventional treatment, thus avoiding the need of another tertiary process (Ma et al. 2018; Jalilnejad et al. 2020). Membrane bioreactors are slightly more efficient than activated sludge for the removal of organic matter because they combine biodegradation and membrane separation. Biodegradation converts minerals, organic matter and organic compounds into less toxic and refractory substances or, ideally, mineralizes them, while the final step using membranes reduces the chemical oxygen demand, promotes the retention of suspended solids and pathogens and salts, depending on the type of membrane used (microfiltration, ultrafiltration, nanofiltration or reverse osmosis). Compared to

other conventional treatment processes, membrane bioreactor technology is also a smaller and simpler integrated process (compact installation), with less sludge production, complete biomass retention, high performance of nutrient removal, low energy density requirements, and much smaller footprint (Jalilnejad et al. 2020). The main shortcomings of membrane filtration are the generation of large volumes of concentrate that must be treated separately and the fouling of the membranes (which can considerably reduce their performance and lifetime), which then leads to a significant increase in maintenance and operating costs (Huang et al. 2010; Iorhemen et al. 2016). A challenge of interest to the scientific community is the search for sustainable strategies to reduce membrane fouling. Other problems often mentioned are the generally longer retention times of the sludge, the higher biomass concentration of the reactors and the high variance of the separation step between the liquid phase and the sludge. It is also important to note that membrane bioreactor technology, like other techniques such as adsorption or membrane filtration, is a simple transfer process rather than a transformation/degradation process (as in the case of advanced oxidation processes). Attention should therefore be paid to the treatment of wastewater sludge (Ma et al. 2018).

Membrane bioreactors were originally designed and used for the treatment of domestic wastewater to remove conventional pollutants (organic matter, minerals, metals) and pollution (suspended solids, chemical oxygen demand, biological oxygen demand) (Radjenovic et al. 2007; González et al. 2008; Huang et al. 2010). They have subsequently been extended to a wide range of wastewaters, including urban runoff, mine wastewater and industrial effluents (González et al. 2008). Research interests in membrane reactor technique have grown rapidly in recent years. Indeed, studies also showed that membrane bioreactors are effective in removing emerging substances, mostly pharmaceuticals (Maeng et al. 2013; Ojajuni et al. 2015; Phan et al. 2015; Sanguanpak et al. 2015; Alvarino et al. 2017; Beshha et al. 2017; Gurung et al. 2017; Abargues et al. 2018; Jiang et al. 2018; Ma et al. 2018; Mert et al. 2018; Bodzek 2019; Borea et al. 2019; Monteoliva-García et al. 2019; Lim et al. 2020; Pathak et al. 2020; Racar et al. 2020; Vieira et al. 2020).

Maeng et al. (2013) demonstrated that membrane bioreactor technology is an excellent approach for removing trace pharmaceuticals from complex wastewater. They reported high removal efficiency (>80–90%) for acetaminophen, ibuprofen, bezafibrate, estrogens (estrone, estradiol, estriol). Phan et al. (2015) reported that membrane bioreactor technology can generally achieve high pollutant removal efficiency with the effluent quality largely complying with the Australian guidelines for water recycling (except for caffeine, estrone and triclosan). Performance is a function of temperature (Suárez et al. 2012; Gurung et al. 2017) and pH-dependent (Sanguanpak et al. 2015). Suárez et al. (2012) evaluated the removal efficiency of sulfamethoxazole and erythromycin as a function of temperature and the results indicated that an increase in temperature resulted in 30% higher removal than in cold weathers. However, an increase in temperature to a high level, e.g. 45 °C, may inhibit metabolic activity (Beshha et al. 2017). Similarly, low temperature impairs treatment efficiency. Gurung et al. (2017) also indicated that the removal efficiency of bisoprolol, diclofenac and bisphenol A was highly dependent on temperature,

with maximum removal of 65%, 38% and >97%, respectively. Sanguanpak et al. (2015) reported that membrane bioreactors performed better for analgesics and anti-inflammatory drugs (e.g. ibuprofen, diclofenac and ketoprofen) under low pH conditions (the optimal pH was about 6), mainly due to the increased lipophilicity and the ionisability of pH-dependent molecules.

Racar et al. (2020) investigated the removal of several emerging substances, mainly pharmaceuticals, from wastewater from a treatment plant located in Čakovec (Croatia) by a membrane bioreactor. A 6-month analytical monitoring of wastewater showed 12 substances were systematically detected with a high variation in concentration. The highest values (up to 500 µg/L) were found in the winter period. Azithromycin (92.54 ± 113.90 µg/L), clarithromycin (50.49 ± 80.95 µg/L), and diclofenac (71.57 ± 57.41 µg/L) were the most prevalent, while the other measured pharmaceuticals showed wide variations in concentration, in particular acetamiprid, clothianidin, imidacloprid and thiamethoxam, a high concentration in November, while the other months had significantly lower concentrations. The authors demonstrated that membrane bioreactor technology achieves high removal rates (to levels below the limit of quantification) for all substances, regardless of the season.

Vieira et al. (2020) recently compared the efficiency of adsorption, membrane separation and biodegradation to remove endocrine disruptors (parabens, bisphenols, phthalates, estrogens and nonylphenols) and pesticides and discussed the advantages and disadvantages of each process.

Literature data shows that the three main removal mechanisms for substances that occur in membrane bioreactors are adsorption/sorption/biosorption (onto sludge flocs and bound microbial products), biological degradation (aerobic degradation, anaerobic degradation, metabolism and co-metabolism, ion trapping mechanisms) and membrane separation. For adsorption process, the efficiency largely depends on the physicochemical characteristics of emerging substances, e.g. hydrophobicity, hydrogen bond, electrostatic interactions, etc. For biological degradation, performance depends also on the biodegradability and bioavailability of the substances, and the condition used (oxidation-reduction potential plays an important role in the microbial diversity, enzymatic functions and activities). Suárez et al. (2012) reported that musks (galaxolide, tonalide and celestolide) and estrogens (estrone and estradiol) can be well degraded under aerobic and anoxic conditions, whereas the transformation of ibuprofen, roxithromycin, erythromycin, citalopram and naproxen occurs only in the aerobic process. In contrast, the degradation of diclofenac, sulfamethoxazole, diazepam, trimethoprim and carbamazepine is much less effective in the presence of oxygen species. Membrane separation is another mechanism (size exclusion, charge repulsion) contributing to pollutant removal and it depends on the type of membrane used. Alvarino et al. (2017) demonstrated that the removal efficiency of diclofenac and roxithromycin in an ultrafiltration membrane bioreactor was higher than that in a microfiltration membrane bioreactor due to the retention by the cake layer. However, ultrafiltration does not eliminate all pollutants. The solution would be to generalize the use of nanofiltration and osmosis membranes, but then there is the problem of energy consumption and maintenance costs of the membranes, which can clog up more quickly.

Most of the studies published in the literature on the behavior of membrane bioreactors in relation to emerging substances (mainly pharmaceuticals) have been conducted on a laboratory scale. Pilot projects at industrial scale have yet to be conducted on a much wider range of substances including different families of pharmaceutical compounds, personal products and cosmetics, pesticides and industrial substances. Another important challenge is the presence of nanoparticles and nano-products in wastewater that can create clogging problems.

The sustainable application of membrane bioreactor technology requires a better understanding of the fate of pollutants, research on biotransformation mechanisms and the combination of bioreactors with emerging technologies such as advanced oxidation processes (Borea et al. 2019; Monteoliva-García et al. 2019). The idea developed in this recent research theme is to use the redox reactions that occur on the surface of a conductive membrane (under anodic or cathodic polarization). These reactions can facilitate the transformation of refractory pollutants, which is a clear advantage over conventional processes, and reduce membrane fouling, while having negligible effects on microbial activities in the effluent.

There are two other aspects that are becoming increasingly important in the field of water treatment. The first is the recycling of water, especially for irrigation of agricultural soils or golf courses. Recycling or reuse of wastewater could also be a way of supplementing available water supplies. Effluents from membrane bioreactor technology are capable of meeting or exceeding current drinking water regulations. However, there are several barriers to water reuse. For example, the public perception of recycled water for drinking water production is less than favorable, while the reuse of water for irrigation is generally accepted. The second is to consider wastewater as a resource and not as a waste. Conventional municipal wastewater treatment plants such as those applying activated sludge are energy-intensive, produce large quantities of residues (sludge) and fail to recover the potential resources available in wastewater. Furthermore, in this respect, wastewater is often considered as a waste. However, wastewater should be considered a resource because it contains organic matter, phosphorus, nitrogen, metals and energy. Membrane techniques could make it possible to recover compounds with high added value. Of course, there is the question of the presence of emerging substances. In this context, biological membrane technologies coupled with other methods could be useful.

1.6 Removal of Emerging Contaminants by Membrane Filtration

Advanced treatment methods such as membrane filtration are potential technologies capable of removing a wide range of pollutants detected in water, even at trace levels, and are already used at industrial scale as tertiary treatment (Kunst and Košutić 2008; Ojajuni et al. 2015; Hu et al. 2017; Warsinger et al. 2018). In simple terms,

the membrane filtration process is a physical separation method characterized by the ability to separate molecules of different sizes and characteristics. Its driving force is the pressure difference between the two sides of a special membrane. The technology involves passing a single feed stream through a membrane system that separates it into two individual streams, called permeate and retentate. The membrane that separates them is a physical barrier with highly specialized characteristics – a barrier that only selected components of the feed stream can pass through. There are four main types of membranes, defined according to the size of the substance they must separate from the feed effluent: reverse osmosis, nanofiltration, ultrafiltration and microfiltration, in order of pore size. For wastewater treatment, the two preferred methods are reverse osmosis and nanofiltration, which are pressure-driven membrane technologies that can remove contaminants to 0.1 nm and 1 nm, respectively. Both methods are diffusion and size exclusion controlled processes. They have the largest treatment capacity but require the greatest degree of pre-treatment. These technologies are known for their capacity to remove pharmaceuticals (ibuprofen, naproxen, trimethoprim, diazepam 17- β -estradiol, testosterone) and personal care products (triclosan, alkylphenols).

Mehran Abtahi et al. (2018) showed that the removal rates of diclofenac, naproxen, ibuprofen and 4-n-nonylphenol by nanofiltration can reach 77%, 56%, 44%, and 70%, respectively. Alonso et al. (2018), investigating the removal of ciprofloxacin in synthetic seawater by a commercial spiral-wound reverse osmosis membrane, showed that more than 90% of ciprofloxacin could be successfully removed by reverse osmosis membrane under constant pressure, and the maximum removal rate was 99.96%. In general, to treat pharmaceuticals and personal care products, nanofiltration has shown to be superior to other conventional filtration methods, in terms of effluent quality, easy operation and maintenance procedures, low cost, and small required operational space (Hu et al. 2017; Mehran Abtahi et al. 2018). However, reverse osmosis is the most effective in removing pesticides. In reality, there are no general rules because the performance depends not only on the membranes used and the pre-treatments undergone by the effluents, but also on several parameters such as the complexity of the effluents, the type(s) of substance(s), or their concentration. It is therefore necessary to carry out numerous tests at pilot scale before defining the choice of the membrane technique to be used.

A recent review by Kim et al. (2018) provides a comprehensive overview of the most relevant works available in literature reporting the use of membrane filtration for the removal of emerging contaminants. The fundamental knowledge of forward osmosis (the force that drives the separation is concentration gradient), reverse osmosis (pressure-driven process), nanofiltration (pressure-driven process) and ultrafiltration (pressure-driven process) technologies has been described. This review also aimed to address several key parameters, including the physicochemical properties of emerging contaminants (solute molecular weight/size/geometry, charge, and hydrophobicity), water quality conditions (pH, solute concentration, temperature, background inorganics, and natural organic matter), and membrane properties and operating conditions (membrane fouling, membrane pore size, porosity, charge, and pressure) that influence the removal of emerging contaminants

during membrane filtration, and separation mechanisms. Overall, the general emerging contaminant removal trend was as follows: (i) the removal efficiency for the membranes follows the declining order: reverse osmosis \geq forward osmosis $>$ nanofiltration $>$ ultrafiltration; (ii) the retention of emerging contaminants by reverse osmosis and forward osmosis membranes is mainly governed by size/steric exclusion, while high retention can still be achieved due to hydrophobic (adsorption) and electrostatic (attraction) interactions for nanofiltration and ultrafiltration membranes; (iii) more polar, less volatile, and less hydrophobic organic emerging contaminants have less retention than less polar, more volatile, and more hydrophobic substances; (iv) while, in general, forward osmosis and reverse osmosis membranes show significant metal/toxic anion retention ($>95\%$) regardless of water quality and operating conditions, metal/toxic anion retention by nanofiltration and ultrafiltration membranes is more efficient at neutral and alkaline conditions than at acidic values; and (v) while ultrafiltration alone may not effectively remove emerging contaminants, it can be employed as a pretreatment step prior to forward osmosis and reverse osmosis.

The advantages of membrane filtration often cited are: a wide range of commercial membranes available from several manufacturers, modular design, small footprint, simple and efficient technologies, production of high quality treated wastewater, no chemicals required, low energy consumption, and well-known separation mechanisms. The main disadvantages are: high investment costs, high energy requirements, high maintenance and operating costs, rapid clogging of the membranes (pre-treatment is essential), formation of separate contaminant concentrates (retentate), which must be removed. A major disadvantage of membrane filtration compared to advanced oxidation processes is indeed that the substances are only transferred into concentrate streams and not destroyed, as in the case of advanced oxidation, and therefore the concentrate requires additional treatment and disposal. Despite this, in Europe, advanced tertiary adsorption processes on activated carbon, combined with a chemical oxidation step, are in competition with membrane technologies because the latter are particularly effective in removing complex mixtures of substances, even in trace amounts and in the presence of many interferents.

1.7 Advanced Oxidation Processes to Degrade Emerging Contaminants

1.7.1 Removal of Emerging Contaminants Through Wastewater Disinfection

The main objective of disinfection is to either eliminate pathogens from water for the production of potable water or to reduce the pathogen content of treated wastewater in wastewater treatment plants. Disinfection is indeed the final treatment step for the production of potable water. It is an important step because the use of water disinfection as a public health measure reduces the spread of diseases.

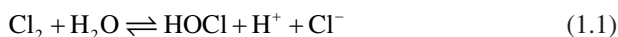
Pathogenic microorganisms are destroyed or inactivated using chemical or physical disinfectants such as chlorine, chlorine dioxide, hypochlorite, ozone, peracetic acid, bromide, iodine, non-ionizing radiation (ultraviolet radiation, ultrasonic radiation), and ionizing radiation (gamma ray). Among chemicals, chlorine and its compounds, chlorine dioxide and ozone, are the most common disinfectants used in the water industry. The main mechanisms of germicidal action of disinfectants are related to the direct oxidation of the cell of microorganisms by the disinfectant or to the alteration of the permeability of the cell wall, or even to the photochemical deterioration of their DNA or RNA (ultraviolet radiation) (Asano et al. 2007). Disinfectants are also known to remove organic contaminants from water, which act as nutrients or shelter for microorganisms. They must also have a residual effect to prevent microorganisms from growing in the pipe after treatment, which would result in recontamination of the water (Collivignarelli et al. 2018). The main problem with disinfection, with the exception of ultraviolet radiation, is that the processes can lead to the formation of organic and inorganic disinfection by-products such as trihalomethanes, chlorite and chlorate, aldehydes, etc. (von Sonntag and von Gunten 2012). Advanced technologies include the combination of ozone and hydrogen peroxide, ozone and ultraviolet radiation, hydrogen peroxide and ultraviolet radiation, ultraviolet radiation with titanium dioxide, alone or combined with other processes, such as sand filtration, membrane technologies, nanotechnology, photovoltaic method, solar photocatalytic, sonodisinfection etc.

Disinfection processes using disinfectants, alone or in combination with additional physical/chemical agents, have also been proposed to eliminate emerging substances (Ikehata et al. 2006, 2008; Snyder et al. 2006; Gagnon et al. 2008; Kim and Tanaka 2009; Hey et al. 2012a, b; Noutsopoulos et al. 2013a; Yang et al. 2013). In municipal wastewater treatment, disinfection is usually the last step (tertiary or final treatment) before the treated wastewater is released to the aquatic environment. However, the treatment can also take place after primary and secondary wastewater treatment. Certain types of pollutants such as diclofenac (anti-inflammatory), boldenone (anabolic steroid), sulfamethoxazole (bacteriostatic antibiotic), and clofibrac acid (lipid-regulating agent), can be effectively degraded at reasonably low doses for drinking water and wastewater treatment. Kim and Tanaka (2009) reported that photodegradation rates of up to 100% were obtained when diclofenac was treated using ultraviolet disinfection, but with ultraviolet dose which is 6 times higher than what typically used to disinfect drinking water. However, in general, direct ultraviolet irradiation at disinfection doses was no effective in removing trace pollutants such as hormones (Rosenfeldt and Linden 2004), bisphenol A (Chen et al. 2006), or ketoprofen (Real et al. 2009).

A review of the abundant literature published over the past 20 years shows that the three main technologies studied for both disinfecting water from pathogens and removing substances are chlorination, ozonation and ultraviolet irradiation. These are the technologies used at industrial scale, either alone or in combination with other chemicals. For example, oxidative removal of trace organic contaminants in water (surface water, wastewater) can be achieved using ozone combined with

hydrogen peroxide or ultraviolet combined with hydrogen peroxide (Kruithof et al. 2007; Gagnon et al. 2008; von Sonntag and von Gunten 2012; Yang et al. 2013).

Chlorination The main chlorination compounds used in the wastewater industry are chlorine (Cl_2), sodium hypochlorite (NaOCl) and calcium hypochlorite ($\text{Ca}(\text{OCl})_2$). Of these, chlorine gas is generally used in large wastewater treatment plants, although a switch to sodium hypochlorite has been noted in many cases over the last decade due to safety concerns, while calcium hypochlorite is allowed in smaller plants. When chlorine gas is dissolved in water, it hydrolyzes according to Eq. (1.1). The hypochlorous acid produced during this reaction is a weak acid which dissociates easily in the aqueous solution according to Eq. (1.2). The sum of hypochlorous acid and the hypochlorite ion forms free chlorine. The relative distribution between the two chlorine species depend on both the temperature and pH of the wastewater (Fig. 1.8) and is very important because the acid form is a much more effective oxidant than the ionic form.



The effect of chlorination on the removal of emerging contaminants has been widely documented (Hu et al. 2002; Petrovic et al. 2003; Westerhoff et al. 2005; Zhang and Grimm 2005; Greyshock and Vikesland 2006; Thurman 2006; Korshin 2006; Stackelberg et al. 2007; Simazaki et al. 2008; Benotti et al. 2009a, b; Acero et al. 2010; Quintana et al. 2010; Chen et al. 2013; Ga et al. 2014; de Jesus Gaffney et al. 2016). The degree of removal varies for different types of emerging contaminants. Nevertheless, all these studies on chlorination experiments are focused on pure water or drinking water rather than in the wastewater matrix. On the other

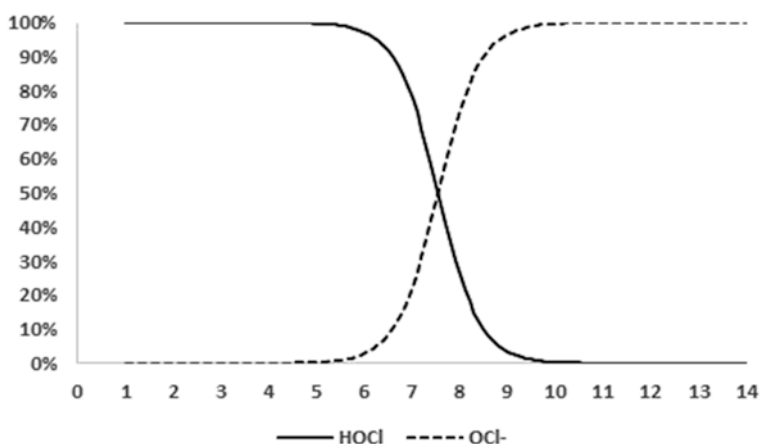


Fig. 1.8 Relative distribution among the dominant chlorine species versus pH at 25 °C for a chlorine concentration of 10 mg/L. (Source: Constantinos Noutsopoulos, Athens, Greece)

hand, studies on the ability of chlorination to remove emerging contaminants from wastewater are rather rare (Renew and Huang 2004; Belgiorno et al. 2007; Nakamura et al. 2007; Ying et al. 2009; Li and Zhang 2011; Noutsopoulos et al. 2013a, b, c, 2015; Nika et al. 2016).

Based on the extensive data in the literature, chlorination appears to be effective in the removal of several non-steroidal anti-inflammatory drugs, antibiotics, estrogens and antidepressants (diclofenac, naproxen, sulfamethoxazole, amitriptyline hydrochloride, methyl salicylate), endocrine disruptors (nonylphenol, bisphenol, triclosan and 17- β -estradiol), benzotriazoles and benzothiazoles, while other chemicals in these categories have significantly lower degradability, e.g. ibuprofen, ketoprofen, 17- β -estradiol and tolytriazole. The performance of the chlorination process in removing emerging contaminants is related both to the characteristics of the matrix (organic matter content of the wastewater, presence of total suspended solids, pH, etc.) and to the physicochemical characteristics of the chemicals. As suggested by Noutsopoulos et al. (2015), the performance of the chlorination process for the removal of targeted endocrine disruptors and non-steroidal anti-inflammatory drugs was not affected by the pH for typical wastewater pH values around 7–8. On the other hand, some studies reported a significant effect of pH on the removal of new contaminants (Acero et al. 2010; Gallard et al. 2004; Pinkston and Sedlak 2004; Deborde and von Gunten 2008) for pH values significantly different from those prevailing in wastewater treated by secondary and tertiary treatment. In general, pH can effectively affect process performance at low values (lower than those prevailing in treated wastewater) that favor the prevalence of the strongest oxidizing species (i.e. hypochlorous acid). In addition, it is expected that not only the available free chlorine species (HOCl and OCl⁻), but also the chemical characteristics (pK_a, chemical structure) of the compounds under different pH conditions may also affect chlorination performance. With respect to other wastewater characteristics, Noutsopoulos et al. (2015) reported that the effect of total suspended solids content of wastewater (and thus organic matter content) on the degradation of emerging contaminants during chlorination is more profound for chemicals with high K_{ow} values (e.g. nonylphenol and its ethoxylates, triclosan), and thus a high affinity to be distributed to the particulate phase. In the same study, the effect of humic acids on the removal of emerging contaminants and non-steroidal anti-inflammatory drugs by wastewater chlorination was rather minimal.

In most studies, degradation of emerging contaminants appears to follow pseudo first-order kinetics and values of rate constant (*k*) and half-lives (*t*_{1/2}) have been determined for many chemicals (Deborde and von Gunten 2008; Quintana et al. 2012). According to Deborde and von Gunten (2008), the reactivity of hypochlorous acid with organic micropollutants refers to (i) oxidation reactions, (ii) addition reactions to unsaturated bonds, and (iii) electrophilic substitution reactions at nucleophilic sites. Thus, as explained by the authors, the effect of chlorine on aliphatic organic compounds (with the exception of compounds with sulfur or nitrogen-containing fractions) is generally small, whereas for the most popular emerging contaminants (nonylphenol, bisphenol A and triclosan) and the steroid hormones estrogen, the reactivity of chlorine occurs mainly on the phenolic ring. A

significant number of studies on endocrine disruptors and chlorination by-products of pharmaceuticals provide an analytical discussion of the relevant mechanisms (Hu et al. 2002; Hu et al. 2003; Petrovic et al. 2003; Gallard et al. 2004; Bedner and MacCrehan 2006; Korshin et al. 2006; Thurman 2006; Lei and Snyder 2007; Sharma 2008; Quintana et al. 2012; Bulloch et al. 2012; Soufan et al. 2012; Noutsopoulos et al. 2015). In many cases, toxicity measurements show that some of the by-products of chlorination are more toxic than the original compounds.

Chlorine Dioxide This chemical agent has a stronger disinfectant activity than chlorine. Considering its higher cost compared to conventional chlorination, disinfection with chlorine dioxide is generally adopted in cases where minimizing the production of chlorine-based disinfection by-products is desirable. Because of its instability, chlorine dioxide (ClO_2) is produced on-site by mixing a chlorine solution with a sodium chlorite solution. The literature on the effectiveness of chlorine dioxide in removing emerging contaminants during wastewater disinfection is rather limited. In their comprehensive review, Hey et al. (2012a) investigate the effect of ClO_2 on the removal of a wide range of 56 pharmaceuticals. According to this study, it was shown that, in addition to the effectiveness of chlorine dioxide in removing many emerging contaminants, approximately one-third of the target compounds studied were virtually unaffected by the oxidant, even at doses as high as 20 mg/L. In their follow-up study, Hey et al. (2012b) reported the effective elimination of three non-steroidal anti-inflammatory drugs (naproxen, diclofenac, mefenamic acid) and a lipid-regulating agent (gemfibrozil), while no elimination was reported for ibuprofen and clofibrac acid. The inability of ClO_2 to remove ibuprofen and carbamazepine has also been reported previously by Lee and van Gunten (2010), while satisfactory removal has been reported for sulfamethoxazole and 17α -ethinyl estradiol. In addition, Huber et al. (2005a, b) showed an effective elimination of estrogenic hormones at very low doses of ClO_2 and a short contact time (5 min). The ability of chlorine dioxide to remove emerging contaminants has also been demonstrated for a range of antibiotics (Navalon et al. 2008; Wang et al. 2011). The variable efficacy of chlorine dioxide on the removal of pharmaceuticals was also recorded in the study by Sharma (2008). According to his conclusions, chlorine dioxide is an effective oxidant.

UV Radiation This process is a well-known disinfection step used to effectively remove bacteria, viruses and protozoa without producing toxic by-products. The main types of lamps are low-intensity low-pressure lamps, high-intensity low-pressure lamps and high-intensity medium-pressure lamps, the former being the most commonly used for disinfection purposes (Asano et al. 2007). The main germicidal mechanism of ultraviolet irradiation is associated with direct DNA damage, while the removal of organic pollutants is based on their direct photolysis during absorption of UV-C photons (at the wavelength of 254 nm). The effectiveness of ultraviolet irradiation on the removal of pathogens and organic micropollutants is highly dependent on the applied dose (in mJ/cm^2 or mWs/cm^2), calculated as the product of average ultraviolet intensity and contact time. The effectiveness of ultra-

violet irradiation for the removal of emerging contaminants has been well documented, primarily for pharmaceuticals and endocrine disruptors (Andreozzi et al. 2003; Doll and Frimmel 2003; Lopez et al. 2003; Rosenfeldt and Linden 2004; Vogna et al. 2004; Chen et al. 2006; Neamtu and Frimmel 2006; Pereira et al. 2007a, b; Canonica et al. 2008; Benotti et al. 2009a, b; Kim et al. 2009a; Kim and Tanaka 2009; Yuan et al. 2009; Rosario-Ortiz et al. 2010; Zhang et al. 2010; Baeza and Knappe 2011; Salgado et al. 2011, 2012, 2013; Hansen and Andersen 2012; Pablos et al. 2013; Bennett et al. 2018; Mole et al. 2019). Kim et al. (2009a, b) reported that of the 42 pharmaceuticals studied under real wastewater conditions, only a few showed high removal (ketoprofen, diclofenac and antipyrine), while several others (particularly antibiotics, e.g. clarithromycin, erythromycin and azithromycin) showed very low degradation due to ultraviolet irradiation, even at doses above 2700 mJ/cm². Consequently, Noutsopoulos et al. (2013c) concluded that with the application of the low-pressure ultraviolet doses generally adopted for pathogen removal (10–80 mJ/cm²), no significant removal should be expected for many emerging contaminants. Based on this study, the endocrine disruptors bisphenol A and nonylphenol and the non-steroidal anti-inflammatory drugs ibuprofen and naproxen showed a low degradability even at doses as high as 1000 mJ/cm², confirming the results of previous studies (Rosenfeldt and Linden 2004; Vogna et al. 2004; Chen et al. 2006, Pereira et al. 2007a, b; Canonica et al. 2008; Yuan et al. 2009; Rosario-Ortiz et al. 2010; Baeza and Knappe 2011; Salgado et al. 2011; Pablos et al. 2012). The moderate effect of ultraviolet has also been confirmed by Bennett et al. (2018) for estrogens. The authors suggested that the complete degradation of estrogens could only be achieved at ultraviolet doses (500–100 mJ/cm²) much higher than those used for pathogen removal. As concluded by many researchers (Kim et al. 2009a; Yuan et al. 2009; Pablos et al. 2013; Noutsopoulos et al. 2013a), the structure of each chemical as well as its physical characteristics (i.e. decadal molar absorption coefficient at 254 nm wavelength) largely govern its sensitivity to degradation. Studies of ultraviolet radiation transformation by-products on emerging contaminants are rather limited (Salgado et al. 2013; Bennett et al. 2018) and the hypothesis that photodegradation intermediates may be more recalcitrant or toxic than parent compounds has therefore yet to be fully demonstrated. Several modifications have been suggested in order to improve the efficiency of ultraviolet irradiation such as the use of medium-pressure lamps (Kim et al. 2009a; Pereira et al. 2017) or the ultraviolet based advanced oxidation processes such as UV/H₂O₂, UV/Cl₂ and VUV/O₃ (Kruithof et al. 2007; Yuan et al. 2009; Xiang et al. 2016; Lian et al. 2017). For example, full-scale application of ultraviolet combined with hydrogen peroxide in an existing water treatment plant in North Holland for a running time of more than 2 years has proven that this practice was effective and reliable to control organic micropollutants (Kruithof et al. 2007). The UV/H₂O₂ process was installed between the sand filtration and granular activated carbon filtration processes. Substances such as mecoprop and diclofenac were removed by 98%, while the removal of the other compounds (pesticides) varied from 60% to 91%. Carbon filters could effectively remove residual hydrogen peroxide and at least conceptually, also any by-products formed in the oxidation process, as well as assim-

lable organic carbon that can feed microbes in biofilm formed within the water distribution lines.

Ozonation Ozone is a very active oxidant and therefore a very effective germicide. It has been widely demonstrated that ozone has a remarkable ability to eliminate not only bacteria and viruses, but also pathogenic protozoa, compared to chlorine and chlorine dioxide. Ozone is produced on site and an ozonation unit consists of the air compressor, including cooling, drying and filtration accessories, the ozone generator, the contact tank for ozonation and the waste gas destruction device. Due to the high cost of the method and the high doses required in the wastewater, compared to natural water treatment, ozonation was not considered before an attractive method for wastewater disinfection and its use was limited to water disinfection. However, after having corroborated its ability to remove emerging contaminants as well as its well-known disinfection performance, ozonation has received much attention over the last decade, especially in cases where specific provisions for the removal of emerging contaminants through wastewater treatment have been regulated (e.g. the Swiss Water Protection Act).

Ozone reacts either through its molecular form (O_3) or through the activity of hydroxyl radicals that are formed during its decomposition reactions in water. The ozone molecule reacts effectively with many compounds, especially those containing aromatic rings, unsaturations or heteroatoms, while hydroxyl radicals are powerful non-selective oxidants. Ozone tends to react preferentially with the hydrophobic fractions of organic compounds such as hydrophobic acid and neutral species. The effectiveness of ozonation is affected by several parameters such as temperature, pH, presence of organic compounds (e.g. chemical oxygen demand), natural organic matter, total suspended solids, nitrates, nitrites, etc. For example, it has been proposed that nitrites act as a radical scavenger, inhibiting the effectiveness of ozonation (Lee and von Gunten 2010). Several studies have been reported on the effectiveness of ozonation in removing emerging contaminants, although the majority of these studies use pure water rather than a wastewater matrix (Gehr et al. 2003; Xu et al. 2002; Huber et al. 2003, 2004, 2005a, b; Ternes et al. 2003; Kim et al. 2004; Larsen et al. 2004; Deborde et al. 2005; Irmak et al. 2005; Westerhoff et al. 2005; Buffle et al. 2006; Ikehata et al. 2006; Snyder et al. 2006; Wert et al. 2007; Benner et al. 2008; Dantas et al. 2008; Gagnon et al. 2008; Maniero et al. 2008; Coelho et al. 2009; Dodd et al. 2009; Lin et al. 2009; Leitner and Roshani 2010; Rosal et al. 2010a, b; Schaar et al. 2010; Stalter et al. 2011; Tay et al. 2010; Thompson et al. 2011; Zimmermann et al. 2011; Altmann et al. 2012, 2014; Lee and von Gunten 2012, 2016; Mawhinney et al. 2012; Reungoat et al. 2012; Kovalova et al. 2013; Lee et al. 2013, 2014; Snyder et al. 2006; Margot et al. 2013; Ahmed et al. 2017; Sun et al. 2017; Bourgin et al. 2018; Lacson et al. 2018; Paucar et al. 2018; Thanekar et al. 2018; Wang et al. 2018a).

Gagnon et al. (2008) studied the degradation of anti-inflammatory and anti-convulsant drugs in treated wastewater from a primary wastewater treatment plant in Montreal using ozonation. The analytical monitoring of treated wastewater before

disinfection revealed concentrations ranging from 42 to 2556 ng/L for several pharmaceutical residues such as salicylic acid, clofibric acid, ibuprofen, naproxen, triclosan, carbamazepine, diclofenac, and 2-hydroxy-ibuprofen. After treatment, most of these substances were eliminated at a rate greater than 50% at an ozone dose of 10 mg/L. Higher elimination rates (up to 70%) were observed when 20 mg/L of ozone was used. The pilot projects carried out by the authors demonstrated that disinfection processes were a potential complementary method to degrade pharmaceutical residues still present after biological treatment.

Snyder et al. (2006) also reported that in drinking water and wastewater experiments, the majority of estrogenic and androgenic steroids, pharmaceuticals, pesticides and industrial chemicals were eliminated by more than 90% in exposures to ozone commonly used for disinfection. Ozone has proven to be very effective in removing the majority of emerging trace substances from water. Pilot-scale experiments also demonstrated that for compounds that are highly resistant to ozone oxidation, such as atrazine, iopromide, meprobamate and tris-chloroethylphosphate, the removal performance was less than 50%. The addition of hydrogen peroxide for advanced oxidation was not very beneficial for contaminant removal compared to ozone alone. In addition, ozone and ozone combined with hydrogen peroxide have been shown to eliminate estrogenicity *in vitro*.

According to extensive data in the literature, ozone has a high reactivity with pesticides, estrogens, endocrine disruptors, beta-blockers and many non-steroidal anti-inflammatory drugs and parabens, while a lower elimination capacity has been recorded for some antidepressants, antiepileptics, benzotriazoles, perfluorooctane-sulfonic acids and perfluorooctanoic acids. Several researchers have postulated that decomposition of emerging contaminants is lower when using real water matrices and especially wastewater (Ternes et al. 2003; Lee and von Gunten 2010), rather than pure water, due to the presence of several parameters that could interfere with process performance. Recently, Kim et al. (2020) proposed new empirical models to predict ozonation kinetics and micropollutant reduction during ozonation. A disadvantage of the method is associated with the low mineralization obtained in some cases, which can lead to the production of reaction by-products that may exhibit stronger refractory behavior and possibly toxicity. Stalter et al. (2010a, b) provided some ecotoxicological evidence of increased toxicity following ozonation. Conversely, Nasuhoglu et al. (2018) showed a decrease in estrogenic and androgenic activity of 98% and 68%, respectively, while anti-estrogenic activity remained unchanged. Several changes have been proposed to improve the efficiency of ozonation, such as the adoption of advanced ozone-based oxidation processes such as catalytic ozonation, O_3/H_2O_2 , O_3/UV , O_3/TiO_2 , ultrasonication aided ozonation, etc. (Comes et al. 2017).

In view of the above, it is anticipated that through wastewater disinfection an appreciable removal of emerging contaminants can be achieved, therefore adding on their total abatement in wastewater treatment plants (when the removal through primary and secondary treatment is taken into consideration as well). Among different disinfection methods, chlorination and ozonation seem to provide better results, with regard to emerging contaminants removal, while ultraviolet as stand-alone

disinfection method (without being upgraded to ultraviolet assisted advanced oxidation process) exhibit rather moderate performance. In order to guarantee satisfactory removal capacities, for as much as possible chemicals, high doses should be applied for all disinfection methods which exceed the ones that are typically used for the removal of pathogens. Further research is needed in order to conclude about the possible toxic characteristics of alternative disinfection methods by-products compared to those of their parent compounds. Conclusively, when disposal of treated wastewater in low dilution water streams (e.g. streams, rivers, lakes, shallow marine waters) is practiced or wastewater reuse is desirable (e.g. for agricultural use), the use of wastewater disinfection is mandatory to ensure a microbiologically acceptable water content. Optimizing disinfection methods to provide the removal of pathogens and the reduction of the emerging contaminant load that is released to the aquatic environment appears to be technologically feasible.

1.7.2 Emerging Contaminants in Industrial Wastewaters: Electrochemical, Photochemical and Ultrasonic Technologies for Their Removal

For the scientific community, it is of great interest not only to study the presence of emerging substances in aqueous compartments (e.g. in terms of identification, quantification, behavior), but also to propose simple, adequate and effective methodologies for their elimination. Indeed, there is an urgent need for effective tertiary treatments capable of eliminating pharmaceuticals in biologically treated wastewater. This research theme is of particular interest to many research groups, as detailed below.

Advanced oxidation processes represent one of the most promising strategies for the removal of emerging contaminants present in wastewater treatment effluents. Although advanced oxidation processes use different reagent systems, all techniques are based on the generation of reactive oxygen species such as the hydroxyl radical, which is a non-selective and very powerful oxidizing agent, used not only to degrade organic and inorganic substances but also to inactivate biological agents such as pathogenic microorganisms. Several types of advanced oxidation processes are presented in Fig. 1.9. The technology can improve biodegradability, enhance color removal, degrade and mineralize recalcitrant molecules, and reduce toxicity. Advanced oxidation processes are potential techniques for industrial wastewater treatment (e.g. removal of pollutants from pulp and paper and textile industry), and for drinking water production (to remove pathogens and organic compounds in combination with an adsorption step). Conventional municipal wastewater treatment plants have serious shortcomings that can also be addressed by advanced oxidation processes. However, these systems are not yet widely used in industry, mainly because of their high cost to treat large volume of effluents. The principles, performances, advantages, drawbacks and applications of advanced oxidation processes

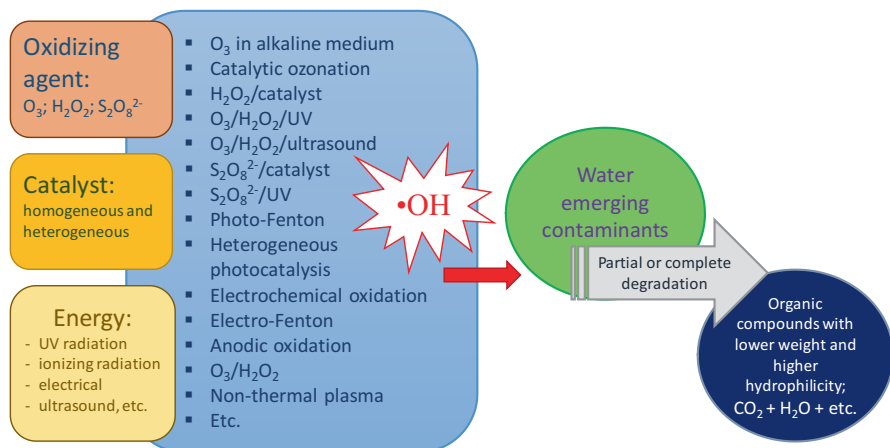


Fig. 1.9 Various types of advanced oxidation processes for wastewater treatment. (Source: Corina Bradu, Bucharest, Romania)

are detailed in numerous reviews (Ikehata et al. 2008; Yang et al. 2013; Oturan and Aaron 2014; Fernández-Castro et al. 2015; Ribeiro et al. 2015; de Araújo et al. 2016; Mishra et al. 2017; Moreira et al. 2017; Miklos et al. 2018; Syam Babu et al. 2019; Wang and Zhuan 2020).

Among the many advanced oxidation processes studied for the elimination of non-biodegradable compounds (the so-called refractory compounds), electrochemical, photochemical, photocatalytic and ultrasonic technologies are subject to particular attention. These technologies use single or combined methods (e.g. electro-Fenton, photo-electro-Fenton, sono-electrolysis etc.) in homogeneous (e.g. photo-Fenton: $Fe^{2+}/H_2O_2/UV$) or heterogeneous systems (heterogeneous photocatalysis: $TiO_2/H_2O_2/UV$; anodic oxidation or photo-electrocatalysis). Different energy sources and catalysts are employed. The heterogeneous catalysis is often preferred to the homogeneous processes, due to the easier recovery of the catalyst. According to the energy source, there are three sub-types of processes, those using: (i) UV radiation (O_3/UV , H_2O_2/UV , $O_3/H_2O_2/UV$, or photo-Fenton $Fe^{2+}/H_2O_2/UV$); (ii) ultrasound energy ($O_3/ultrasound$, $H_2O_2/ultrasound$) and (iii) electrical energy (electrochemical oxidation, anodic oxidation and electro-Fenton).

The general aspects of Fenton and photo-Fenton processes, electrochemical oxidation processes and sonochemistry were recently published by Ameta et al. (2018), by Radha and Sirisha (2018) and by Torres-Palma and Serna-Galvis (2018), respectively. Briefly, the Fenton process, based on the Fenton reagent, uses H_2O_2 and an iron soluble salt, generating hydroxyl radicals at atmospheric pressure and room temperature. High efficiency, relatively cheap reagents, no need of energy to activate H_2O_2 and the consequent easy implementation and operation are the advantages of such treatment. Some disadvantages are the generation of a secondary waste (sludge) and the narrow range of optimal pH (2.5–3.0). The photo-assisted Fenton process can be more efficient than Fenton alone, mainly due to the faster

regeneration of Fe^{2+} . Other related options are electro-Fenton, where Fe^{2+} is produced from sacrificial cast iron anodes, or even photo-electro-Fenton. Heterogeneous photocatalysis is another process that has been extensively investigated for water/wastewater treatment and is based on the use of wide band-gap semiconductors which generate electrons and holes (and subsequent chain reactions including hydroxyl radicals) when irradiated with photons of energy higher than the semiconductor band-gap. The most widely used photocatalyst is TiO_2 , due to its outstanding activity, photochemical stability, good band gap energy, low cost and relatively low toxicity. Nevertheless, a drawback of the photo-assisted processes is the limited thickness of the water layer that is effectively penetrated by the UV radiation. Therefore, to increase the treatment efficiency shallow bed reactors should be used. These methods (Fenton process, photo-Fenton process, photocatalysis, ozonation-based processes) have been commonly studied, while others such as electrochemical technologies and sonolysis are less applied but deserve special attention in the literature.

Advanced oxidation processes methods constitute a potential additional (secondary or tertiary) treatment for the elimination of pharmaceuticals, for example in wastewaters from the cities of Bogotá and Medellín (Colombia), due to their high elimination percentages. A chemical wastewater treatment using advanced oxidation processes may ideally produce the complete mineralization of organic pollutant, generating H_2O , CO_2 and other inorganic substances, or at least their transformation into more innocuous by-products. For example, the partial degradation of non-biodegradable organic substances can lead to biodegradable intermediates. For this reason, advanced oxidation processes can be used as pre-treatments before biological processes in a wastewater treatment plant. The electrochemical advanced oxidation processes have also been proposed for the degradation of pesticides and dyes, for the degradation of organic pollutants from wastewater and for water disinfection. Advantages often cited are: ease operation, high efficiency with possibility to mineralize compounds, no sludge production, possible coupling with other process, low temperature required for its operation, and possibility to use solar panel to decrease the energy consumption. Electrochemical technologies emerge also as a good alternative to carry out the *on-site* generation of disinfectant agents from the species naturally contained in wastewater. These technologies can be applied as a pre-treatment to transform recalcitrant compounds in biological wastewaters or in post-treatment before their discharge. However, until now most studies are conducted at laboratory scale and under controlled conditions. Further research and operational and investment costs assessment are necessary for scale-up new electrochemical technologies.

Promising results using electrochemical, photochemical/photocatalytic and sonochemical processes have been published by Torres-Palma and collaborators (Giraldo et al. 2015; Serna-Galvis et al. 2016, 2019; Jojoa-Sierra et al. 2017; Valero et al. 2017; Villegas-Guzman et al. 2017; Torres-Palma and Serna-Galvis 2018). The authors studied the degradation of the antibiotic oxacillin in water by anodic oxidation with Ti/IrO_2 anodes using an undivided stirred tank reactor (Giraldo et al. 2015). By using the best electrolyte and current density, complete oxacillin removal

and total loss of antimicrobial activity was achieved after only 4 min of treatment and with low energy consumption. The degradation route and kinetics were indeed strongly affected by the supporting electrolyte (NaHCO_3 , Na_2SO_4 , NaCl or NaNO_3). Direct pathway was the most important route when NaHCO_3 and Na_2SO_4 were used as supporting electrolytes. In presence of NaNO_3 , basic hydrolysis also contributed to the elimination of the pollutant. In the case of NaCl , the best supporting electrolyte, degradation *via* chlorinated oxidative species (mainly HOCl) was the most important route. The efficiency in the oxacillin degradation was not significantly affected by the initial pH (in the pH range of 3–9). Unfortunately, no mineralization was observed even after long exposure times (8 h). However, a decrease of 70% of the initial chemical oxygen demand was obtained and the level of biodegradability increased from 0.03 to 0.84, indicating that the system was able to transform the pollutant into highly oxidized and more biodegradable products with less antimicrobial activity. Additionally, different substances and radical scavengers present in wastewaters and natural water (glucose, isopropanol, and inorganic species) did not significantly affect the efficiency of the process. Finally, the more relevant initial aromatic by-products were identified and a degradation pathway of the electrochemical oxidation of the oxacillin antibiotic was proposed. Giraldo et al. (2015) concluded that electrochemical oxidation had a high potential to eliminate antibiotics.

In another work, Serna-Galvis and co-workers demonstrated that high frequency ultrasound in the presence of additives was a selective and efficient advanced oxidation process to remove penicillinic antibiotics and to eliminate its antimicrobial activity from water (Serna-Galvis et al. 2016). The ultrasound is a sound wave with frequencies above 18 kHz and therefore cannot be heard by human ear. There are ultrasounds of high frequency, mainly used for medical applications, and ultrasounds of low frequency or power ultrasound, responsible for the phenomenon of cavitation. The sonochemical degradation of oxacillin was studied in simulated pharmaceutical wastewater. Oxacillin was transformed into by-products without antimicrobial activity and sonotreated water was completely mineralized using a subsequent biological process. Experiments showed that the antimicrobial activity was eliminated after 120 min of treatment and additives such as mannitol, calcium carbonate or their combination did not affect the sonochemical abatement of antimicrobial activity in terms of efficiency. A sonodegradation mechanism of oxacillin was proposed based on the evolution of four main by-products identified and their chemical structure. The identified by-products showed that the attack of the hydroxyl radical modified the penicillinic nucleus, which is the moiety responsible for the activity of the antibiotic. Although the ultrasound action also degraded part of by-products, the process was unable to achieve mineralization of the initial pollutant, even after a long period of ultrasonic irradiation (360 min). Nevertheless, the mineralization of the organic pollutants was completed through a subsequent biological treatment with a non-adapted microorganism from a municipal wastewater treatment plant. These results showed that the sonochemical treatment transformed the initial pollutant into substances that are biotreatable with a typical aerobic biological system. The authors concluded that the combination of a biological system with

a sonochemical process was a promising alternative for the remediation of water containing oxacillin and other pharmaceutical additives.

Torres-Palma's group also studied the degradation of isoxazolyl penicillins by photo-Fenton, photocatalysis and ultrasound. The three processes achieved total removal of the antibiotic and antimicrobial activity, and increased the biodegradability level of the solutions (Villegas-Guzman et al. 2017). However, significant differences concerning the mineralization extent was observed depending on solution pH, chemical nature of additives (water matrix characteristics) and contaminant concentration. With TiO₂ photocatalysis almost complete mineralization was reached, while ~10% mineralization was obtained for photo-Fenton and practically zero for ultrasound activated process. Photo-Fenton and ultrasound processes were improved in acidic media (pH = 3), while natural pH favored TiO₂ photocatalysis system. Bicarbonate and oxalic acid also improved photo-Fenton and ultrasound processes, respectively. According to both the nature of the added organic compound (e.g. glucose, 2-propanol and oxalic acid) and the pH of the process, inhibition, no effect or enhancement of the degradation rate was observed. The degradation in natural mineral water showed contrasting results according to the antibiotic concentration: ultrasound process was enhanced at low concentration of dicloxacillin followed by detrimental effects at high substrate concentrations. A contrary effect was observed during photo-Fenton, while TiO₂ photocatalysis was inhibited in all of cases (Villegas-Guzman et al. 2017).

In another work, Torres-Palma's group investigated the elimination of the antibiotic norfloxacin in municipal wastewater, urine and seawater by electrochemical oxidation on Ti/IrO₂ anodes (Jojoa-Sierra et al. 2017). This treatment was able to eliminate antimicrobial activity and the pollutant in all matrices. However, the results showed that matrices such as seawater or municipal wastewater containing chloride or bicarbonate ions exhibited a better degradation rate, while nitrate ions or urea, found in urine, reduced the efficiency of the process. Concerning the pH, the efficiency of the process in the presence of chloride ions followed the order: 9.0 > 7.5 > 6.5 > 3.0, showing a strong dependence on the antibiotic speciation. Anionic antibiotic form was more easily degraded than the zwitterionic and cationic forms. The antibiotic degradation occurred through both direct elimination at the electrode surface and mediated oxidation, *via* the electrogeneration of oxidative agents, such as active chlorine species and percarbonate ions, which came from chloride and bicarbonate oxidation, respectively. The mechanism of by-product formation was also studied to understand the efficiency of the technology to eliminate norfloxacin and its associated antimicrobial activity in complex matrices. The identification of three primary norfloxacin by-products demonstrated that the initial attack of the active chlorine species, mainly HOCl, occurred at the secondary amine of the piperazine ring followed by chlorination of the benzene ring.

Torres-Palma's group also demonstrated that electrochemical advanced oxidation was a pertinent approach for *Staphylococcus aureus* disinfection in municipal wastewater treatment plants (Valero et al. 2017). *Staphylococcus aureus* is a facultative anaerobic, Gram-positive, coccoid bacterium, which has the capacity to colonize almost every tissue of the human body, causing different diseases. Pathogenic

organisms can be found in municipal effluents at relatively high concentration since the elimination of microbes is not an objective of conventional wastewater treatment plants. Thus, antibiotic-resistant pathogens and their genes can be easily spread through wastewaters. The results published by Valero et al. (2017) showed that the photo-electro-Fenton process led to a bacterial reduction of -0.9 log units and a dissolved organic carbon reduction of 14%, while -5.2 log units of bacteria and 26% of dissolved organic carbon were removed by using the photo-electro-Fenton process. The increase in current intensity in the photoelectro-Fenton system augmented the production of H_2O_2 , resulting in increased bacterial inactivation. However, mineralization extent slightly increased or remained practically the same. When comparing the influence of Fe^{2+} and Fe^{3+} on photo-electro-Fenton, similar *Staphylococcus aureus* inactivation was observed, while dissolved organic carbon removal was higher with Fe^{2+} (31%) than with Fe^{3+} (19%). This water disinfection technology is of interest because in the reclamation of municipal wastewater, a disinfection stage is always required to obtain a high quality effluent, as established by the Colombian legislation.

The degradation of seventeen contaminants of emerging concern in real effluents from the municipal wastewater treatment plant of Bogotá by sonochemical advanced oxidation processes, was studied by Serna-Galvis et al. (2019). The municipal water treatment plant operates at $4\text{ m}^3/\text{s}$, about $350,000\text{ m}^3/\text{day}$, with a removal efficiency of 40% biological oxygen demand and 60% of suspended solids. However, it is not efficient to completely remove emerging contaminants, as confirmed by a previous work of the same research group (Botero-Coy et al. 2018). Analytical monitoring of the effluents showed the presence of several pharmaceuticals with variable concentrations, in the range of $0.01\text{--}2\text{ }\mu\text{g/L}$ (Serna-Galvis et al. 2019). Among the substances, the antihypertensives (valsartan, losartan) were those at the highest concentrations followed by a cocaine metabolite (benzoylecgonine), an anti-inflammatory (diclofenac) and the antibiotics ciprofloxacin and norfloxacin. The obtained results confirmed that ultrasound water treatment is an efficient alternative method for the treatment of these emerging contaminants present in low concentrations in the effluent of the municipal wastewater of Bogotá treatment plant. For example, after 30 min of treatment the concentration of sulfamethoxazole, an antibiotic used to treat a variety of bacterial infections, notably diminished from 0.37 to $0.14\text{ }\mu\text{g/L}$. The ultrasonic system complemented with iron (II), UVA light and oxalic acid presented a strong potential for the contaminant elimination in real and complex effluents. The main disadvantage of the method is however the high consumption of electrical energy.

Martínez-Pachón et al. (2019) studied the advanced oxidation of antihypertensives losartan and valsartan by photo-electro-Fenton at near-neutral pH using natural organic acids and a dimensional stable anode-gas diffusion electrode system under light emission diode lighting. Valsartan and losartan are used in the treatment of hypertension diseases, and are considered among the emerging contaminants that are difficult to treat. In their experiments, organic acids as citric, tartaric and oxalic acids were used as complexing agents of iron ions in order to maintain the performance of the Fenton reaction at near-neutral pH value. The authors showed that

after 90 min of electro-Fenton treatment using the optimized conditions, a degradation of 70% of valsartan and 100% of losartan were achieved. The total degradation of the two antihypertensives was achieved with a photo-electro-Fenton for the same time period. The degradation performance was attributed to the increase of the initial dissolved iron in the system in the presence of the organic ligands, facilitating the $\text{Fe}^{3+}/\text{Fe}^{2+}$ turnover in the catalytic photo-Fenton reaction and consequently, hydroxyl radical production. The increased photo-activity of the complexes was also associated with their high capability to complex Fe^{3+} and to promote ligand-to-metal charge transfer, which was of key importance to feed Fe^{2+} to the Fenton process. The results showed that the system evaluated was more efficient to eliminate sartan family compounds using light emission diode lighting in comparison with traditional UV-A lamps used in this type of works. Moreover, three transformation products of valsartan degradation and two transformation products of losartan degradation were identified by high-resolution mass spectrometry using hybrid quadrupole-time-of-flight mass spectrometry. The several organic compounds still present at the end of the photo-electro-Fenton treatment were effectively treated in a subsequent aerobic biological system (Martínez-Pachón et al. 2019).

The review of the literature related to wastewater treatment issue revealed that the electrochemical, photochemical and ultrasonic based technologies have a tremendous power to degrade emerging pollutants such as antibiotics, although some processes are not capable to completely mineralize the organic pollutants. The two main advantages of these advanced oxidation processes are: (i) the oxidizing species are generated *in situ* (no need of chemicals storage and handling) and (ii) most of processes (except the Fenton type) do not require a rigorous control of solution pH. Other advantages are: operation control simplicity, reactor design compactness, adaptability of the technology to various organic loads of wastewater and effectiveness in disinfection. For the electrochemical treatment, one of the main challenges to its successful implementation for industrial application is to reduce energy consumption and cost (including the cost of electrodes). Another important challenge is to improve the understanding of the reaction mechanisms and in particular to identify potential toxic intermediates. It is also important to improve the long-term stability and electrolytic efficiency of the materials. In this respect, progress is expected from the application of nanotechnologies.

1.7.3 Carbon Nanomaterials in Catalytic Ozonation of Emerging Contaminants

An effective technology to destroy organic emerging contaminants is catalytic ozonation. This treatment uses a catalyst to decompose ozone into a number of strong oxidant radicals such as $\cdot\text{OH}$ (Wang et al. 2016c). These radicals quickly oxidize organic compounds (Fig. 1.10).

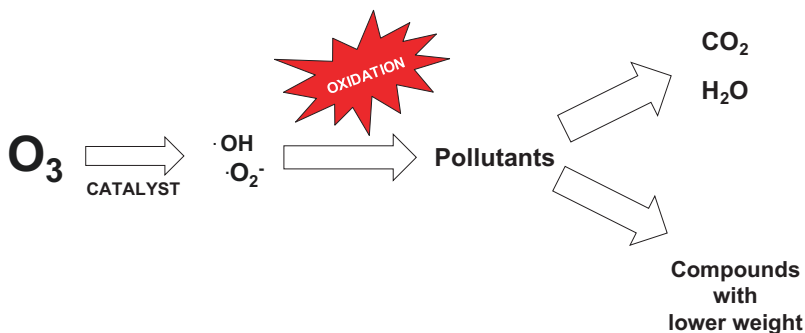


Fig. 1.10 Radical pathway of catalytic ozonation process. (Source: Mohammad Mahmudul Huq, Saskatoon, Canada)

The principal component of a catalytic ozonation process is the catalyst. These catalysts could primarily be categorized into two: homogenous or heterogeneous. Homogeneous catalysts are water soluble metal salts which are not recoverable after an ozonation process, thus their application involves chemical costs as well as further pollution. On the contrary, heterogeneous catalysts are solid particles that can be recovered, regenerated and reused. Numerous works have reported different kinds of materials as catalysts in water treatment processes, namely metal oxides, activated carbon and carbon nanomaterials (Restivo et al. 2012, 2013, 2016; Rocha et al. 2015; Wang et al. 2016b, c). Many reports have shown superior performance of metal oxide-based catalysts. However, these catalysts can be subject to metal leaching into effluent water (Rocha et al. 2015). Consequently, increasingly more research effort has been made for the development of metal-free catalyst. Among metal-free catalysts, carbon materials such as activated carbon, multi-walled carbon nanotubes, graphene oxide and reduced-graphene oxide are the most studied ones. These materials have been studied both as sole catalysts and as support materials. This section focuses fundamentally on the studies that concern application of carbon-based nanomaterials (i.e. multi-walled carbon nanotubes, graphene oxide and reduced-graphene oxides) both as catalysts and catalyst support materials in catalytic ozonation processes.

Among carbon nanomaterials, multi-walled carbon nanotubes are the most widely studied catalyst for ozonation processes due to their strong catalytic activity and re-usability. Multi-walled carbon nanotubes were first reported as catalyst in ozonation process by Liu et al. (2009). These materials achieved 80% conversion of oxalic acid in 40 min as compared to around 2% conversion by non-catalytic ozonation. The authors also studied the catalytic performance of oxidized multi-walled carbon nanotubes. For this purpose, nanotubes were oxidized by pre-ozonation treatment at various degrees. This pre-ozonation treatment implanted different acidic groups (such as $-COOH$, $-OH$, etc.) on catalyst surface leading to inferior performance of multi-walled carbon nanotubes. The catalytic activity decrease can be attributed to the negative charge generated by the acidic groups which causes a

drop of pH_{pzc} value nearly to the pH of oxalic acid aqueous solution. This leads to less adsorption of anion species of oxalic acid, eventually to less degradation of oxalic acid during catalytic ozonation.

In a similar study, Gonçalves et al. (2010) investigated the role of surface chemistry of multi-walled carbon nanotubes on catalytic ozonation of oxalic acid. This study gave a very similar picture as the previous one in which the surface acidic sites hinder multi-walled carbon nanotubes' catalytic ability. The authors also compared the performances of multi-walled carbon nanotubes with those of commercial activated carbon, concluding that multi-walled carbon nanotubes are more effective catalysts since they impose less internal mass transfer limitations on the reactants during the catalytic ozonation reaction. A catalytic reaction is mass transfer limited when the participating reactants experience mass transfer resistance inside micro-pores before reaching the active sites. Activated carbons possess a large quantity of micro-pores, which is likely to impose significant mass transfer resistance. On the other hand, multi-walled carbon nanotubes barely possess any micro-pores. The same research group compared the catalytic performance of commercial multi-walled carbon nanotubes with that of activated carbon in catalytic oxidative degradation of sulfamethoxazole, an antibiotic (Gonçalves et al. 2013). In terms of sulfamethoxazole degradation, catalytic ozonation with multi-walled carbon nanotubes was comparable to non-catalytic ozonation. Nevertheless, catalytic ozonation led to higher degree of mineralization expressed as total organic carbon removal. Surprisingly, activated carbon showed superior catalytic activity compared to multi-walled carbon nanotubes in terms of total organic carbon removal. This result was ascribed to the fact that sulfamethoxazole is more readily adsorbed in micro-pores and not to its oxidative degradation. The authors also studied the toxicity effects of sulfamethoxazole oxidation by-products by Microtox® bioassays. It was found that the lowest toxicity is achieved when the ozonation was carried on in the presence of multi-walled carbon nanotubes.

Restivo et al. (2012) studied the activity of multi-walled carbon nanotubes in the ozonation of metolachlor, an herbicide. The use of the carbon based material did not show much improvement of the single ozonation process in the removal of target pollutant. Both catalytic and non-catalytic oxidation products of metolachlor showed higher toxicity when compared to the toxicity of non-treated metolachlor, as shown by Microtox® bioassay test. However, the end-products were found less toxic with catalytic ozonation when compared to the non-catalytic ozonation. The degradation of atrazine (an herbicide) by multi-walled carbon nanotubes catalyzed ozonation was found to be somewhat slower (lower apparent reaction rate constant) than single ozonation (Fan et al. 2014). Nevertheless, in terms of total organic carbon and toxicity reduction, catalytic ozonation was found superior.

One of the main research directions in this field is to improve the catalytic activity of carbon nanotubes by modifying their surface chemistry and specific surface area by different methods (e.g. heteroatom-doping, oxidation, grinding, etc.). Qu et al. (2015) studied carboxylated carbon nanotubes in catalytic ozonation of indigo. The modified nanotubes showed higher indigo removal in terms of indigo concentration, total organic carbon and toxicity removal. Yet, this study is inconclusive as

it did not compare the results with those obtained with pristine carbon nanotubes. Soares et al. (2015) improved multi-walled carbon nanotubes' catalytic performance by increasing their specific surface area by shortening their tube size. This size reduction was achieved by ball-milling. The ball-milled multi-walled carbon nanotubes showed fairly improved performance in catalytic ozonation of oxalic acid.

Rocha et al. (2015) showed that reduced graphene oxide works as a catalyst in ozonation of oxalic acid. Catalytic ozonation with reduced-graphene oxide turned out to be 50% more efficient in the pollutant removal than non-catalytic ozonation (for 120 min reaction time). Wang et al. (2016b) used reduced-graphene oxide as catalyst for ozonation of p-hydroxybenzoic acid when nearly full mineralization of p-hydroxybenzoic acid was achieved in 60 min. This study identified carbonyl groups as the active sites and suggested that superoxide radicals (O_2^-) and singlet oxygen ($^1\text{O}_2$) are the dominant species responsible for p-hydroxybenzoic acid degradation. Graphene oxide, the parent material of reduced-graphene oxide, can also be catalytically active in many reactions as its surface is rich in oxygen functional groups. For instance, the ozonation of N,N-diethyl-m-toluamide, a widely used pesticide, in the presence of graphene oxide was investigated by Liu et al. (2016). This process showed increased removal of the target pollutant as compared to non-catalytic ozonation. But lack of mineralization data raises doubts on its applicability.

Ahn et al. (2017) showed that over-oxidized graphene oxide produces significantly higher amounts of $\cdot\text{OH}$ than graphene oxide or reduced-graphene oxide, which is likely to lead to higher removal of recalcitrant organics. Song et al. (2019b) studied both graphene oxide and reduced-graphene oxide as catalysts for catalytic ozonation of p-chlorobenzoic acid and benzotriazoles. They found graphene oxide more efficient in degrading p-chlorobenzoic acid while reduced-graphene oxide showed higher activity in the case of benzotriazole. However, the authors noted that graphene oxide suffers from gradual degradation during the catalytic ozonation process. This deterioration of graphene oxide material is most likely caused by corrosive attack of ozone or $\cdot\text{OH}$ (Radich et al. 2014). In an extensive study, Wang et al. (2018c) synthesized reduced-graphene oxide starting from graphite from used lithium ion battery. The obtained material showed higher removal of oxalic acid than commercially reduced-graphene oxide. A strong correlation between the amount of defective sites on reduced-graphene oxide and its catalytic activity was found. This correlation was again justified by density functional theory calculations.

Heteroatom doping of graphene oxide and of reduced-graphene oxide can significantly improve their catalytic activity. N, B, P and S have been studied as dopants for reduced-graphene oxides. Rocha et al. (2015) doped reduced-graphene oxide with N from different nitrogen precursors such as melamine and urea. This doping process implanted three N containing functionalities into the reduced-graphene oxide namely, pyridinic, pyrrolic and quaternary-N. The improved performance of the N-doped reduced-graphene oxide in mineralizing oxalic acid and phenol was attributed to these functional groups which are said to work as active centers. Moreover, these N-functional groups increase the pH_{PZC} , making the material more positively charged at the pH of oxalic acid solution (3.0). This enables

increased adsorption of oxalate anions (which is the dissociated form of oxalic acid at pH of 3.0), favoring its catalytic surface reaction. This could also explain the lack of improvement in the phenol degradation, which is found in molecular form at the aqueous solution pH (pK_a around 10).

Bao et al. (2016) also confirmed improved catalytic ozonation performance of N-doped reduced-graphene oxide. Yin et al. (2017) showed catalytic ozonation using N and P doped reduced-graphene oxides is far more efficient than non-catalytic ozonation in the degradation of sulphamethoxazole. Wang et al. (2019a, b) used a novel microwave method to dope N into reduced-graphene oxide. This method generates higher amounts of N-doping that eventually leads to higher removal of 4-nitrophenol and oxalic acid. The improved performance of this microwave method was attributed to the higher degree of graphene oxide reduction and generation of more defects and carbon dangling bonds.

In a very detailed study, Song et al. (2019a) synthesized and tested N, P, B and S-doped reduced-graphene oxide or catalytic ozonation degradation of p-chlorobenzoic acid and benzotriazole. They also studied bromate (BrO_3^-) elimination capacities of these processes. Bromates are carcinogenic by-products of many ozonation processes. Although P-doped reduced-graphene oxides showed the fastest elimination of both p-chlorobenzoic acid and benzotriazole, the authors concluded that in terms of normalized pseudo-first order reaction constant (k_{obs}), N-doped reduced-graphene oxide shows the fastest removal. The normalization was done by dividing the k_{obs} by atomic percentage of the corresponding heteroatoms in each of the as prepared reduced-graphene oxide. On the other hand, S-doped reduced-graphene oxide is found to be unstable as it increases the total organic carbon content of the aqueous solution during the catalytic ozonation process.

Wang et al. (2018b) doped multi-walled carbon nanotubes with F using HF as F precursor. The materials showed significantly increased catalytic activity in ozonation of oxalic acid as compared to N-doped multi-walled carbon nanotubes. Highly electronegative active sites like N and O are inferred to decompose ozone by nucleophilic attack. Interestingly, this study showed that an excessive doping of electronegative atoms is counter productive. Nevertheless, given the difficulty in handling highly toxic HF, F doping may not be feasible at commercial level.

Usually, catalytically active metals and metal oxides are deposited on porous materials such as alumina, zeolite, activated carbon, silica and various metal oxides (Ghughe and Saroha 2018). Carbon nanomaterials such as multi-walled carbon nanotubes and graphene oxide/reduced-graphene oxides have also been used as support materials because of their excellent compatibility with metals and metal oxides, resistance to adverse environment, mechanical strength and excellent electron transfer ability (Lin et al. 2011; Khan et al. 2015). Studies have also shown synergy between active catalyst materials and these carbon materials (Sampaio et al. 2015). This synergy has been exploited in a few catalytic ozonation studies as well.

The greatest number of works deals with the synthesis of supported manganese and iron oxides and their use in the oxidative degradation of emerging pollutants such as pesticides and pharmaceuticals (Sui et al. 2012; Li et al. 2015; Bai et al. 2017; Wang et al. 2016a). Sui et al. (2012) synthesized a MnO_x /multi-walled carbon

nanotube composite for catalytic ozonation of ciprofloxacin, a persistent antibacterial agent. MnO_x /multi-walled carbon nanotube showed 87.5% ciprofloxacin removal in 15 min as opposed to 40.2% removal with unsupported MnO_x and 26.7% removal with non-catalytic ozonation. Li et al. (2015) reported the synthesis of a sea urchin-like α - MnO_2 /reduced-graphene oxide composite for catalytic ozonation of bisphenol A. The process showed significantly higher bisphenol A removal efficiency compared to that with pristine α - MnO_2 , pristine reduced-graphene oxide and non-catalytic ozonation. The authors concluded that reduced-graphene oxide is inactive in catalytic ozonation of bisphenol A. Wang et al. (2016a) synthesized γ - MnO_2 /reduced-graphene oxide composite for catalytic ozonation of 4-nitrophenol, showing improved degradation and mineralization compared to non-catalytic ozonation. Prepared γ - MnO_2 /reduced-graphene oxide showed improved performance over commercial MnO_2 . Wang et al. (2019a) prepared a CeO_2 /oxidized-carbon nanotube composite for catalytic ozonation of phenol. The composite catalyst achieved nearly 100% total organic carbon removal in 60 min with virtually no activity loss up to 5 cycles. Depositing reduced-graphene oxide on metal oxide can also be fruitful as shown by Ren et al. (2018). In this report, MnFe_2O_4 nano-fiber catalyst was improved by reduced-graphene oxide doping.

Overall, catalytic ozonation processes with carbon nanomaterial-based catalysts offer the following advantages: (i) higher degree of organic pollutant degradation as compared to activated carbon catalysts (ii) minimal metal leaching issue and (iii) compatibility under a wide range of conditions. However, the separation method of catalyst from treated water is an important issue to be addressed before technology scale-up for industrial application.

1.7.4 Non-thermal Plasma: A New Candidate Water Treatment for the Removal of Emerging Contaminants

Growing interest in finding effective solutions for the removal of emerging contaminants from water led to the investigation of unconventional water treatment methods. Among them, non-thermal plasma is a promising approach and is now considered the youngest member of the so-called advanced oxidation processes family. Recently, significant research efforts were devoted to enhancing the efficiency of plasma treatment of water contaminated with harmful organic pollutants such as pharmaceuticals and pesticides (Magureanu et al. 2018). The efforts are directed to elaborate technical and economical feasible solution, but also to bring new insight from the point of view of reaction mechanism and final characteristics and quality of the treated water.

Non-thermal plasma can be generated directly in the liquid or in the gas phase. Plasmas in contact with water are very complex systems, which produce a diversity of molecular, ionic and radical reactive species responsible for the degradation of organic pollutants. In these systems, the generation of reactive species is initiated by the collision of highly energetic electrons (formed by the electrical discharge) with

the gas constituents and water molecules (in the gas phase, or at the gas-liquid interface). The nature of active species and their availability in the liquid phases depend on the plasma reactor configuration (e.g. corona, dielectric barrier discharges, gliding arc, plasma jet etc.), on the discharge characteristics, solution properties and gas composition (Park et al. 2013). A number of reactive oxygen species and reactive nitrogen species have been detected in gas and liquid phase of the cold plasma discharge systems, such as: $\bullet\text{OH}$, $\text{HO}_2\bullet$, H_2O_2 , $\text{O}\bullet$, $\bullet\text{O}_2^-$, O_3 , $\bullet\text{NO}$, $\bullet\text{NO}_2$, NO_2^- , NO_3^- , ONO_2^- etc. (Lukes et al. 2012; Locke et al. 2012; Bruggeman et al. 2016).

Ozone, hydrogen peroxide and hydroxyl radical are the most investigated reactive oxygen species in the plasmas in contact with water systems. Numerous studies deal with the identification and quantification of these three species by different spectrophotometric and chromatographic methods (Ono and Oda 2002; Park et al. 2006; Xiong et al. 2015; Guo et al. 2019a; Kanazawa et al. 2013; Marotta et al. 2011; Lukes et al. 2004; Bilea et al. 2019).

The hydroxyl radical is a key reactive oxygen species, considered to be the main actor in the oxidative degradation of organic pollutants. It is actually the species that makes the plasma process to be framed as an advanced oxidation process. Due to its short lifetime, $\bullet\text{OH}$ interacts with organic pollutants very near the gas-water interface (Kanazawa et al. 2011; Marotta et al. 2011; Ajo et al. 2015). In the bulk liquid phase, hydrogen peroxide, a stable molecular reactive oxygen species, is formed mainly by recombination of hydroxyl radicals (Locke and Shih 2011). The accumulation of H_2O_2 in water during the plasma treatment was highlighted by numerous works (Locke and Shih 2011; Magureanu et al. 2016; Bradu et al. 2017; Bilea et al. 2019). The production and loss mechanisms of $\bullet\text{OH}$ in discharges formed over water are discussed in detail in (Bruggeman and Schram 2010). The radical recombination reaction leading to stable molecular species may limit the process effectiveness (Locke et al. 2012). However, the hydrogen peroxide is a potential source of hydroxyl radicals, which could be used judiciously. For instance, H_2O_2 decomposition with the regeneration of $\bullet\text{OH}$ radicals could be promoted by an adequate catalyst. Indeed, numerous research groups report advantages of the combined plasma-catalytic oxidation process in the degradation of recalcitrant pollutants in water (Parvulescu et al. 2012; Jović et al. 2014; He et al. 2014; Hama Aziz et al. 2018; Guo et al. 2019a). The proposed catalysts are soluble transitional metal salts (e.g. Fe^{2+} , Fe^{3+} , Mn^{2+} and Co^{2+} salts) (Dojčinović et al. 2011; Jović et al. 2014) or heterogeneous catalysts (e.g. TiO_2 , activated carbon and graphene based materials) (He et al. 2015; Hama Aziz et al. 2018, Vanraes et al. 2015, 2017; Guo et al. 2019a, b, c).

Another long-lived species generated in non-thermal plasma in oxygen-containing gaseous atmosphere is ozone. Appreciable O_3 concentrations were detected in the gas phase of electrical discharges in contact with water (Lukes et al. 2005; Marotta et al. 2011; Magureanu et al. 2016). However, ozone diffusion across the gas-liquid interface is limited and its concentration in water is often under the detection limit of employed analytical methods (Marotta et al. 2011; Dobrin et al. 2013; Magureanu et al. 2016). Nevertheless, the transfer of plasma generated O_3 from the gas to the liquid could be improved to facilitate its reaction with the target

organic pollutants or their degradation by-products (both by direct: involving molecular ozone attack; and indirect path-way: involving $\bullet\text{OH}$). In this respect, plasma-ozonation systems were proposed (Magureanu et al. 2016; Bradu et al. 2017). In this case, the water to be treated is continuously circulated between the two reactors: a plasma reactor (in which the electrical discharge is produced over water surface) and second reactor in which the effluent gas from the plasma reactor was bubbled into the aqueous solution (Fig. 1.11). With this combined plasma-ozonation system faster removal of the target compound (e.g. methylparaben and herbicide 2,4-D) and higher degree of mineralisation was obtained compared to the single plasma or ozonation processes. The improvement was attributed to the

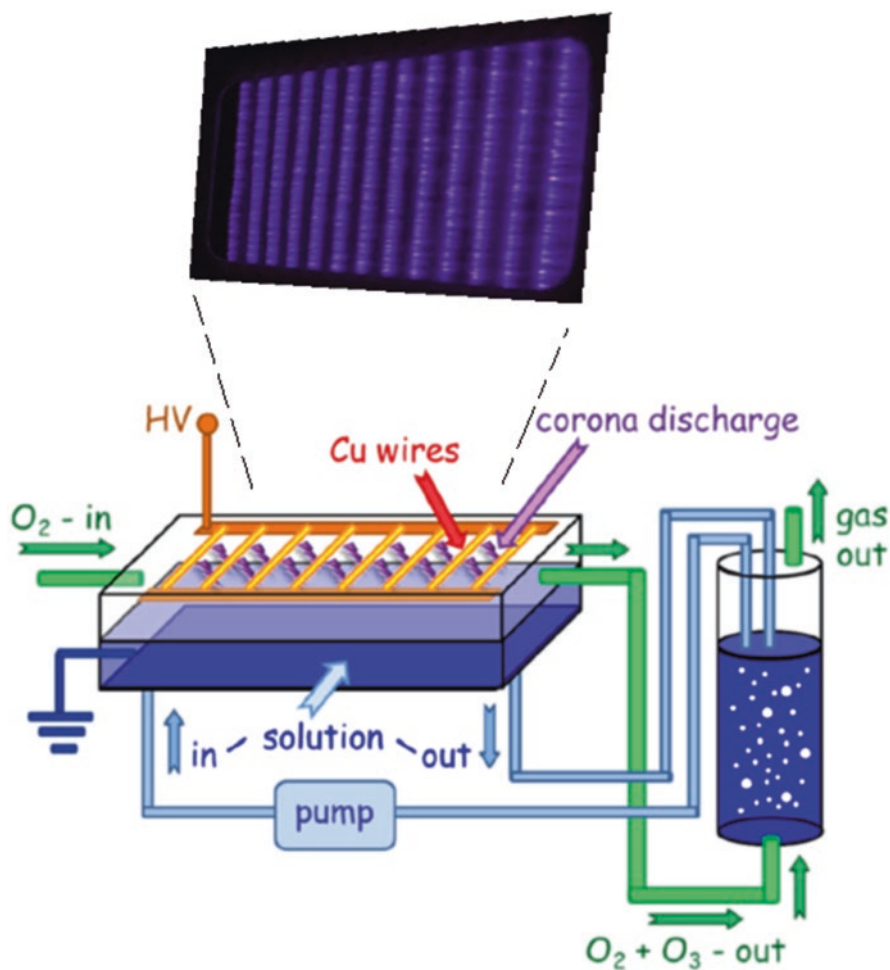


Fig. 1.11 Experimental set-up for plasma-ozonation system. (Monica Magureanu, Magurele, Romania)

enhanced transfer of O_3 in the water and its further interaction with the H_2O_2 accumulated in solution, leading to increased generation of $\bullet OH$ (peroxone reaction).

When non-thermal plasma is generated in air, beside reactive oxygen species, reactive nitrogen species can be formed in significant amounts. Nitric oxide ($\bullet NO$) is an important secondary species, produced through the interaction of the parent (N_2) and/or primary species ($N\bullet$, $O\bullet$, $\bullet OH$) in gas phase. In further reactions, $\bullet NO$ can effectively fix oxygen atoms through the interaction with $O\bullet$ or with O-donor species produced in the discharge (e.g. O_3 and $HO_2\bullet$) to form nitrogen dioxide ($\bullet NO_2$) (Brisset and Pawlat 2016; Aritoshi et al. 2002). In humid air and in the aqueous phase, the formation of nitrous and nitric acids (HNO_2 and HNO_3) takes place. The presence of peroxyxynitrous acid ($ONOOH$) in water was also reported. It was suggested that this peroxy-acid is produced in the reaction between nitrous acid and hydrogen peroxide (reaction favoured in acidic pH), or *via* the reaction between dissolved nitric and nitrous oxides and different radical reactive oxygen species ($\bullet OH$, $HO_2\bullet$ and $\bullet O_2^-$) (Goldstein et al. 2005; Moussa et al. 2007; Lukes et al. 2012; Tian and Kushner 2014). The generation of peroxyxynitric acid (O_2NOOH) through the reaction between peroxyxynitrous acid and hydrogen peroxide has also been proposed (Boehm et al. 2018; Ikawa et al. 2016; Nakashima et al. 2016). Thus, a variety of nitrogen-containing species is present in the aqueous phase as well. The reactive nitrogen species accumulation in water depends on their solubility and their lifetime. The dominant species for electrical discharges in contact with water are considered to be the nitrogen oxy- and peroxy-acids and their conjugate ions: HNO_x/NO_x^- (Tian and Kushner 2014). Detailed analysis of the generation, transport and interactions of reactive nitrogen species in plasma in contact with water can be found in (Locke et al. 2012; Bruggeman et al. 2016; Bradu et al. 2020).

Even if the reactive nitrogen species involvement in the organic compounds degradation was less studied, there are solid evidences that these species participate in the degradative oxidation pathway of water pollutants. As an example, nitro-substituted by-products and N,N-dimethyl-nitroaniline have been detected in the degradation of methyl orange in corona discharge in contact with water by Cadornin et al. (2015). It was assumed that the organic molecules interact with peroxyxynitrous acid either directly or indirectly *via* dissociation into $\bullet NO_2$ and $\bullet OH$ (Moussa et al. 2007; Cadornin et al. 2015).

A general scheme for the reactive oxygen species and reactive nitrogen species dynamic in a non-thermal plasma system for water treatment is presented in Fig. 1.12.

A large variety of discharge configurations has been used to produce plasma in liquid or gas-liquid environments, and can be classified into two categories: discharges generated directly in liquid (i.e. with both electrodes submerged in liquid) and discharges generated in the gas phase, in contact with liquid (Bruggeman and Leys 2009; Jiang et al. 2014; Magureanu and Parvulescu 2016; Locke et al. 2012). The early studies on plasma removal of aqueous pollutants addressed mainly organic dyes, due to facile observation of the solution decolorization (Malik et al. 2002; Sugiarto et al. 2003; Burlica et al. 2004; Grabowski et al. 2007; Magureanu et al. 2007, 2008; Stará et al. 2009). An analysis of reported results revealed that the

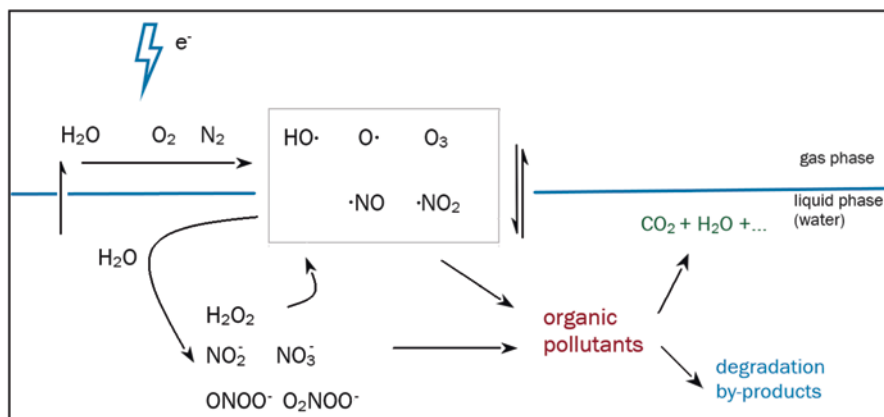


Fig. 1.12 Schematic representation of reactive oxygen species and reactive nitrogen species dynamic for non-thermal plasma in contact with water. (Monica Magureanu, Magurele, Romania; Corina Bradu, Bucharest, Romania)

energy efficiency of the process is significantly higher for the plasma in gas phase as compared to discharges directly in liquid, especially for large surface to volume ratio of the solution to be treated, i.e. in case of thin liquid films or liquid spray (Malik 2010).

Most of the recent studies on plasma degradation of water contaminants have been carried out using electrical discharges generated in gas phase in contact with liquid. Very simple geometries, such as corona, dielectric barrier discharges or gliding arc above liquid, have often been reported for the removal of antibiotics (El Shaer et al. 2020; Smith et al. 2018; Sarangapani et al. 2019; Xu et al. 2020; Zhang et al. 2018; Acayanka et al. 2019) and pesticides (Hijos-Valsero et al. 2013; Hu et al. 2013; Li et al. 2013; Singh et al. 2016, 2017). Since the penetration depth of the plasma-generated reactive species into the solution is very small, in such configurations the volume of plasma-treated solution is generally very small, in the milliliter range (Smith et al. 2018; Zhang et al. 2018; Xu et al. 2020). Smith et al. (2018) reported the complete removal of ampicillin in 1 mL solution of high concentration (20 mM) after only 3 min of treatment with a dielectric barrier discharge above liquid. No information on the discharge power is provided, and thus an evaluation of the degradation efficiency is not possible. If treatment of larger solution volumes is attempted the time required for pollutant removal becomes much longer. Using a pin-to-water corona discharge, El Shaer et al. (2020) obtained almost complete removal of doxycycline with concentration of 50 mg/L in 50 mL water after 90 min treatment, while the degradation of oxytetracycline was even slower. Acayanka et al. (2019) needed 120 min to remove approximately 80% of the initial amoxicillin in 500 mL 0.1 mM aqueous solution using a gliding arc above liquid. Obviously, the treatment time is not an accurate measure of the efficiency of the plasma process, since the degradation depends on a number of factors, such as the molecular structure of the target compound, its concentration, the solution volume

and properties, the gaseous atmosphere, the input power and the discharge characteristics, to name only a few. An example to illustrate the large extent of this influence is the comparison between the above-mentioned results of El Shaer et al. (2020) and the data reported by Singh et al. (2016, 2017), who also used a pin-to-water corona to degrade the pesticides carbofuran and 2,4-D and achieved complete removal within less than 10 min treatment. Information on the energy efficiency of the removal process was provided by Xu et al. (2020), research group that investigated the degradation of norfloxacin (initial concentration 10 mg/L in 10 mL water) by a dielectric barrier discharge. Although fast removal of the antibiotic has been achieved (4 min), the reported efficiency (defined as the amount of pollutant removed per unit of energy consumed in the process) was rather low, i.e. in the range of tens of mg/kWh. The addition of H₂O₂ and Fe²⁺ significantly improved the results, optimum catalyst concentration leading to the reduction of treatment time to 0.5 min. The positive effect of iron catalyst was attributed to the Fenton reaction in the presence of plasma-generated H₂O₂ (Li et al. 2013; Jović et al. 2014; Hama Aziz et al. 2018; Xu et al. 2020).

A comparison between the corona discharge above liquid and a corona generated in gas bubbles inside the solution demonstrated much faster degradation of the target antibiotics in the second case (El Shaer et al. 2020). This discharge geometry, with one or several hollow needles submerged in liquid as high voltage electrode and plasma produced in gas bubbles at the tip of the needles, has been employed by several research groups for the removal of antibiotics, mostly in combination with catalysts (Wang et al. 2018d; Guo et al. 2019a, b, c). A slightly different configuration, with the gas blown through a tube containing the high voltage needle electrode has also been used (He et al. 2014, 2015; Hu et al. 2019). Several authors produce plasma in the gas and bubble the effluent gas through the solution to be treated (Kim et al. 2013; Kim et al. 2015; Lee et al. 2018; Tang et al. 2018a, b, 2019; Wang et al. 2019c; Li et al. 2020). It is unlikely that highly reactive species with short lifetime would reach the liquid, so in this case plasma is simply used as a source of ozone.

Besides the generation of large amounts of reactive species in the plasma, their efficient transfer to the treated liquid is essential for the enhancement of pollutants removal efficiency. This has been demonstrated for instance in the experiments of Acayanka et al. (2019), where the authors compared the degradation of amoxicillin by a gliding arc plasma above the target solution with the results obtained when the solution is sprayed through the discharge region. Faster degradation of the antibiotic has been reported for the spray configuration than in the batch mode (i.e. three times larger rate constant) and 2.5 times higher energy yield. Hijosa-Valsero et al. (2013) have also confirmed the importance of large surface-to-volume area by comparing the removal of several pesticides in water using either a batch dielectric barrier discharge geometry or a dielectric barrier discharge with falling liquid film. The energy efficiency for the removal of atrazine is 10 times higher in the configuration with liquid circulation, while for the insecticides lindane and chlorfenvinfos, it exceeds one order of magnitude. Such more elaborated reactor design has been extensively investigated for the degradation of various pesticides (Hijosa-Valsero et al. 2013; Jović et al. 2013, 2014; Vanraes et al. 2015, 2017; Bradu et al. 2017; Yu et al. 2017;

Hama Aziz et al. 2018) and antibiotics (Magureanu et al. 2011; Rong and Sun 2014; Rong et al. 2014; Xin et al. 2016; Iervolino et al. 2019). Most authors used coaxial geometry, with the liquid pumped upwards through a cylindrical inner electrode and then flowing as a thin film on the outer surface of this tube, thus being in direct contact with plasma. However, planar geometries have also been employed, with the liquid film flowing either horizontally (Xin et al. 2016) or vertically (Hama Aziz et al. 2018) between the electrodes. One of the challenges in the dielectric barrier discharge with falling liquid film is to produce a stable thin film of liquid. Hama Aziz et al. (2018) obtained a homogeneous and stable solution layer of thickness estimated to 150 μm , flowing along large area ($68 \times 29 \text{ cm}$) glass sheets and used this planar dielectric barrier discharge configuration to degrade the herbicide 2,4-D. A comparison between plasma treatment and other advanced oxidation processes from the point of view of the energy yield revealed that the dielectric barrier discharge in combination with Fenton oxidation is the most efficient treatment process, followed in this order by ozonation, plasma alone, photocatalytic ozonation and, at last photocatalysis. Although the good removal efficiency of ozonation is confirmed, the authors mention its major drawback related to low mineralization. For improved degradation of the target compound and its intermediate oxidation products, either photocatalytic ozonation, or plasma combined with Fenton oxidation are recommended (Hama Aziz et al. 2018).

It is now generally accepted that the addition of Fe^{2+} to the plasma treatment significantly improves the removal of aqueous contaminants, another example being the herbicides mesotrione and sulcotrione (Jović et al. 2013; Jović et al. 2014). In this case it has been found that the effect of Fe^{2+} exceeds that of Mn^{2+} and Co^{2+} . The combination of plasma with TiO_2 catalysts also appears successful for pollutants removal. He et al. (2014) reports a considerable rise in the removal rate of the antibiotic tetracycline, from 61.9% to 85.1%, accompanied by the enhancement of total organic carbon removal, from 25.3% with the plasma alone to 53.4% in the presence of TiO_2 .

Another approach to increase the efficiency of pollutants removal by plasma adopted by Vanraes et al. (2015, 2017) is to locally enhance the pollutant concentration in the plasma region. They used a coaxial dielectric barrier discharge with falling film and added an activated carbon textile mesh with extremely large surface area over the inner electrode. This highly adsorptive material was found to significantly contribute to the removal of target compounds in plasma.

A method to improve the mass transfer of the plasma-generated ozone into the treated liquid is to bubble the effluent gas from the plasma through the solution (Gerrity et al. 2010; Magureanu et al. 2011; Bradu et al. 2017). Therefore, as presented earlier, dual plasma-ozonation systems have been developed. Very high energy efficiency has been reported in such systems, either employing dielectric barrier discharge with falling liquid film for the removal of β -lactam antibiotics (reaching 105 g/kWh for amoxicillin) (Magureanu et al. 2011), or with a corona discharge above liquid to degrade the herbicide 2,4-D (5 g/kWh) (Bradu et al. 2017).

One of the most efficient plasma systems reported up to now is based on a pulsed corona reactor similar to an electrostatic precipitator, with the liquid introduced as

droplets or jets through the plasma zone and short high voltage pulses (Panorel et al. 2013; Preis et al. 2013). Energy yields of tens of g/kWh have been achieved in this system for the removal of various pharmaceuticals and these high values have been attributed to the large contact area between the plasma and the liquid (Ajo et al. 2015). This configuration has recently been adapted for the treatment of hospital wastewater at pilot scale (50 L) (Ajo et al. 2018) and tests have been run with promising results for both untreated sewage of a public hospital and for biologically treated wastewater effluent of a healthcare institute.

Another report of a pilot-scale plasma system has been done by Gerrity et al. (2010) using the reactor developed by Aquapure Technologies Ltd. for the degradation of several pharmaceuticals in trace concentrations. The pilot unit contains a plasma reactor, based on a pulsed corona above water, and an ozone contactor which uses the ozone-rich gas from the plasma reactor. The tests have been done on tertiary-treated wastewater and spiked surface water with contaminants concentrations of tens to hundreds of ng/L. Rapid degradation of the target compounds has been demonstrated and the authors concluded that plasma treatment may be a possible alternative to more common advanced oxidation processes, since the energy requirements for pollutants degradation are comparable and no additional feed chemicals are needed.

To increase the performance of non-thermal plasma processes for the degradation of harmful water pollutants, significant research efforts have been focused on the optimisation of the electrical discharge, including reactor design, aimed at improving the energy yield. Numerous studies have been dedicated to the understanding of the process chemistry through investigation of the plasma-generated reactive species, as well as the identification and quantification of the intermediate degradation products.

An issue that requires more attention is the characterisation of the plasma treated water from both chemical and (eco)toxicological points of view. There are only few studies dealing with this complex characterisation and more efforts are needed in order to correctly evaluate the plasma treatment performances. Nevertheless, it is worth mentioning that progress has been made in developing new combined processes such as plasma-ozonation or plasma-catalysis and performing tests on real wastewater effluents (like those from hospitals) at pilot-scale. In this context, non-thermal plasma appears to be a new potential candidate for water treatment used for emerging contaminants removal.

1.8 Conclusion

The remediation of contaminated water in general, and that of emerging substances in particular, is not only a source of concern for our societies, but also a major subject of debate, at both industrial and political levels for all water stakeholders, and of research for scientists. Indeed, emerging substances study and their treatment have become a relevant research topic for scientists focused on water engineering

issues. However, the challenge is not simple, as it is difficult to remove trace contaminants from complex mixtures of substances in a way that is chemically effective, technologically simple, economically viable, and environmentally friendly. In this chapter, we have described advanced treatment methods that have been proposed for this purpose, including wastewater disinfection, adsorption onto conventional or non-conventional materials, constructed wetlands, membrane bioreactors and other biological-based strategies, membrane filtration, and advanced oxidation processes such as electrochemical technologies and catalytic ozonation.

Of the various disinfection methods, chlorination and ozonation appear to give better results in terms of removing both pathogens and emerging contaminants. However, further research is needed to determine the possible toxic characteristics of disinfection by-products compared to their parent compounds. The approach consisting in the use of ozonation and adsorption on activated carbon has been used for about 10 years in countries such as Switzerland and Germany, due to its efficiency, simplicity and technical feasibility at industrial scale, and also for economic reasons. Another feature of these technologies is the fact that they can be easily integrated into existing treatment facilities. One disadvantage is the rapid saturation of the carbon filters, which must then be regenerated. This step is difficult and expensive.

Extensive research on non-conventional adsorbents highlights the growing interest of scientists in developing systems that are increasingly effective in removing mixtures of trace pollutants, simple to implement from a technological point of view, economically viable and environmentally friendly, with little or no impact on the environment. Materials such as cyclodextrin polymers, metal-organic frameworks, molecularly imprinted polymers, chitosan-based materials and nanocelluloses have great potential in environmental applications. However, they are still at the laboratory study stage. Further research is needed to determine the means of integration of these adsorbents into treatment plants.

Biological technologies used for the degradation of new contaminants and the reduction of their negative impact on the environment are also a field of research in full development and significant advances are expected in the future. Biological approaches include constructed wetlands, biomembrane reactors, strategies based on the use of algae, fungi and bacteria, and enzymatic degradation. Membrane filtration is already used as a tertiary treatment capable of removing a wide range of pollutants and pathogens detected in water, but this treatment has not become widespread due in part to its high cost but also to problems of membrane clogging.

Finally, advanced oxidation processes also represent one of the most promising strategies because of their efficiency and simplicity (they can also be integrated into plants as primary, secondary and tertiary methods). Significant advances are expected in the next few years, although here again, investment, operation and maintenance costs must be taken into account. Industrialists will now have to be convinced to use these technologies in their municipal wastewater treatment plants.

What are the prospects for the management of emerging substances? Firstly, increased political measures to tackle pollution at source would help mitigate the impact of pollution. Pollution reduction requires the application of good practices

for water users and industrialists: reduction of industrial discharges, avoid mixing domestic (containing antibiotics) and industrial water (containing metals; recent studies have shown a relationship between the presence of metals and the phenomenon of bacterial resistance), reduction of pesticides and other plant protection products, regulation of soil fertilization, more control or prohibition of hazardous substances, etc. All of this obviously has a cost. Secondly, the implementation of complementary water treatment systems (known as tertiary decontamination) in wastewater treatment plants would make it possible to move towards zero pollution discharge and thus increase the availability of water resources. In addition, the microbiological quality of treated wastewater is a parameter that is increasingly being taken into account. These effluents represent, in some cases, a significant source of contamination by pathogens and/or antimicrobial resistant bacteria for the receiving environment. However, in many countries, most wastewater treatment plants do not apply any disinfection step before the discharge of their water. Finally, wastewater is still an undervalued resource of water, energy, nutrients and other valuable by-products (metals). Recycling, reuse and recovery of what is normally considered waste could alleviate water stress and bring many social, economic and environmental benefits. In this context, advanced oxidation processes combined with biodegradation, adsorption and membrane filtration are promising, effective and environmentally friendly treatments to remove new pollutants and pathogens from wastewater and can be part of wastewater reuse policies, even if their high cost still prevents their widespread use.

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References

- Abargues MR, Ferrer J, Bouzas A, Seco A (2018) Fate of endocrine disruptor compounds in an anaerobic membrane bioreactor (AnMBR) coupled to an activated sludge reactor. *Environ Sci Water Res Technol* 4:226–233. <https://doi.org/10.1039/c7ew00382j>
- Abouzeid RE, Khiari R, El-Wakil N, Dufresne A (2018) Current state and new trends in the use of cellulose nanomaterials for wastewater treatment. *Biomacromolecules* 20:573–597. <https://doi.org/10.1021/acs.biomac.8b00839>

- Abujaber F, Zougagh M, Jodeh S, Ríos A, Javier F, Bernardo G, Martín-Doimeadios RCR (2018) Magnetic cellulose nanoparticles coated with ionic liquid as a new material for the simple and fast monitoring of emerging pollutants in waters by magnetic solid phase extraction. *Microchem J* 137:490–495. <https://doi.org/10.1016/j.microc.2017.12.007>
- Acayanka E, Tarkwa JB, Laminsi S (2019) Evaluation of energy balance in a batch and circulating non-thermal plasma reactors during organic pollutant oxidation in aqueous solution. *Plasma Chem Plasma P* 39:75–87. <https://doi.org/10.1007/s11090-018-9946-7>
- Acero JL, Benitez FJ, Real J, Roldan G (2010) Kinetics of aqueous chlorination of pharmaceuticals and their elimination from water matrices. *Water Res* 44:4158–4170. <https://doi.org/10.1016/j.watres.2010.05.012>
- Acero JL, Benitez FJ, Real FJ, Roldan G, Rodriguez E (2013) Chlorination and bromination kinetics of emerging contaminants in aqueous systems. *Chem Eng J* 219:43–50. <https://doi.org/10.1016/j.cej.2012.12.067>
- Adams C, Wang Y, Loftin K, Meyer M (2002) Removal of antibiotics from surface and distilled water in conventional water treatment processes. *J Environ Eng* 128:253–260
- Adriano WS, Veredas V, Santana CC, Gonçalves LRB (2005) Adsorption of amoxicillin on chitosan beads: kinetics, equilibrium and validation of finite bath models. *Biochem Eng J* 27:132–137. <https://doi.org/10.1016/j.bej.2005.08.010>
- Afzal MZ, Sun X, Liu J, Song C, Wang S, Javed A (2018) Enhancement of ciprofloxacin sorption on chitosan/biochar hydrogel beads. *Sci Total Environ* 639:560–569
- Ahmaruzzaman MD (2008) Adsorption of phenolic compounds on low-cost adsorbents: a review. *Adv Colloid Int Sci* 143:48–67. <https://doi.org/10.1016/j.cis.2008.07.002>
- Ahmed MB, Zhou JL, Ngo HH, Guo W (2015) Adsorptive removal of antibiotics from water and wastewater: Progress and challenges. *Sci Total Environ* 532:112–126. <https://doi.org/10.1016/j.scitotenv.2015.05.130>
- Ahmed I, Iqbal DK (2017) Enzyme-based biodegradation of hazardous pollutants – an overview. *J Exp Biol Agricultural Sci* 5:402–411. [https://doi.org/10.18006/2017.5\(4\).402.411](https://doi.org/10.18006/2017.5(4).402.411)
- Ahmed M, Zhou J, Ngo H, Guo W, Thomaidis N, Xu J (2017) Progress in the biological and chemical treatment technologies for emerging contaminants removal from wastewater: a critical review. *J Hazard Mater* 323:274–298. <https://doi.org/10.1016/j.jhazmat.2016.04.045>
- Ahn Y, Oh H, Yoon Y, Park WK, Yang WS, Kang JW (2017) Effect of graphene oxidation degree on the catalytic activity of graphene for ozone catalysis. *J Environ Chem Eng* 5:3882–3894. <https://doi.org/10.1016/j.jece.2017.07.038>
- Ajo P, Kornev I, Preis S (2015) Pulsed corona discharge in water treatment: the effect of hydrodynamic conditions on oxidation energy efficiency. *Ind Eng Chem Res* 54:7452–7458. <https://doi.org/10.1021/acs.iecr.5b01915>
- Ajo P, Preis S, Vornamo T, Mänttari M, Kallioinen M, Louhi-Kultanen M (2018) Hospital wastewater treatment with pilot-scale pulsed corona discharge for removal of pharmaceutical residues. *J Environ Chem Eng* 6:1569–1577. <https://doi.org/10.1016/j.jece.2018.02.007>
- Aksu Z (2005) Application of biosorption for the removal of organic pollutants: a review. *Process Biochem* 40:997–1026. <https://doi.org/10.1016/j.procbio.2004.04.008>
- Alexander C, Andersson HS, Andersson LI, Ansell RJ, Kirsch N, Nicholls IA, O'Mahony J, Whitcombe MJ (2006) Molecular imprinting science and technology: a survey of the literature for the years up to and including 2003. *J Mol Recognit* 19:106–180
- Ali I (2012) New generation adsorbents for water treatment. *Chem Rev* 112:5073–5091. <https://doi.org/10.1021/cr300133d>
- Ali MEM, Abd El-Aty AM, Badawy MI, Ali RK (2018) Removal of pharmaceutical pollutants from synthetic wastewater using chemically modified biomass of green alga *Scenedesmus obliquus*. *Ecotoxicol Environ Saf* 151:144–152. <https://doi.org/10.1016/j.ecoenv.2018.01.012>
- Almeida CAP, Debacher NA, Downs AJ, Cottet L, Mello CAD (2009) Removal of methylene blue from colored effluents by adsorption on montmorillonite clay. *J Colloid Interf Sc* 332:46–53. <https://doi.org/10.1016/j.jcis.2008.12.012>

- Alonso JSJ, Kori NE, Melian-Martel N, Del Río-Gamero B (2018) Removal of ciprofloxacin from seawater by reverse osmosis. *J Environ Manag* 217:337–345
- Alsaibee A, Smith BJ, Xiao L, Ling Y, Helbling DE, Dichtel WR (2016) Rapid removal of organic micropollutants from water by a porous β -cyclodextrin polymer. *Nature* 529:190–194. <https://doi.org/10.1038/nature16185>
- Alsudir S, Iqbal Z, Lai EPC (2012) Competitive CE-UV binding tests for selective recognition of bisphenol A by molecularly imprinted polymer particles. *Electrophoresis* 33:1255–1262
- Alvarino T, Torregrosa N, Omil F, Lema J, Suarez S (2017) Assessing the feasibility of two hybrid MBR systems using PAC for removing macro and micropollutants. *J Environ Manag* 203:831–837
- Alvaro M, Carbonell E, Ferrer B, Llabrés IXFX, Garcia H (2007) Semiconductor behavior of a metal-organic framework (MOF). *Chem Eur J* 13:5106–5112
- Altmann D, Schaar H, Bartel C, Schorkopf DLP, Miller I, Kreuzinger N, Möstl E, Grillitsch B (2012) Impact of ozonation on ecotoxicity and endocrine activity of tertiary treated wastewater effluent. *Water Res* 46:3693–3702. <https://doi.org/10.1016/j.watres.2012.04.017>
- Altmann J, Ruhl AS, Zietzschmann F, Jekel M (2014) Direct comparison of ozonation and adsorption onto powdered activated carbon for micropollutant removal in advanced wastewater treatment. *Water Res* 55:185–193. <https://doi.org/10.1016/j.watres.2014.02.025>
- Ameta R, Chohadia AK, Jain A, Punjabi PB (2018) Chapter 3: Fenton and photo-Fenton processes. In: *Advanced oxidation processes for waste water treatment*, pp 49–87. <https://doi.org/10.1016/B978-0-12-810499-6.00003-6>
- Anastopoulos I, Pashalidis I, Orfanos AG, Manariotis ID, Tatarchuk T, Sellaoui L, Bonilla-Petriciolet A, Mittal A, Núñez-Delgado A (2020) Removal of caffeine, nicotine and amoxicillin from (waste)waters by various adsorbents. *A Rev J Environ Manag* 261:110236. <https://doi.org/10.1016/j.jenvman.2020.110236>
- Andreozzi R, Raffaele M, Nicklas R (2003) Pharmaceuticals in STP effluents and their solar photodegradation in aquatic environment. *Chemosphere* 50:1319–1330. [https://doi.org/10.1016/S0045-6535\(02\)00769-5](https://doi.org/10.1016/S0045-6535(02)00769-5)
- Aoki N, Kinoshita K, Mikuni K, Nakanishi K, Hattori K (2007) Adsorption of 4-nonylphenol ethoxylates onto insoluble chitosan beads bearing cyclodextrin moieties. *J Inclusion Phenomena Macrocyclic Chem* 57:237–241. <https://doi.org/10.1007/s10847-006-9190-2>
- Aritoshi K, Fujiwara M, Ishida M (2002) Production and removal mechanisms of discharge NO_x treatment in N₂/O₂ gas mixture. *Jpn J Appl Phys* 41:3936–3942. <https://doi.org/10.1143/JJAP.41.3936>
- Asano T, Burton FL, Leverenz HL, Tsuchihashi R, Tchobanoglous G (2007) *Water reuse: issues, technologies, and applications*. McGraw Hill, Metcalf Eddy Inc. AECO, New York. ISBN: 978-0-007-145927-3
- Asif MB, Hai FI, Singh L, Price WE, Nghiem LD (2017) Degradation of pharmaceuticals and personal care products by white-rot-fungi – a critical review. *Cur Pollut Rep* 3:88–103. <https://doi.org/10.1007/s40726-017-0049-5>
- Badia-Fabregat M, Lucas D, Gros M, Rodríguez-Mozaz S, Barceló D, Caminal G, Vicent T (2015) Identification of some factors affecting pharmaceutical active compounds (PhACs) removal in real wastewater. Case study of fungal treatment of reverse osmosis concentrate. *J Hazard Mater* 283:663–671
- Baeza C, Knappe DR (2011) Transformation kinetics of biochemically active compounds in low-pressure UV photolysis and UV/H₂O₂ advanced oxidation processes. *Water Res* 45:4531–4543. <https://doi.org/10.1016/j.watres.2011.05.039>
- Bai X, Acharya K (2017) Algae-mediated removal of selected pharmaceutical and personal care products (PPCPs) from Lake Mead water. *Sci Total Environ* 581–582:734–740. <https://doi.org/10.1016/j.scitotenv.2016.12.192>
- Bai Z, Yang Q, Wang J (2017) Catalytic ozonation of dimethyl phthalate using Fe₃O₄/multi-wall carbon nanotubes. *Environ Technol* 38:2048–2057. <https://doi.org/10.1080/09593330.2016.1245360>

- Baille WE, Huang WQ, Nichifor M, Zhu XX (2000) Functionalized β -cyclodextrin polymers for the sorption of bile salts. *J Macromol Sci A* 37:677–690. <https://doi.org/10.1081/ma-100101117>
- Bao Q, Hui KS, Duh JG (2016) Promoting catalytic ozonation of phenol over graphene through nitrogenation and Co_3O_4 compositing. *J Environ Sci* 50:38–48. <https://doi.org/10.1016/j.jes.2016.03.029>
- Barbosa MO, Moreira NFF, Ribeiro AR, Pereira MFR, Silva AMT (2016) Occurrence and removal of organic micropollutants: an overview of the watch list of EU Decision 2015/495. *Water Res* 94:257–279. <https://doi.org/10.1016/j.watres.2016.02.047>
- Basile T, Petrella A, Petrella M, Boghetich G, Petruzzelli V, Colasuonno S, Petruzzelli D (2011) Review of endocrine-disrupting-compound removal technologies in water and wastewater treatment plants: an EU perspective. *Ind Eng Chem Res* 50:8389–8401. <https://doi.org/10.1021/ie101919v>
- Batt AL, Aga DS (2005) Simultaneous analysis of multiple classes of antibiotics by ion trap LC/MS/MS for assessing surface water and ground water contamination. *Anal Chem* 77:2940–2947
- Beall GW (2003) The use of organo-clays in water treatment. *Appl Clay Sci* 24:11–20. <https://doi.org/10.1016/j.clay.2003.07.006>
- Bedia J, Muelas-Ramos V, Peñas-Garzón M, Gómez-Avilés A, Rodríguez JJ, Bolver C (2019) A review on the synthesis and characterization of metal organic frameworks for photocatalytic water purification. *Catalysts* 9:52. <https://doi.org/10.3390/catal9010052>
- Bedner M, MacCrehan WA (2006) Transformation of acetaminophen by chlorination produces the toxicants 1,4-benzoquinone and n-acetyl-pbenzoquinone imine. *Environ Sci Technol* 40:516–522. <https://doi.org/10.1021/es0509073>
- Bedoya-Ríos DF, Lara-Borrero JA (2018) Occurrence of endocrine disruptor chemicals in the urban cycle of Colombia. In: Ahmed RG (ed) *Endocrine disruptors*. IntechOpen. <https://doi.org/10.5772/intechopen.78325>
- Bekçi Z, Seki Y, Yurdakoç MK (2006) Equilibrium studies for trimethoprim adsorption on montmorillonite KSF. *J Hazard Mater* 133:233–242. <https://doi.org/10.1016/j.jhazmat.2005.10.029>
- Bekçi Z, Seki Y, Yurdakoç MK (2007) A study of equilibrium and FTIR, SEM/EDS analysis of trimethoprim adsorption onto K10. *J Mol Struct* 827:67–74. <https://doi.org/10.1016/j.molstruc.2006.04.054>
- BelBruno JJ (2019) Molecularly imprinted polymers. *Cehm Rev* 119:94–119. <https://doi.org/10.1021/acs.chemrev.8b00171>
- Belgiorno V, Rizzo L, Fatta D, Della Rocca C, Lofrano G, Nikolaou A, Naddeo V, Meric S (2007) Review on endocrine disrupting-emerging compounds in urban wastewater: occurrence and removal by photocatalysis and ultrasonic irradiation for wastewater reuse. *Des* 215:166–176. <https://doi.org/10.1016/j.desal.2006.10.035>
- Benner J, Salhi E, Ternes T, von Gunten U (2008) Ozonation of reverse osmosis concentrate: kinetics and efficiency of beta blocker oxidation. *Water Res* 42:3003–3012. <https://doi.org/10.1016/j.watres.2008.04.002>
- Bennett JL, Mackie AL, Park Y, Gagnon GA (2018) Advanced oxidation processes for treatment of 17[beta]-estradiol and its metabolites in aquaculture wastewater. *Aquacultural Eng* 83:40
- Benotti M, Trenholm R, Vanderford B, Holady J, Stanford B, Snyder S (2009a) Pharmaceuticals and endocrine disrupting compounds in U.S drinking water. *Environ Sci Technol* 43:597–603. <https://doi.org/10.1021/es801845a>
- Benotti MJ, Stanford BD, Wert EC, Snyder SA (2009b) Evaluation of a photocatalytic reactor membrane pilot system for the removal of pharmaceuticals and endocrine disrupting compounds from water. *Water Res* 43:1513–1522. <https://doi.org/10.1016/j.watres.2008.12.049>
- Besha AT, Gebreyohannes AY, Tufa RA, Bekele DN, Curcio E, Giorno L (2017) Removal of emerging micropollutants by activated sludge process and membrane bioreactors and the effects of micropollutants on membrane fouling: a review. *J Environ Chem Eng* 5:2395–2414
- Bhattacharyya KG, Gupta SS (2008) Adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite: a review. *Adv Colloid Int Sci* 140:114–131. <https://doi.org/10.1016/j.cis.2007.12.008>

- Bhattarai B, Manickavachagam M, Suri R (2012) Development of novel cyclodextrin adsorbents for the removal of emerging contaminants from water. In: Abstracts of papers, 244th ACS national meeting and exposition, Philadelphia, 19–23 August 2012, ENV-5
- Bilal M, Adeel M, Rasheed T, Zhao Y, Iqbal HMN (2019a) Emerging contaminants of high concern and their enzyme-assisted biodegradation – a review. *Environ Int* 124:336–353. <https://doi.org/10.1016/j.envint.2019.01.011>
- Bilal M, Rasheed T, Nabeel F, Iqbal HMN, Zhao YP (2019b) Hazardous contaminants in the environment and their laccase-assisted degradation – a review. *J Environ Manag* 234:253–264. <https://doi.org/10.1016/j.jenvman.2019.01.001>
- Bilea F, Bradu C, Mandache NB, Magureanu M (2019) Characterization of the chemical activity of a pulsed corona discharge above water. *Chemosphere* 236:124302. <https://doi.org/10.1016/j.chemosphere.2019.07.033>
- Bodzek M (2019) Membrane separation techniques - removal of inorganic and organic admixtures and impurities from water environment - review. *Arch Environ Protection* 45:4–19. <https://doi.org/10.24425/aep.2019.130237>
- Boehm D, Curtin J, Cullen PJ, Bourke P (2018) Hydrogen peroxide and beyond-the potential of high-voltage plasma activated liquids against cancerous cells. *Anti Cancer Agents Med Chem* 18:815–823. <https://doi.org/10.2174/1871520617666170801110517>
- Bolong N, Ismail AF, Salim MR, Matura T (2009) A review of the effects of emerging contaminants in wastewater and options for their removal. *Des* 239:229–246. <https://doi.org/10.2016/j.desal.2008.03.20>
- Borea L, Ensano BMB, Hasan SW, Balakrishnan M, Belgiorno V, de Lun DG, Ballesteros FC Jr, Nadeo V (2019) Are pharmaceuticals removal and membrane fouling in electromembrane bioreactor affected by current density? *Sci Total Environ* 692:732–740. <https://doi.org/10.1016/j.scitotenv.2019.07.149>
- Botero-Coy AM, Martínez-Pachón D, Boix C, Rincón RJ, Castillo N, Arias-Marín NL, Manrique-Losada L, Torres-Palma R, Moncayo-Lasso A, Hernández F (2018) An investigation into the occurrence and removal of pharmaceuticals in wastewater Colombian. *Sci Total Environ* 642:842–853. <https://doi.org/10.1016/j.scitotenv.2018.06.088>
- Bourgin M, Beck B, Boehler M, Borowska E, Fleiner J, Salhi E, Teichler R, von Gunten U, Siegrist H, McDardell CS (2018) Evaluation of a full-scale wastewater treatment plant upgraded with ozonation and biological post-treatments: abatement of micropollutants, formation of transformation products and oxidation by-products. *Water Res* 129:486–498. <https://doi.org/10.1016/j.watres.2017.10.036>
- Bradu C, Magureanu M, Parvulescu VI (2017) Degradation of the chlorophenoxyacetic herbicide 2,4-D by plasma-ozonation system. *J Hazard Mater* 336:52–56. <https://doi.org/10.1016/j.jhazmat.2017.04.050>
- Bradu C, Kutasi K, Magureanu M, Puač N, Živković S (2020) Reactive nitrogen species in plasma-activated water: generation, chemistry and application in agriculture. *J Phys D: Appl Phys* 53:223001. <https://doi.org/10.1088/1361-6463/ab795a>
- Braga FG, Pinto S, Antunes MCG (2011) Comparative study of 17 β -estradiol removal from aqueous solutions using pine bark and almond shell as adsorbents. *Microchim Acta* 173:111–117. <https://doi.org/10.1007/s00604-010-0531-x>
- Brisset JL, Pawlat J (2016) Chemical effects of air plasma species on aqueous solutes in direct and delayed exposure modes: discharge, post-discharge and plasma activated water. *Plasma Chem Plasma Process* 36:355–381. <https://doi.org/10.1007/s11090-015-9653-6>
- Bruggeman P, Leys C (2009) Non-thermal plasmas in and in contact with liquids. *J Phys D Appl Phys* 42:053001. <https://doi.org/10.1088/0022-3727/42/5/053001>
- Bruggeman P, Schram DC (2010) On OH production in water containing atmospheric pressure plasmas. *Plasma Sources Sci Technol* 19:45025. <https://doi.org/10.1088/0963-0252/19/4/045025>
- Bruggeman PJ, Kushner MJ, Locke BR, Gardeniers JGE, Graham WG, Graves DB, Hofman-Caris RCHM, Maric D, Reid JP, Ceriani E, Fernandez Rivas D, Foster JE, Garrick SC, Gorbanev Y, Hamaguchi S, Iza F, Jablonowski H, Klimova E, Kolb J, Krca F, Lukes P, Machala Z,

- Marinov I, Mariotti D, Mededovic Thagard S, Minakata D, Neyts EC, Pawlat J, ZLj P, Pflieger R, Reuter S, Schram DC, Schröter S, Shiraiwa M, Tarabová B, Tsai PA, JRR V, von Woedtke T, Wilson KR, Yasui K, Zvereva G (2016) Plasma-liquid interactions: a review and roadmap. *Plasma Sources Sci Technol* 25:053002. <https://doi.org/10.1088/0963-0252/25/5/053002>
- Buffe M, Schumacher J, Salhi E, Jekel M, von Gunten U (2006) Measurement of the initial phase of ozone decomposition in water and wastewater by means of continuous quench flow system: application of disinfection and pharmaceutical oxidation. *Water Res* 40:1884–1894. <https://doi.org/10.1016/j.watres.2006.02.026>
- Burlica R, Kirkpatrick MJ, Finney WC, Clark RJ, Locke BR (2004) Organic dye removal from aqueous solution by glidarc discharges. *J Electrostat* 62:309–321. <https://doi.org/10.1016/j.elstat.2004.05.007>
- Bulloch DN, Lavado R, Forsgren KL, Beni S, Schlenk D, Larive CK (2012) Analytical and biological characterization of halogenated gemfibrozil produced through chlorination of wastewater. *Environ Sci Technol* 46:5583–5589. <https://doi.org/10.1021/es3006173>
- Cadorin BM, Tralli D, Ceriani E, de Brito Benetoli LO, Marotta E, Ceretta C, Debacher NA, Paradisi C (2015) Treatment of methyl orange by nitrogen non-thermal plasma in a corona reactor: the role of reactive nitrogen species. *J Hazard Mater* 300:754–764. <https://doi.org/10.1016/j.jhazmat.2015.08.009>
- Canonica S, Meunier L, von Gunten U (2008) Phototransformation of selected pharmaceuticals during UV treatment of drinking water. *Water Res* 42:121–128
- Cantarella M, Carroccio S, Dattilo S, Avolio R, Castaldo R, Puglisi C, Privitera V (2019) Molecularly imprinted polymer for selective adsorption of diclofenac from contaminated water. *Chem Eng J* 367:180–188. <https://doi.org/10.1016/j.cej.2019.02.146>
- Cantarella M, Impellizzeri G, Privitera V (2017) Functional nanomaterials for water purification. *Riv Nuovo Cimento* 40:595–632
- Castiglioni S, Bagnati R, Fanelli R, Pomati F, Calamari D, Zuccato E (2006) Removal of pharmaceuticals in sewage treatment plants in Italy. *Environ Sci Technol* 40:357–363. <https://doi.org/10.1021/es050991m>
- Charles J, Crini G, Morin-Crini N, Badot PM, Trunfio G, Sancey B, de Carvalho M, Bradu C, Avramescu S, Winterton P, Gavaille S, Torri G (2014) Advanced oxidation (UV-ozone) and cyclodextrin sorption: effects of individual and combined action on the chemical abatement of organic pollutants in industrial effluents. *J Taiwan Institute Chem Eng* 45:603–608. <https://doi.org/10.1016/j.jtice.2013.06.023>
- Chen PJ, Linden KG, Hinton DE, Kashiwada S, Rosenfeldt EJ, Kullman SW (2006) Biological assessment of bisphenol A degradation in water following direct photolysis and UV advanced oxidation. *Chemosphere* 65:1094–1102. <https://doi.org/10.1016/j.chemosphere.2006.04.048>
- Chen HW, Liang CH, Wu ZM, Lin TF, Chiang PC, Wang GS (2013) Occurrence and assessment of treatment efficiency of nonylphenol, octylphenol and bisphenol A on drinking water in Taiwan. *Sci Total Environ* 449:20–28. <https://doi.org/10.1016/j.scitotenv.2013.01.038>
- Chen W, Xue M, Xue F, Mu X, Xu Z, Meng Z, Zhu G, Shea KJ (2015) Molecularly imprinted hollow spheres for the solid phase extraction of estrogens. *Talanta* 140:68–72
- Chen L, Wang X, Lu W, Wu X, Li J (2016a) Molecular imprinting: perspectives and applications. *Chem Soc Rev* 45:2137
- Chen J, Wei XD, Liu YS, Ying GG, Liu SS, He LY, Su HC, Hu LX, Chen FR, Yang YQ (2016b) Removal of antibiotics and antibiotic resistance genes from domestic sewage by constructed wetlands: optimization of wetland substrates and hydraulic loading. *Sci Total Environ* 565:240–248. <https://doi.org/10.1016/j.scitotenv.2016.04.176>
- Chung YC, Chen CY (2009) Competitive adsorption of a phthalate esters mixture by chitosan bead and α -cyclodextrin-linked chitosan bead. *Environ Technol* 30:1343–1350. <https://doi.org/10.1080/09593330902858914>
- Coelho AD, Sans C, Agüera A, Gómez MJ, Esplugas S, Dezotti M (2009) Effects of ozone pre-treatment on diclofenac: intermediates, biodegradability and toxicity assessment. *Sci Total Environ* 407:3572–3578. <https://doi.org/10.1016/j.scitotenv.2009.01.013>

- Collivignarelli MC, Abbà A, Benigna I, Sorlini S, Torretta V (2018) Overview of the main disinfectin processes for wastewater and drinking water treatment plants. *Sustainability* 10:86. <https://doi.org/10.3390/su10010086>
- Comes J, Costa R, Quinta-Ferreira RM, Martins RC (2017) Application of ozonation for pharmaceuticals and personal care products removal from water. *Sci Total Environ* 586:265–283. <https://doi.org/10.1016/j.scitotenv.2017.01.216>
- Couto OM, Matos I, da Fonseca IM, Arroyo PA, da Silva EA, de Barros MASD (2015) Effect of solution pH and influence of water hardness on caffeine adsorption onto activated carbons. *Can J Chem Eng* 93:68–77. <https://doi.org/10.1002/cjce.22104>
- Crini (2005) Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment. *Prog Polym Sci* 30:38–70. <https://doi.org/10.1016/j.progpolymsci.2004.11.002>
- Crini G (2006) Non-conventional low-cost adsorbents for dye removal. *Bioresour Technol* 97:1061–1085. <https://doi.org/10.1016/j.biortech.2005.05.001>
- Crini G (2010) Chapter 2: Wastewater treatment by sorption. In: Sorption processes and pollution. PUFC, Besançon, pp 39–78
- Crini G (2014) Review: a history of cyclodextrins. *Chem Rev* 114:10940–10975. <https://doi.org/10.1021/cr500081p>
- Crini G (2015) Non-conventional adsorbents for dye removal. In: Sharma SK (ed) *Green chemistry for dyes removal from wastewater*. Scrivener Publishing LLC, pp 359–407
- Crini G, Badot PM (2007) *Traitement et épuration des eaux industrielles polluées* (in French). Presses Universitaires de Franche-Comté, France, Besançon. ISBN 978-2-84867-197-0
- Crini G, Badot PM (2010) Sorption processes and pollution. Presses Universitaires de Franche-Comté, France, Besançon. ISBN 978-2-84867-304-2
- Crini G, Morcellet M (2002) Synthesis and applications of adsorbents containing cyclodextrins. *J Sep Sci* 25:789–813. [https://doi.org/10.1002/1615-9314\(20020901\)25:13<789::aid-jssc789>3.0.co;2-j](https://doi.org/10.1002/1615-9314(20020901)25:13<789::aid-jssc789>3.0.co;2-j)
- Crini G, Lichtfouse E (2018a) Chapter 1: Wastewater treatment: an overview. In: Crini G, Lichtfouse E (eds) *Green adsorbents for pollutant removal*. Springer, Cham, pp 1–21. https://doi.org/10.1007/978-3-319-92111-2_1
- Crini G, Lichtfouse E (eds) (2018b) Chitin and chitosan: applications in food, agriculture, pharmacy, medicine and wastewater treatment. *Sustainable Agriculture Review* 36. Springer. <https://doi.org/10.1007/978-3-030-16581-9>
- Crini G, Lekchiri Y, Morcellet M (1995) Separation of structural isomers using cyclodextrin-polymers coated on silica beads. *Chromatographia* 40:296–302. <https://doi.org/10.1007/bf02290360>
- Crini G, Janus L, Morcellet M, Torri G, Naggi A, Bertini S, Vecchi C (1998) Macroporous polyamines containing cyclodextrin: synthesis, characterization, and sorption properties. *J Appl Polym Sci* 69:1419–1427. [https://doi.org/10.1002/\(sici\)1097-4628\(19980815\)69:7<1419::aid-app17>3.0.co;2-o](https://doi.org/10.1002/(sici)1097-4628(19980815)69:7<1419::aid-app17>3.0.co;2-o)
- Crini G, Euvrard E, Druart C, Morin-Crini N, Lagarrigue C, Gavoille S (2016) Alkylphénols et rejets de la filière traitement de surface (in French). *GalvanoOrgano* 845:53–55
- Crini G, Fourmentin S, Fenyvesi É, Torri G, Fourmentin M, Morin-Crini N (2018) Cyclodextrins, from molecules to applications. *Environ Chem Lett* 16:1361–1375. <https://doi.org/10.1007/s10311-018-0763-2>
- Crini G, Lichtfouse E, Wilson LD, Morin-Crini N (2019) Conventional and non-conventional adsorbents for wastewater treatment. *Environ Chem Lett* 17:145–155. <https://doi.org/10.1007/s10311-018-0785-9>
- Cruz del Álamo A, Pariente MI, Vasiliadou I, Padrino B, Puyol D, Molina R, Martínez F (2018) Removal of pharmaceutical compounds from urban wastewater by an advanced bio-oxidation process based on fungi *Trametes versicolor* immobilized in a continuous RBC system. *Environ Sci Pollut Res* 25:34884–34892. <https://doi.org/10.1007/s11356-017-1053-4>
- Cruz-Morató C, Ferrando-Climent L, Rodríguez-Mozaz S, Barceló D, Marco-Urrea E, Vicent T, Sarà M (2013) Degradation of pharmaceuticals in non-sterile urban wastewater by *Trametes*

- versicolor* in a fluidized bed bioreactor. *Water Res* 47:5200–5210. <https://doi.org/10.1016/j.watres.2013.06.007>
- Cruz-Morató C, Lucas D, Llorca M, Rodriguez-Mozaz S, Gorga M, Petrovic M, Barceló D, Vicent T, Sarrà M, Marco-Urrea E (2014) Hospital wastewater treatment by fungal bioreactor: removal efficiency for pharmaceuticals and endocrine disruptor compounds. *Sci Total Environ* 493:365–376. <https://doi.org/10.1016/j.scitotenv.2014.05.117>
- Cruz-Tato P, Ortiz-Quiles EO, Vega-Figueroa K, Santiago-Martoral L, Flynn M, Diaz-Vázquez LM, Nicolau E (2017) Metalized nanocellulose composites as a feasible material for membrane supports: design and applications for water treatment. *Environ Sci Technol* 51:4585–4595
- CycloLab (2020). www.cyclolab.hu
- Cyclopure (2020). www.cyclopure.com
- Dąbrowski A, Podkościelny P, Hubicki Z, Barczak M (2005) Adsorption of phenolic compounds by activated carbon – a critical review. *Chemosphere* 58:1049–1070. <https://doi.org/10.1016/j.chemosphere.2004.09.067>
- Dantas R, Contreras S, Sans C, Esplugas S (2008) Sulfamethoxazole abatement by means of ozonation. *J Hazard Mater* 150:790–794
- de Andrade JR, Oliveira MF, da Silva MGC, Vieira MGA (2018) Adsorption of pharmaceuticals from water and wastewater using nonconventional low-cost materials: a review. *Ind Eng Chem Res* 57:3103–3127. <https://doi.org/10.1021/acs.iecr.7b05137>
- de Andrade JR, Vieira MGA, Silva MGC, Wang S (2020) Oxidative degradation of pharmaceutical losartan potassium with N-doped hierarchical porous carbon and peroxymonosulfate. *Chem Eng J* 382:1–11. <https://doi.org/10.1016/j.cej.2019.122971>
- de Araújo KS, Antonelli R, Gaydeczka B, Granato AC, Malpass GRP (2016) Advanced oxidation processes: a review regarding the fundamentals and applications in wastewater treatment and industrial wastewater. *Ambiente e Agua Int J Appl Sci* 11. <https://doi-org.inec.bib.cnrs.fr/10.4136/1980-993X>
- de Godos I, Muñoz R, Guieysse B (2012) Tetracycline removal during wastewater treatment in high-rate algal ponds. *J Hazard Mater* 229–230:446–449. <https://doi.org/10.1016/j.jhazmat.2012.05.106>
- de Jesus GV, Cardoso VV, Joao Benoliel M, Almeida CMM (2016) Chlorination and oxidation of sulfonamides by free chlorine: identification and behaviour of reaction products by UPLC-MS/MS. *J Environ Manag* 166:466–477. <https://doi.org/10.1016/j.jenvman.2015.10.048>
- de Oliveira M, Frihling BEF, Velasques J, Magalhaes FJG, Cavalheri PS, Migliolo L (2020) Pharmaceuticals residues and xenobiotics contaminants: occurrence, analytical techniques and sustainable alternatives for wastewater treatment. *Sci Total Environ* 705:135568. <https://doi.org/10.1016/j.scitotenv.2019.135568>
- de Souza FM, Dos Santos OAA, Vieira MGA (2019) Adsorption of herbicide 2,4-D from aqueous solution using organo-modified bentonite clay. *Environ Sci Pollut Res* 26:18329–18342. <https://doi.org/10.1007/s11356-019-05196-w>
- de Souza FM, Lazarin AM, Vieira MGA, Santos OAA (2018) Kinetic, equilibrium and thermodynamic study on atrazine adsorption in organophilic clay. *Des Water Treat* 123:240–252. <https://doi.org/10.5004/dwt.2018.22767>
- de Wilt A, Butkovskiy A, Tuantet K, Leal LH, Fernandes TV, Langenhoff A, Zeeman G (2016) Micropollutant removal in an algal treatment system fed with source separated wastewater streams. *J Hazard Mater* 304:84–92. <https://doi.org/10.1016/j.jhazmat.2015.10.033>
- Deborde M, Von Gunten U (2008) Reactions of chlorine with inorganic and organic compounds during water treatment – kinetics and mechanism: a critical review. *Water Res* 42:13–51. <https://doi.org/10.1016/j.watres.2007.07.025>
- Dehghani MH, Ghadermazi M, Bhatnagar A, Sadighara P, Jahed-Khaniki G, Heibati B, McKay G (2016) Adsorptive removal of endocrine disrupting bisphenol a from aqueous solution using chitosan. *J Environ Chem Eng* 4:2647–2655

- Dhaka S, Kumar R, Deep A, Kurade MB, Ji SW, Jeon BH (2019) Metal-organic frameworks (MOFs) for the removal of emerging contaminants from aquatic environments. *Coordination Chem Rev* 380:330–352. <https://doi.org/10.1016/j.ccr.2018.10.003>
- Dias EM, Petit C (2015) Towards the use of metal-organic frameworks for water reuse: a review of the recent advances in the field of organic pollutants removal and degradation and the next steps in the field. *J Mater Chem A* 3:22484–22506. <https://doi.org/10.1039/C5TA05440K>
- Dobrin D, Bradu C, Magureanu M, Mandache NB, Parvulescu VI (2013) Degradation of diclofenac in water using a pulsed corona discharge. *Chem Eng J* 234:389e396. <https://doi.org/10.1016/j.cej.2013.08.114>
- Dodd MC, Kohler HPE, von Gunten U (2009) Oxidation of antibacterial compounds by ozone and hydroxyl radical: elimination of biological activity during aqueous ozonation processes. *Environ Sci Technol* 43:2498–2504. <https://doi.org/10.1021/es8025424>
- Doll TE, Frimmel FH (2003) Fate of pharmaceuticals – photodegradation by simulated solar UV-light. *Chemosphere* 52:1757–1769. [https://doi.org/10.1016/S0045-6535\(03\)00446-6](https://doi.org/10.1016/S0045-6535(03)00446-6)
- Dojčinović BP, Roglič GM, Obradović BM, Kuraica MM, Kostić MM, Nešić J, Manojlović DD (2011) Decolorization of reactive textile dyes using water falling film dielectric barrier discharge. *J Hazard Mater* 192:763–771
- Domańska M, Boral A, Hamal K, Kuśnierz M, Łomotowski J, Płaza-Ożóg P (2007) Efficiency of municipal wastewater treatment with membrane bioreactor. *J Water Land Dev*. <https://doi.org/10.2478/jwld-2019-0026>
- Dordio AV, Miranda S, Prates Ramalho JP, Palace Carvalho AJ (2016) Mechanisms of removal of three widespread pharmaceuticals by two clay materials. *J Hazard Mater* 323:575–583. <https://doi.org/10.1016/j.jhazmat.2016.05.091>
- El Shaer M, Eldaly M, Heikal G, Sharaf Y, Diab H, Mobasher M, Rousseau A (2020) Antibiotics degradation and bacteria inactivation in water by cold atmospheric plasma discharges above and below water surface. *Plasma Chem Plasma Process*. <https://doi.org/10.1007/s11090-020-10076-0>
- EMA (European Medicines Agency) (2017) Background review for cyclodextrins used as excipient. EMA/CHMP/333892/2013. https://www.ema.europa.eu/en/documents/scientific-guideline/questions-answers-cyclodextrins-used-excipients-medicinal-products-human-use_en.pdf
- Escapa C, Coimbra RN, Paniagua S, García AI, Otero M (2017a) Paracetamol and salicylic acid removal from contaminated water by microalgae. *J Environ Manag* 203:799–806. <https://doi.org/10.1016/j.jenvman.2016.06.051>
- Escapa C, Coimbra RN, Paniagua S, García AI, Otero M (2017b) Comparison of the culture and harvesting of *Chlorella vulgaris* and *Tetradesmus obliquus* for the removal of pharmaceuticals from water. *J Appl Phycol* 29:1179–1193. <https://doi.org/10.1007/s10811-016-1010-5>
- Fan X, Restivo J, Órfão JJM, Pereira MFR, Lapkin AA (2014) The role of multiwalled carbon nanotubes (MWCNTs) in the catalytic ozonation of atrazine. *Chem Eng J* 241:66–76. <https://doi.org/10.1016/j.cej.2013.12.023>
- Fenyvesi É, Zsádon B, Szejtli J, Tüdős F (1979) Preparation of cyclodextrin polymers in bead form and control of their characteristics by the parameters of preparation. *Ann Univ Sci Budap Rolando Eotvos Nominatae Sect Chim* 15:13–22
- Fenyvesi É, Ujházy A, Szejtli J, Putter S, Gan TG (1996) Controlled release of drugs from CD polymers substituted with ionic groups. *J Incl Phenom Mol Recogn Chem* 25:185–189. <https://doi.org/10.1007/bf01041566>
- Fenyvesi É, Puskás I, Szente L (2019) Applications of steroid drugs entrapped in cyclodextrins. *Environ Chem Lett* 17:375–391. <https://doi.org/10.1007/s10311-018-0807-7>
- Fenyvesi É, Barkács K, Gruiz K, Kenyeres I, Zárny G, Szente L (2020) Removal of hazardous micropollutants from treated wastewater using cyclodextrin bead polymer – a pilot demonstration case. *J Hazard Mater* 383:121181. <https://doi.org/10.1016/j.jhazmat.2019.121181>
- Fernández C, González-Doncel M, Pro J, Carbonell G, Tarazona JV (2010) Occurrence of pharmaceutically active compounds in surface waters of the henares-jarama-tajo river system

- (Madrid, Spain) and a potential risk characterization. *Sci Total Environ* 408:543–551. <https://doi.org/10.1016/j.scitotenv.2009.10.009>
- Fernández-Alvarez P, Le Noir M, Guieysse B (2009) Removal and destruction of endocrine disrupting contaminants by adsorption with molecularly imprinted polymers followed by simultaneous extraction and phototreatment. *J Hazard Mater* 163:1107–1112
- Fernández-Castro P, Vallejo M, San Román MF, Ortiz I (2015) Insight on the fundamentals of advanced oxidation processes. Role and review of the determination methods of reactive oxygen species. *J Chem Technol Biotechnol* 90:796–820. <https://doi.org/10.1002/jctb.4634>
- Ferreira RC, De Lima HHC, Cândido AA, Couto Junior OM, Arroyo PA, De Carvalho KQ, Gauze GF, Barros MASD (2015) Adsorption of paracetamol using activated carbon of Dende and Babassu coconut mesocarp. *World Academy of Science, Engineering and Technology, International Science Index. Chem Mol Eng* 9:717–722
- Fomina M, Gadd GM (2014) Biosorption: current perspectives on concept, definition and application. *Bioresour Technol* 160:3–14. <https://doi.org/10.1016/j.biortech.2013.12.102>
- Foo KY, Hameed BH (2010) Detoxification of pesticide waste *via* activated carbon adsorption process. *J Hazard Mater* 175:1–11
- Fountoulakis MS, Daskalakis G, Papadaki A, Kalogerakis N, Manios T (2017) Use of halophytes in pilot-scale horizontal flow constructed wetland treating domestic wastewater. *Environ Sci Pollut Control Ser* 24:16682e16689. <https://doi.org/10.1007/s11356-017-9295-8>
- Freitas ED, Carmo ACR, Almeida Neto AF, Vieira MGA (2017) Binary adsorption of silver and copper on Verde-lodo bentonite: kinetic and equilibrium study. *Appl Clay Sci* 137:69–76. <https://doi.org/10.1016/j.clay.2016.12.016>
- Frömring KH, Szejtli J (1994) *Cyclodextrins in pharmacy*. Kluwer Academic Publishers, Dordrecht
- Gagnon C, Lajeunesse A, Cejka P, Gagné F, Hausler R (2008) Degradation of selected acidic and neutral pharmaceutical products in a primary-treated wastewater by disinfection processes. *Ozone Sci Eng* 30:387–392. <https://doi.org/10.1080/01919510802336731>
- Gallard H, Leclercq A, Croué JP (2004) Chlorination of bisphenol A: kinetics and by-products formation. *Chemosphere* 56:465–473. <https://doi.org/10.1016/j.chemosphere.2004.03.001>
- Geankoplis CJ (1993) *Transport and unit operations*, vol 3. Prentice-Hall International Editions, New Jersey
- Gehr R, Wagner M, Veerasubramanian P, Payment P (2003) Disinfection efficiency of peracetic acid, UV and ozone after enhanced primary treatment of municipal wastewater. *Water Res* 37:4573–4586. [https://doi.org/10.1016/S0043-1354\(03\)00394-4](https://doi.org/10.1016/S0043-1354(03)00394-4)
- Genç N, Dogan EC, Yurtseve M (2013) Bentonite for ciprofloxacin removal from aqueous solution. *Water Sci Technol* 68:848–855
- Gentili FG, Fick J (2017) Algal cultivation in urban wastewater: an efficient way to reduce pharmaceutical pollutants. *J Appl Phycol* 29:255–262. <https://doi.org/10.1007/s10811-016-0950-0>
- 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>
- Ghughe SP, Saroha AK (2018) Catalytic ozonation for the treatment of synthetic and industrial effluents – application of mesoporous materials: a review. *J Environ Manag* 211:83–102. <https://doi.org/10.1016/j.jenvman.2018.01.052>
- Gilabert-Alarcón C, Salgado-Méndez SO, Walter Daesslé L, Mendoza-Espinosa LG, Villada-Canela M (2018) Regulatory challenges for the use of reclaimed water in Mexico: a case study in Baja California. *Water* 10:1432. <https://doi.org/10.3390/w10101432>
- Giraldo AL, Erazo-Erazo ED, Flórez-Acosta OA, Serna-Galvis T-PRA (2015) Degradation of the antibiotic oxacillin in water by anodic oxidation with Ti/IrO₂ anodes: evaluation of degradation routes, organic by-products and effects of water matrix components. *Chem Eng J* 279:103–114. <https://doi.org/10.1016/j.cej.2015.04.140>

- Githinji LJM, Musey MK, Ankumah RO (2011) Evaluation of the fate of ciprofloxacin and amoxicillin in domestic wastewater. *Water Air Soil Pollut* 219:191–201. <https://doi.org/10.1007/s11270-010-0697-1>
- Gogoi A, Mazumder P, Tyagi VK, Tushara Chaminda GGT, An AK, Kumar M (2018) Occurrence and fate of emerging contaminants in water environment: a review. *Groundw Sustain Dev* 6:169–180. <https://doi.org/10.1016/j.gsd.2017.12.009>
- Goldstein S, Lind J, Merenyi G (2005) Chemistry of peroxyxynitrites as compared to peroxyxynitrites. *Chem Rev* 105:2457–2470. <https://doi.org/10.1021/cr0307087>
- Goméz JM, Mezcuca M, Martínez MJ, Fernández-Alba AR, Agüera A (2006) A new method for monitoring estrogens, N-octylphenol, and bisphenol A in wastewater treatment plants by solid-phase extraction-gas chromatography-tandem mass spectrometry. *Int J Environ Anal Chem* 86:3–13
- Gonçalves AG, Figueiredo JL, Órfão JJM, Pereira MFR (2010) Influence of the surface chemistry of multi-walled carbon nanotubes on their activity as ozonation catalysts. *Carbon* 48:4369–4381. <https://doi.org/10.1016/j.carbon.2010.07.051>
- Gonçalves AG, Órfão JJM, Pereira MFR (2013) Ozonation of sulfamethoxazole promoted by MWCNT. *Cat Com* 35:82–87. <https://doi.org/10.1016/j.catcom.2013.02.012>
- González S, Petrovic M, Barceló D (2008) Evaluation of two pilot scale membrane bioreactors for the elimination of selected surfactants from municipal wastewaters. *J Hydrol* 356:46–55. <https://doi.org/10.1016/j.jhydrol.2008.03.023>
- Gonzalez S, Lopez-Roldan R, Cortina JL (2012) Presence and biological effects of emerging contaminants in Llobregat River basin: a review. *Environ Poll* 161:83–92. <https://doi.org/10.1016/j.envpol.2011.10.002>
- Gorito AM, Ribeiro AR, Almeida CMR, Silva AMT (2017) A review on the application of constructed wetlands for the removal of priority substances and contaminants of emerging concern listed in recently launched EU legislation. *Environ Pollut* 227:428–443. <https://doi.org/10.1016/j.envpol.2017.04.060>
- Gorito AM, Ribeiro AR, Gomes CR, Almeida CMR, Silva AMT (2018) Constructed wetland microcosms for the removal of organic micropollutants from freshwater aquaculture effluents. *Sci Total Environ* 644:1171–1180. <https://doi.org/10.1016/j.scitotenv.2018.06.371>
- Gouveia L, Graça S, Sousa C, Ambrosano L, Ribeiro B, Botrel EP, Neto PC, Ferreira AF, Silva CM (2016) Microalgae biomass production using wastewater: treatment and costs. Scale-up considerations. *Algal Res* 16:167–176. <https://doi.org/10.1016/j.algal.2016.03.010>
- Grabowski LR, van Veldhuizen EM, Pemen AJM, Rutgers WR (2007) Breakdown of methylene blue and methyl orange by pulsed corona discharge. *Plasma Sources Sci Technol* 16:226–232. <https://doi.org/10.1088/0963-0252/16/2/003>
- Greychock AE, Vikesland PJ (2006) Triclosan reactivity in chloraminated waters. *Environ Sci Technol* 40:2615–2622. <https://doi.org/10.1021/es051952d>
- Gruiz K, Molnár M, Fenyvesi É, Cs H, Atkári A, Barkács K (2011) Cyclodextrins in innovative engineering tools for risk-based environmental management. *J Incl Phenom Macrocycl Chem* 70:299–306. <https://doi.org/10.1007/s10847-010-9909-y>
- Grundgeiger E, Lim YH, Frost RL, Ayoko GA, Yunfei X (2015) Application of organo-beidellites for the adsorption of atrazine. *Appl Clay Sci* 105-106:252–258. <https://doi.org/10.1016/j.clay.2015.01.003>
- Gupta SS, Bhattacharyya KG (2014) Adsorption of metal ions by clays and inorganic solids. *RSC Adv* 4:28537–28586. <https://doi.org/10.1039/C4RA03673E>
- Guo H, Jiang N, Wang H, Lu N, Shang K, Li J, Wu Y (2019a) Pulsed discharge plasma assisted with graphene-WO₃ nanocomposites for synergistic degradation of antibiotic enrofloxacin in water. *Chem Eng J* 372:226–240. <https://doi.org/10.1016/j.cej.2019.04.119>
- Guo H, Jiang N, Wang H, Shang K, Lu N, Li J, Wu Y (2019b) Enhanced catalytic performance of graphene-TiO₂ nanocomposites for synergetic degradation of fluoroquinolone antibiotic in pulsed discharge plasma system. *Appl Catal B Environ* 248:552–566. <https://doi.org/10.1016/j.apcatb.2019.01.052>

- Guo H, Jiang N, Wang H, Lu N, Shang K, Li J, Wu Y (2019c) Degradation of antibiotic chloramphenicol in water by pulsed discharge plasma combined with TiO₂/WO₃ composites: mechanism and degradation pathway. *J Haz Mater* 371:666–676. <https://doi.org/10.1016/j.jhazmat.2019.03.051>
- Gurung K, Ncibi MC, Sillanpää M (2017) Assessing membrane fouling and the performance of pilot-scale membrane bioreactor (MBR) to treat real municipal wastewater during winter season in Nordic regions. *Sci Total Environ* 579:1289–1297
- Hama Aziz KH, Miessner H, Mueller S, Mahyar A, Kalass D, Moeller D, Khorshid I, MAM R (2018) Comparative study on 2,4-dichlorophenoxyacetic acid and 2,4-dichlorophenol removal from aqueous solutions *via* ozonation, photocatalysis and non-thermal plasma using a planar falling film reactor. *J Hazard Mater* 343:107–115. <https://doi.org/10.1016/j.jhazmat.2017.09.025>
- Hansen R, Andersen HR (2012) Energy effectiveness of direct UV and UV/H₂O₂ treatment of estrogenic chemicals in biologically treated sewage. *Int J Photoenergy* 270320. <https://doi.org/10.1155/2012/270320>
- Haque E, Lee JE, Jang IT, Hwang YK, Chang JS, Jegal J, Jung SH (2010) Adsorptive removal of methyl orange from aqueous solution with metal-organic frameworks, porous chromium-benzenedicarboxylates. *J Hazard Mater* 181:535–542
- He J, Ding L, Deng J, Yang W (2012) Oil-absorbent beads containing beta-cyclodextrin moieties: preparation *via* suspension polymerization and high oil absorbency. *Polym Adv Technol* 23:810–816. <https://doi.org/10.1002/pat.1975>
- He D, Sun Y, Xin L, Feng J (2014) Aqueous tetracycline degradation by non-thermal plasma combined with nano-TiO₂. *Chem Eng J* 258:18–25. <https://doi.org/10.1016/j.cej.2014.07.089>
- He D, Sun Y, Li S, Feng J (2015) Decomposition of tetracycline in aqueous solution by corona discharge plasma combined with a Bi₂MoO₆ nanocatalyst. *J Chem Technol Biotechnol* 90:2249–2256. <https://doi.org/10.1002/jctb.4540>
- Hemine K, Skwierawska A, Kernstein A, Kozłowska-Tylingo K (2020) Cyclodextrin polymers as efficient adsorbents for removing toxic non-biodegradable pimavanserin from pharmaceutical wastewaters. *Chemosphere* 250:126250. <https://doi.org/10.1016/j.chemosphere.2020.126250>
- Herrera-Morales J, Morales K, Ramos D, Ortiz-Quiles EO, Lopez-Encarnación JM, Nicolau E (2017) Examining the use of nanocellulose composites for the sorption of contaminants of emerging concern: an experimental and computational study. *ACS Omega* 2:7714–7722. <https://doi.org/10.1021/acsomega.7b01053>
- Herrera-Morales J, Turley TA, Betancourt-Ponce M, Nicolau E (2019) Nanocellulose-block copolymer films for the removal of emerging organic contaminants from aqueous solutions. *Materials* 12:230. <https://doi.org/10.3390/ma12020230>
- Hey C, Grabi R, Ledin A, la Cour JJ, Andersen HR (2012a) Oxidation of pharmaceuticals by chlorine dioxide in biologically treated wastewater. *Chem Eng J* 185–186:236–242. <https://doi.org/10.1016/j.cej.2012.01.093>
- Hey G, Ledin A, la Cour JJ, Andersen HR (2012b) Removal of pharmaceuticals in biologically treated wastewater by chlorine dioxide or peracetic acid. *Environ Technol* 33:1041–1047. <https://doi.org/10.1080/09593330.2011.606282>
- Hijosa-Valsero M, Molina R, Schikora H, Müller M, Bayona JM (2013) Removal of priority pollutants from water by means of dielectric barrier discharge atmospheric plasma. *J Hazard Mater* 262:664–667. <https://doi.org/10.1016/j.jhazmat.2013.09.022>
- Hokkanen S, Repo E, Sillanpää M (2013) Removal of heavy metals from aqueous solutions by succinic anhydride modified mercerized nanocellulose. *Chem Eng J* 223:40–47
- Hu JY, Aizawa T, Ookubo S (2002) Products of aqueous chlorination of bisphenol A and their estrogenic activity. *Environ Sci Technol* 36:1980–1987
- Hu J, Cheng S, Aizawa T, Terao Y, Kunikane S (2003) Products of aqueous chlorination of 17 α -estradiol and their estrogenic activities. *Environ Sci Technol* 37:5665–5670. <https://doi.org/10.1021/es034324+>

- Hu Y, Bai Y, Yu H, Zhang C, Chen J (2013) Degradation of selected organophosphate pesticides in wastewater by dielectric barrier discharge plasma. *Bull Environ Contam Toxicol* 91:314–319. <https://doi.org/10.1007/s00128-013-1048-x>
- Hu Y, Peng Y, Liu W, Zhao D, Fu J (2017) Chapter 4: Removal of emerging contaminants from water and wastewater using nanofiltration technology. In: Joo SH (ed) *Applying nanotechnology for environmental sustainability*. <https://doi.org/10.4018/978-1-5225-0585-3.ch004>
- Hu S, Liu X, Xu Z, Wang J, Li Y, Shen J, Lan Y, Cheng C (2019) Degradation and mineralization of ciprofloxacin by gas-liquid discharge nonthermal plasma. *Plasma Sci Technol* 21:015501. <https://doi.org/10.1088/2058-6272/aade82>
- Huang X, Xiao K, Shen Y (2010) Recent advances in membrane bioreactor technology for wastewater treatment in China. *Front Environ Sci Eng China* 4:245–271. <https://doi.org/10.1007/s11783-010-0240-z>
- Huang DL, Wang RZ, Liu YG, Zeng GM, Lai C, Xu P, Lu BA, Xu JJ, Wang C, Huang C (2015) Application of molecularly imprinted polymers in wastewater treatment: a review. *Environ Sci Pollut Res* 22:963–977
- Huang X, Ye G, Yi N, Lu L, Zhang L, Yang L, Xiao L, Liu J (2019) Effect of plant physiological characteristics on the removal of conventional and emerging pollutants from aquaculture wastewater by constructed wetlands. *Ecol Eng* 135:45–53. <https://doi.org/10.1016/j.ecoleng.2019.05.017>
- Huang Q, Chai K, Zhou L, Ji H (2020) A phenyl-rich β -cyclodextrin porous crosslinked polymer for efficient removal of aromatic pollutants: insight into adsorption performance and mechanism. *Chem Eng J* 387:124020. <https://doi.org/10.1016/j.cej.2020.124020>
- Huber M, Canonica S, Park G, von Gunten U (2003) Oxidation of pharmaceuticals during ozonation and advanced oxidation processes. *Environ Sci Technol* 37:1016–1024
- Huber MM, Ternes TA, von Gunten U (2004) Removal of estrogenic activity and formation of oxidation products during ozonation of 17 α -ethynylestradiol. *Environ Sci Technol* 38:5177–5186. <https://doi.org/10.1021/es035205x>
- Huber MM, Korhonen S, Ternes TA, von Gunten U (2005a) Oxidation of pharmaceuticals during water treatment with chlorine dioxide. *Water Res* 39:3607–3617
- Huber M, Göbel A, Joss A, Hermann N, Löffler D, Mc Ardell C, Ried A, Siegrist H, Ternes T, von Gunten U (2005b) Oxidation of pharmaceuticals during ozonation of municipal wastewater effluents: a pilot study. *Environ Sci Technol* 39:4290–4299
- Iervolino G, Vaiano V, Palma V (2019) Enhanced removal of water pollutants by dielectric barrier discharge nonthermal plasma reactor. *Sep Purif Technol* 215:155–162. <https://doi.org/10.1016/j.seppur.2019.01.007>
- Ikawa S, Tani A, Nakashima Y, Kitano K (2016) Physicochemical properties of bactericidal plasma-treated water. *J Phys D-Appl Phys* 49:425401. <https://doi.org/10.1088/0022-3727/49/42/425401>
- Ikehata K, Naghashkar NJ, 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.inee.bib.cnrs.fr/10.1080/01919510600985937>
- Ikehata K, Gamal El-Din M, Snyder SA (2008) Ozonation and advanced oxidation treatment of emerging organic pollutants in water and wastewater. *Ozone Sci Eng* 30:21–26. <https://doi-org.inee.bib.cnrs.fr/10.1080/01919510701728970>
- Iorhemen OT, Hamza RA, Tay JH (2016) Membrane bioreactor (MBR) technology for wastewater treatment and reclamation: membrane fouling. *Membranes* 6:33. <https://doi.org/10.3390/membranes6020033>
- Irmak S, Erbaturo O, Akgerman A (2005) Degradation of 17 β -estradiol and bisphenol A in aqueous medium by using ozone and ozone/UV techniques. *J Hazard Mater B* 126:54–62
- Jalilnejad E, Sadeghpour P, Ghasemzadeh K (2020) Advances in membrane bioreactor technology. In: current trends and future developments on (bio-)membranes. *Ceramic membranes bioreactors*. Basile A, Ghasemzadeh and Jalilnejad E (Eds.). Elsevier. Chapitre 1:1–29. <https://doi.org/10.1016/B978-0-12-816822-6.00001-X>

- Janus L, Crini G, El-Rezzi V, Morcellet M, Cambiagli A, Torri G, Naggi A, Vecchi C (1999) New sorbents containing beta-cyclodextrin. Synthesis, characterization, and sorption properties. *React Funct Polym* 42:173–180. [https://doi.org/10.1016/s1381-5148\(98\)00066-2](https://doi.org/10.1016/s1381-5148(98)00066-2)
- Jeirani Z, Niu CH, Soltan J (2017) Adsorption of emerging pollutants on activated carbon. *Rev Chem Eng* 33:491–522. <https://doi.org/10.1515/revce-2016-0027>
- Jelic A, Gros M, Ginebreda A, Cespedes-Sánchez R, Ventura F, Petrovic M, Barcelo D (2011) Occurrence, partition and removal of pharmaceuticals in sewage water and sludge during wastewater treatment. *Water Res* 45:1165–1176. <https://doi.org/10.1016/j.watres.2010.11.010>
- Jiang B, Zheng J, Qiu S, Wu M, Zhang Q, Yan Z, Xue Q (2014) Review on electrical discharge plasma technology for wastewater remediation. *Chem Eng J* 236:348–368. <https://doi.org/10.1016/j.cej.2013.09.090>
- Jiang L, Liu Y, Liu S, Li M, Hu X, Zeng G, Hu X, Liu S, Liu S, Huang B, Li M (2016) Fabrication of β -cyclodextrin/poly(l-glutamic acid) supported magnetic graphene oxide and its adsorption behavior for 17 β -estradiol. *Chem Eng J* 308:597–605. <https://doi.org/10.1016/j.cej.2016.09.067>
- Jiang Q, Ngo HH, Nghiem LD, Hai FI, Price WE, Zhang J, Guo W (2018) Effect of hydraulic retention time on the performance of a hybrid moving bed biofilm reactor-membrane bioreactor system for micropollutants removal from municipal wastewater. *Bioresour Technol* 247:1228–1232. <https://doi.org/10.1016/j.biortech.2017.09.114>
- Johnson AC, Sumpter JP (2001) Removal of endocrine-disrupting chemicals in activated sludge treatment works. *Environ Sci Technol* 35:4697–4703
- Jojoa-Sierra SD, Silva-Agredo J, Herrera-Calderon E, Torres-Palma RA (2017) Elimination of the antibiotic norfloxacin in municipal wastewater, urine and seawater by electrochemical oxidation on IrO₂ anodes. *Sci Total Environ* 575:1228–1238. <https://doi.org/10.1016/j.scitotenv.2016.09.201>
- Jović M, Manojlović D, Stanković D, Dojčinović B, Obradović B, Gašić U, Roglić G (2013) Degradation of triketone herbicides, mesotrione and sulcotrione, using advanced oxidation processes. *J Hazard Mater* 260:1092–1099. <https://doi.org/10.1016/j.jhazmat.2013.06.073>
- Jović MS, Dojčinović BP, Kovačević VV, Obradović BM, Kuraica M, Gašić UM, Roglić GM (2014) Effect of different catalysts on mesotrione degradation in water falling film DBD reactor. *Chem Eng J* 248:63–70. <https://doi.org/10.1016/j.cej.2014.03.031>
- Judd S (2008) The status of membrane bioreactor technology. *Trends Biotechnol* 26:109–116. <https://doi.org/10.1016/j.tibtech.2007.11.005>
- Jurecska L, Dobosy P, Barkács K, Fenyvesi É, Záray G (2014) Characterization of cyclodextrin containing nanofilters for removal of pharmaceutical residues. *J Pharm Biomed Anal* 98:90–93. <https://doi.org/10.1016/j.jpba.2014.05.007>
- Jux U, Baginski RM, Arnold HG, Krönke M, Seng PN (2002) Detection of pharmaceutical contaminations of river, pond, and tap water from Cologne (Germany) and surroundings. *Int J Hyg Environ Health* 205:393–398
- Kanazawa S, Furuki T, Nakaji T, Akamine S, Ichiki R (2013) Application of chemical dosimetry to hydroxyl radical measurement during underwater discharge. *J Phys Conf Ser* 418. <https://doi.org/10.1088/1742-6596/418/1/012102>
- Kang J, Liu H, Zheng YM, Qu J, Chen JP (2010) Systematic study of synergistic and antagonistic effects on adsorption of tetracycline and copper onto a chitosan. *J Colloid Interf Sci* 344:117–125. <https://doi.org/10.1016/j.jcis.2009.11.049>
- Karigár CS, Rao SS (2011) Role of microbial enzymes in the bioremediation of pollutants: a review. *Enzyme Res* 805187. <https://doi.org/10.4061/2011/805187>
- Karthikeyan KG, Meyer MT (2006) Occurrence of antibiotics in wastewater treatment facilities in Wisconsin, USA. *Sci Total Environ* 361:196–207. <https://doi.org/10.1016/j.scitotenv.2005.06.030>
- 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

- Katsigiannis A, Noutsopoulos C, Mantziaras J, Gioldasi M (2015) Removal of emerging pollutants through granular activated carbon. *Chem Eng J* 280:49–57. <https://doi.org/10.1016/j.cej.2015.05.109>
- Khan M, Tahir MN, Adil SF, Khan HU, Siddiqui MRH, Al-Warthan AA, Tremel W (2015) Graphene based metal and metal oxide nanocomposites: synthesis, properties and their applications. *J Mater Chem A* 3:18753–18808. <https://doi.org/10.1039/C5TA02240A>
- 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. *Trends Anal Chem* 122:115744. <https://doi.org/10.1016/j.trac.2019.115744>
- Khalaf MN (2016) Green polymers and environmental pollution control. CRC Press; Apple Academic Press, Inc, Oakville, 436 p
- Kim I, Tanaka H (2009) Photodegradation characteristics of PPCPs in water with UV treatment. *Environ Int* 35:793–802. <https://doi.org/10.1016/j.envint.2009.01.003>
- Kim SE, Yamada H, Tsuno H (2004) Evaluation of estrogenicity for 17 β -estradiol decomposition during ozonation. *Ozone-Sci Eng* 26:563–571
- Kim I, Yamashita N, Tanaka H (2009a) Performance of UV and UV/H₂O₂ processes for the removal of pharmaceuticals detected in secondary effluent of a sewage treatment plant in Japan. *J Hazard Mater* 166:1134–1140. <https://doi.org/10.1016/j.jhazmat.2008.12.020>
- Kim I, Yamashita N, Tanaka H (2009b) Photodegradation of pharmaceuticals and personal care products during UV and UV/H₂O₂ treatments. *Chemosphere* 77:518–525. <https://doi.org/10.1016/j.chemosphere.2009.07.041>
- Kim KS, Yang CS, Mok YS (2013) Degradation of veterinary antibiotics by dielectric barrier discharge plasma. *Chem Eng J* 219:19–27. <https://doi.org/10.1016/j.cej.2012.12.079>
- Kim KS, Kamb SK, Mok YS (2015) Elucidation of the degradation pathways of sulfonamide antibiotics in a dielectric barrier discharge plasma system. *Chem Eng J* 271:31–42. <https://doi.org/10.1016/j.cej.2015.02.073>
- Kim S, Chu KH, Al-Hamadani YAJ, Park CM, Jang M, Kim DH, Yu M, Heo J, Yon Y (2018) Removal of contaminants of emerging concern by membranes in water and wastewater: a review. *Chem Eng J* 335:896–914. <https://doi.org/10.1016/j.cej.2017.11.044>
- Kim MS, Cha D, Lee KM, Lee HJ, Kim T, Lee C (2020) Modeling of ozone decomposition, oxidant exposures, and the abatement of micropollutants during ozonation processes. *Water Res* 169:115230. <https://doi.org/10.1016/j.watres.2019.115230>
- 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* 36:1202–1211. <https://doi.org/10.1021/es011055j>
- Kono H, Onishi K, Nakamura T (2013) Characterization and bisphenol A adsorption capacity of beta- cyclodextrin-carboxymethylcellulose-based hydrogels. *Carbohydr Polym* 98:784–792. <https://doi.org/10.1016/j.carbpol.2013.06.065>
- Korshin G, Kim J, Gan L (2006) Comparative study of reactions of endocrine disruptors bisphenol A and diethylstilbestrol in electrochemical treatment and chlorination. *Water Res* 40:1070–1078
- Kovalova L, Siegrist H, von Gunten U, Eugster J, Hagenbuch M, Wittmer A, Moser R, McArdeil CS (2013) Elimination of micropollutants during post-treatment of hospital wastewater with powdered activated carbon, ozone and UV. *Environ Sci Technol* 47:7899–7908. <https://doi.org/10.1021/es400708w>
- Kunst B, Košutić K (2008) Removal of emerging contaminants in water treatment by nanofiltration and reverse osmosis. In: Hutzinger O, Barceló D, Kostianoy A (eds) *Handbook of environmental chemistry*. Volume 5: water Pollution, vol 5. Springer, Berlin, pp 103–125. https://doi.org/10.1007/698_5_100
- Kurwadkar S, Hoang TV, Malwade K, Kanel SR, Harper WF Jr, Struckhoff G (2019) Application of carbon nanotubes for removal of emerging contaminants of concern in engineered water and wastewater treatment systems. *Nanotechnol Environ Eng* 4:12. <https://doi.org/10.1007/s41204-019-0059-1>

- Kruithof JC, Kamp PC, Martijn BJ (2007) UV/H₂O₂ treatment: a practical solution for organic contaminant control and primary disinfection. *Ozone Sci Eng* 29:273–280
- Kyzas GZ, Kostoglou M (2014) Green adsorbents for wastewaters: a critical review. *Materials* 7:333–364. <https://doi.org/10.3390/ma7010333>
- Lacson CFZ, de Luna MDG, Dong C, Garcia-Segura S, Lu MC (2018) Fluidized-bed Fenton treatment of imidacloprid: optimization and degradation pathway. *Sustainable Environ Res* 28:309–314. <https://doi.org/10.1016/j.serj.2018.09.001>
- Lam E, Male KB, Chong JH, Leung ACW, Luong JHT (2012) Applications of functionalized and nanoparticle-modified nanocrystalline cellulose. *Trends Biotechnol* 30:283–290
- Landy D, Mallard I, Ponchel A, Monflier E, Fourmentin S (2012) Remediation technologies using cyclodextrins: an overview. *Environ Chem Lett* 10:225–237
- Larsen TA, Lienert J, Joos A, Siegrist H (2004) How to avoid pharmaceuticals in the aquatic environment. *J Biotechnol* 113:295–304. <https://doi.org/10.1016/j.jbiotec.2004.03.033>
- Le Noir M, Lepeuple AS, Guieysse B, Mattiasson B (2007) Selective removal of 17beta-estradiol at trace concentration using a molecularly imprinted polymer. *Water Res* 41:2825–2831
- Lee Y, von Gunten U (2010) Oxidative transformation of micropollutants during municipal wastewater treatment: comparison of kinetic aspects of selective (chlorine, chlorine dioxide, ferrate VI, and ozone) and non-selective oxidants (hydroxyl radical). *Water Res* 44:555–566
- Lee Y, von Gunten U (2012) Quantitative structure-activity relationships (QSARs) for the transformation of organic micropollutants during oxidative water treatment. *Water Res* 46:6177–6195
- Lee Y, von Gunten U (2016) Advances in predicting organic contaminant abatement during ozonation of municipal wastewater effluent: reaction kinetics, transformation products, and changes of biological effects. *Environ Sci Water Res Technol* 2:421–442. <https://doi.org/10.1039/C6EW00025H>
- Lee Y, Gerrity D, Lee M, Bogeat AE, Salhi E, Gamage S, Trenholm RA, Wert EC, Snyder SA, von Gunten U (2013) Prediction of micropollutant elimination during ozonation of municipal wastewater effluents: use of kinetic and water specific information. *Environ Sci Technol* 47:5872–5881. <https://doi.org/10.1021/es400781r>
- Lee Y, Kovalova L, McArdell C, von Gunten U (2014) Prediction of micropollutant elimination during ozonation of a hospital wastewater effluent. *Water Res* 64:134–148. <https://doi.org/10.1016/j.watres.2014.06.027>
- Lee D, Lee JC, Nam JY, Kim HW (2018) Degradation of sulfonamide antibiotics and their intermediates toxicity in an aeration-assisted non-thermal plasma while treating strong wastewater. *Chemosphere* 209:901–907. <https://doi.org/10.1016/j.chemosphere.2018.06.125>
- Lei H, Snyder SA (2007) 3D QSPR models for the removal of trace organic contaminants by ozone and free chlorine. *Water Res* 41:4051–4060. <https://doi.org/10.1016/j.watres.2007.05.010>
- Leitner N, Roshani B (2010) Kinetic of benzotriazole oxidation by ozone and hydroxyl radicals. *Water Res* 44:2058–2066. <https://doi.org/10.1016/j.watres.2009.12.018>
- Li B, Zhang T (2011) Mass flows and removal of antibiotics in two municipal wastewater treatment plants. *Chemosphere* 83:1284–1289
- Li SP, Jiang YY, Cao XH, Dong YW, Dong M, Xu J (2013) Degradation of nitenpyram pesticide in aqueous solution by low-temperature plasma. *Environ Technol* 34:1609–1616. <https://doi.org/10.1080/09593330.2013.765914>
- Li G, Lu Y, Lu C, Zhu M, Zhai C, Du Y, Yang P (2015) Efficient catalytic ozonation of bisphenol-a over reduced graphene oxide modified sea urchin-like α -MnO₂ architectures. *J Hazard Mater* 294:201–208
- Li X, Wang B, Cao Y, Zhao S, Wang H, Feng X, Zhou J, Ma X (2019a) Water contaminant elimination based on metal-organic frameworks and perspective on their industrial applications. *Sustain ACS Chem Eng* 7:4548–4563. <https://doi.org/10.1021/acssuschemeng.8b05751>
- Li X, Wang B, Cao Y, Zhao S, Wang H, Feng X, Zhou J, Ma X (2019b) Water contaminant elimination based on metal-organic frameworks and perspective on their industrial applications. *ACS Sustain Chem Eng* 7:4548–4563. <https://doi.org/10.1021/acssuschemeng.8b05751>

- Li H, Li T, He S, Zhou J, Wang T, Zhu L (2020) Efficient degradation of antibiotics by non-thermal discharge plasma: highlight the impacts of molecular structures and degradation pathways. *Chem Eng J* 395:125091. <https://doi.org/10.1016/j.cej.2020.125091>
- Lian F, Sun B, Song Z, Zhu L, Qi X, Xing B (2014) Physicochemical properties of herb-residue biochar and its sorption to ionizable antibiotic sulfamethoxazole. *Chem Eng J* 248:128–134. <https://doi.org/10.1016/j.cej.2014.03.021>
- Lian L, Yao B, Hou S, Fang J, Yan S, Song W (2017) Kinetic study of hydroxyl and sulfate radical-mediated oxidation of pharmaceuticals in wastewater effluents. *Environ Sci Technol* 51:2954–2962. <https://doi.org/10.1021/acs.est.6b05536>
- Lim M, Patureau D, Heran M, Lesage G, Kim J (2020) Removal of organic micropollutants in anaerobic membrane bioreactors in wastewater treatment: critical review. *Environ Sci Water Res.* <https://doi.org/10.1039/C9EW01058K>
- Lin Y, Peng Z, Zhang X (2009) Ozonation of estrone, estradiol, diethylstilbestrol in waters. *Des* 249:235–240. <https://doi.org/10.1016/j.desal.2008.06.034>
- Lin Y, Baggett DW, Kim JW, Siochi EJ, Connell JW (2011) Instantaneous formation of metal and metal oxide nanoparticles on carbon nanotubes and graphene *via* solvent-free microwave heating. *Appl Mater Interfaces* 3:1652–1664. <https://doi.org/10.1021/am200209e>
- Lindberg R, Jarnheimer PA, Olsen B, Johansson M, Tysklind M (2004) Determination of antibiotic substances in hospital sewage water using solid phase extraction and liquid chromatography/mass spectrometry and group analogue internal standards. *Chemosphere* 57:1479–1488. <https://doi.org/10.1016/j.chemosphere.2004.09.015>
- Ling Y, Klemes MJ, Xiao L, Alsaiee A, Dichtel WR, Helbling DE (2017) Benchmarking micropollutant removal by activated carbon and porous β -cyclodextrin polymers under environmentally relevant scenarios. *Environ Sci Technol* 51:7590–7598. <https://doi.org/10.1021/acs.est.7b00906>
- Liu DHF, Liptak BG (eds) (2000) *Wastewater treatment*. CRC Press, Boca Raton
- 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* 407:731–748
- Liu N, Wang M, Liu M, Liu F, Weng L, Koopal LK, Tan W (2012a) Sorption of tetracycline on organo-montmorillonites. *J Hazard Mater* 225-226:28–35. <https://doi.org/10.1016/j.jhazmat.2012.04.060>
- Liu P, Liu WJ, Jiang H, Chen JJ, Li WW, Yu HQ (2012b) 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. <https://doi.org/10.1016/j.biortech.2012.06.085>
- Liu JN, Chen Z, Wu QY, Li A, Hu HY, Yang C (2016) Ozone/graphene oxide catalytic oxidation: a novel method to degrade emerging organic contaminant N, N-diethyl-m-toluamide (DEET). *Sci Rep* 6:1–9
- Locke BR, Shih KY (2011) Review of the methods to form hydrogen peroxide in electrical discharge plasma with liquid water. *Plasma Sources Sci Technol* 20:034006. <https://doi.org/10.1088/0963-0252/20/3/034006>
- Locke BR, Lukes P, Brisset JL (2012) Chapter 6: Elementary chemical and physical phenomena in electrical discharge plasma in gas-liquid environments and in liquids. In: Parvulescu VI, Magureanu M, Lukes P (eds) *Plasma chemistry and catalysis in gases and liquids*. Wiley VCH, Weinheim, pp 185–241
- Lofrano G (2012) *Emerging compounds removal from wastewater: natural and solar based treatments*. Springer, Dordrecht. <https://doi.org/10.1007/978-94-007-3916-1>
- Lofthsson T, Jarho P, Måsson M, Järvinen T (2005) Cyclodextrins in drug delivery (review). *Expert Opin Drug Delivery* 2:335–351. <https://doi.org/10.1517/17425247.2.1.335>
- Lopez A, Anna B, Giuseppe M, John K (2003) Kinetic investigation on UV and UV/H₂O₂ degradations of pharmaceutical intermediates in aqueous solution. *J. Photochem Photobiol* 156:121–126

- Lukes P, Appleton AT, Locke BR (2004) Hydrogen peroxide and ozone formation in hybrid gas-liquid electrical discharge reactors. *IEEE Trans Ind Appl* 40:60–67. <https://doi.org/10.1109/TIA.2003.821799>
- Lukes P, Clupek M, Babicky V, Janda V, Sunka P (2005) Generation of ozone by pulsed corona discharge over water surface in hybrid gas liquid electrical discharge reactor. *J Phys D Appl Phys* 38:409e416. <https://doi.org/10.1088/0022-3727/38/3/010>
- Lukes P, Locke BR, Brisset JL (2012) Chapter 7: Aqueous-phase chemistry of electrical discharge plasma in water and in gas-liquid environments. In: Parvulescu VI, Magureanu M, Lukes P (eds) *Plasma chemistry and catalysis in gases and liquids*. Wiley-VCH, Weinheim, pp 243–308
- Ma JX, Dai RB, Chen M, Khan SJ, Wang ZW (2018) Applications of membrane bioreactors for water reclamation: micropollutant removal, mechanisms and perspectives. *Bioresour Technol* 269:532–543. <https://doi.org/10.1016/j.biortech.2018.08.121>
- Macedo CC, de Andrade JR, da Silva MGC, Vieira MGA (2020) Removal of propranolol hydrochloride by batch biosorption using remaining biomass of alginate extraction from *Sargassum filipendula* algae. *Environ Sci Pollut Res* 28:1–13. <https://doi.org/10.1007/s11356-020-08109-4>
- Machado KC, Grassi MT, Vidal C, Pescara IC, Jardim WF, Fernandes AN, Sodré FF, Almeida FV, Santana JS, Canela CC, Nunes CRO, Bichinho KM, Severo FJR (2016) A preliminary nationwide survey of the presence of emerging contaminants in drinking and source waters in Brazil. *Sci Total Environ* 572:138–146. <https://doi.org/10.1016/j.scitotenv.2016.07.210>
- Madikizela LM, Tavengwa NT, Chimuka L (2018) Applications of molecularly imprinted polymers for solid-phase extraction of non-steroidal anti-inflammatory drugs and analgesics from environmental waters and biological samples. *J Pharm Biomed Anal* 147:624–633
- Maeng SK, Choi BG, Lee KT, Song KG (2013) Influences of solid retention time, nitrification and microbial activity on the attenuation of pharmaceuticals and estrogens in membrane bioreactors. *Water Res* 47:3151–3162
- Magureanu M, Mandache NB, Parvulescu VI (2007) Degradation of organic dyes in water by electrical discharges. *Plasma Chem Plasma Process* 27:589–598. <https://doi.org/10.1007/s11090-007-9087-x>
- Magureanu M, Piroi D, Gherendi F, Mandache NB, Parvulescu VI (2008) Decomposition of methylene blue in water by corona discharges. *Plasma Chem Plasma Process* 28:677–688. <https://doi.org/10.1007/s11090-008-9155-x>
- Magureanu M, Piroi D, Mandache NB, David V, Medvedovici A, Bradu C, Parvulescu VI (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>
- Magureanu M, Dobrin D, Bradu C, Gherendi F, Mandache NB, Parvulescu VI (2016) New evidence on the formation of oxidizing species in corona discharge in contact with liquid and their reactions with organic compounds. *Chemosphere* 165:507e514. <https://doi.org/10.1016/j.chemosphere.2016.09.073>
- Magureanu M, Parvulescu VI (2016) Plasma in liquids and gas-liquid environment. In: Shohet L (ed) *Encyclopedia of plasma technology*. Taylor and Francis
- Magureanu M, Bradu C, Parvulescu VI (2018) Plasma processes for the treatment of water contaminated with harmful organic compounds. *J Phys D Appl Phys* 51:313002. <https://doi.org/10.1088/1361-6463/aacd9c>
- Mahfoudhi N, Boufi S (2017) Nanocellulose as a novel nanostructured adsorbent for environmental remediation: a review. *Cellulose* 24:1171–1197
- Mahmood Q, Pervez A, Zeb BS, Zaffar H, Yaqoob H, Waseem M, Zahidullah AS (2013) Natural treatment systems as sustainable ecotechnologies for the developing countries. *Biomed Res Int* 796373. <https://doi.org/10.1155/2013/796373>
- Maia GS, de Andrade JR, Oliveira MF, Vieira MGA, da Silva MGC (2017) Affinity studies between drugs and clays as adsorbent material. *Chem Eng Trans* 57:583–588. <https://doi.org/10.33031/CET1757098>

- Maia GS, de Andrade JR, da Silva MGC, Vieira MGA (2019) Adsorption of diclofenac sodium onto commercial organoclay: kinetic, equilibrium and thermodynamic study. *Powder Technol* 345:140–150. <https://doi.org/10.1016/j.powtec.2018.12.097>
- Mailler R, Gasperi J, Coquet Y, Buleté A, Vulliet E, Deshayes S, Zedek S, Mirande-Bret C, Eudes V, Bressy A, Caupos E, Moilleron R, Chebbo G, Rocher V (2016) Removal of a wide range of emerging pollutants from wastewater treatment plant discharges by micro-grain activated carbon in fluidized bed as tertiary treatment at large pilot scale. *Sci Total Environ* 542:983–996. <https://doi.org/10.1016/j.scitotenv.2015.10.153>
- Malik MA, ur-Rehman U, Ghaffar A, Ahmed K (2002) Synergistic effect of pulsed corona discharges and ozonation on decolourization of methylene blue in water. *Plasma Sources Sci Technol* 11:236–240. <https://doi.org/10.1088/0963-0252/11/3/302>
- Malik MA (2010) Water purification by plasmas: which reactors are most energy efficient? *Plasma Chem Plasma Process* 30:21–31. <https://doi.org/10.1007/s11090-009-9202-2>
- Maniero MG, Bila DM, Dezotti M (2008) Degradation and estrogenic activity removal of 17 β -estradiol and 17 α -ethinylestradiol by ozonation and O₃/H₂O₂. *Sci Total Environ* 407:105–115
- Marco-Urrea E, Perez-Trujillo M, Vicent T, Caminal G (2009) Ability of White-rot fungi to remove selected pharmaceuticals and degradation products of ibuprofen by *Trametes versicolor*. *Chemosphere* 74:765–772
- Margot J, Kienle C, Magnet A, Weil M, Rossi L, de Alencastro LF, Abegglen C, Thonney D, Chevre N, Scharer M, Barry DA (2013) Treatment of micropollutants in municipal wastewater: ozone or powdered activated carbon? *Sci Total Environ* 461-462:480–498
- Marotta E, Schiorlin M, Ren X, Rea M, Paradisi C (2011) Advanced oxidation process for degradation of aqueous phenol in a dielectric barrier discharge reactor. *Plasma Process Polym* 8:867e875. <https://doi.org/10.1002/ppap.201100036>
- Martínez-Pachón D, Espinosa-Barrera P, Rincón-Ortíz J, Moncayo-Lasso A (2019) Advanced oxidation of antihypertensives losartan and valsartan by photo-electro-Fenton at near-neutral pH using natural organic acids and a dimensional stable anode-gas diffusion electrode (DSA-GDE) system under light emission diode (LED) lighting. *Environ Sci Pollut Res* 26:4426–4437. <https://doi.org/inee.bib.cnrs.fr/10.1007/s11356-018-2645-3>
- Matamoros V, Gutiérrez R, Ferrer I, García J, Bayona JM (2015) Capability of microalgae-based wastewater treatment systems to remove emerging organic contaminants: a pilot-scale study. *J Hazard Mater* 288:34–42. <https://doi.org/10.1016/j.jhazmat.2015.02.002>
- Mautner A (2020) Nanocellulose water treatment membranes and filters: a review. *Polym Int*. <https://doi.org/10.1002/pi.5993>
- Mawhinney DB, Vanderford BJ, Snyder SA (2012) Transformation of 1H-benzotriazole by ozone in aqueous solution. *Environ Sci Technol* 46:7102–7111. <https://doi.org/10.1021/es300338e>
- Meffe R, Bustamante I (2014) Emerging organic contaminants in surface water and groundwater: a first overview of the situation in Italy. *Sci Total Environ* 481:280–295
- Mehran Abtahi S, Ilyas S, Joannis Cassan C, Albasi C, Vos WM (2018) Micropollutants removal from secondary-treated municipal wastewater using weak polyelectrolyte multilayer based nanofiltration membranes. *J Membrane Sci* 548:654–666
- Meneghetti Campos J, Queiroz SCN, Roston DM (2019) Removal of the endocrine disruptors ethinyl estradiol, bisphenol A, and levonorgestrel by subsurface constructed wetlands. *Sci Total Environ* 693:133514. <https://doi.org/10.1016/j.scitotenv.2019.07.320>
- Meneses-Jácome A, Díaz-Chavez R, Velásquez-Arredondo IH, Cárdenas-Chávez DL, Parra R, Ruiz-Colorado AA (2016) Sustainable energy from agro-industrial wastewaters in Latin America. *Renew Sust Energ Rev* 56:1249–1262. <https://doi.org/10.1016/j.rser.2015.12.036>
- Mercurio M, Sarkar B, Langella A (2019) Modified clay and zeolite nanocomposite materials. Environmental and pharmaceutical applications. Elsevier Science Publishing Co. Inc, pp 167–196. ISBN: 978-0-12-814617-0

- Mert BK, Ozengin N, Dogan EC, Aydiner C (2018) Efficient removal approach of micropollutants in wastewater using membrane bioreactor. In: Yonar T (ed) Wastewater and water quality. IntechOpen. <https://doi.org/10.5772/intechopen.75183>
- Mezzelani M, Gorbi S, Regoli F (2018) Pharmaceuticals in the aquatic environments: evidence of emerged threat and future challenges for marine organisms. *Marine Environ Res* 140:41–60. <https://doi.org/10.1016/j.marenvres.2018.05.001>
- Miklos DB, Remy C, Jekel M, Linden KG, Drewes JE, Hübner U (2018) Evaluation of advanced oxidation processes for water and wastewater treatment – a critical review. *Water Res* 139:118–131. <https://doi.org/10.1016/j.watres.2018.03.042>
- Mishra NS, Reddy R, Kuila A, Rani A, Mukherjee P, Nawaz A, Pichiah S (2017) A review on advanced oxidation processes for effective water treatment. *Curr World Environ* 12. <https://doi.org/10.12944/CWE.12.3.02>
- Mocanu G, Miah D, LeCerf D, Picton L, Moscovici M (2009) Cyclodextrins anionic polysaccharide hydrogels: synthesis, characterization, and interaction with some organic molecules (water pollutants, drugs, proteins). *J Appl Polym Sci* 112:1175–1183. <https://doi.org/10.1002/app.29580>
- Mohammed N, Grishkewich N, Tam KC (2018) Cellulose nanomaterials: promising sustainable nanomaterials for application in water/wastewater treatment processes. *Environ Sci Nano* 5:623–658
- Mole RA, Good CJ, Stebel EK, Higgins JF, Pitel SA, Welch AR, Minarik TA, Schoenfuss HL, Edmiston PL (2019) Correlating effluent concentrations and bench-scale experiments to assess the transformation of endocrine active compounds in wastewater by UV or chlorination disinfection. *Chemosphere* 226:565–575. <https://doi.org/10.1016/j.chemosphere.2019.03.145>
- Molu ZB, Yurdaoç K (2010) Preparation and characterization of aluminum pillared K10 and KSF for adsorption of trimethoprim. *Microporous Mesoporous Mater* 127:50–60. <https://doi.org/10.1016/j.micromeso.2009.06.027>
- Mon M, Bruno R, Ferrando-Soria J, Armentano D, Pardo E (2018) Metal-organic framework technologies for water remediation: towards a sustainable ecosystem. *J Mater Chem A* 6:4912–4947. <https://doi.org/10.1039/C8TA00264A>
- Monteoliva-García A, Martín-Pascual J, Muñío MM, Poyatos JM (2019) Removal of a pharmaceutical mix from urban wastewater coupling membrane bioreactor with advanced oxidation processes. *J Environ Eng* 145. [https://doi.org/10.1061/\(ASCE\)EE.1943-7870.0001571](https://doi.org/10.1061/(ASCE)EE.1943-7870.0001571)
- Moon RJ, Martini A, Nairn J, Simonsen J, Youngblood J (2011) Cellulose nanomaterials review: structure, properties and nanocomposites. *Chem Soc Rev* 40:3941–3994
- Moreira NFF, Sousa JM, Macedo G, Ribeiro AR, Barreiros L, Pedrosa M, Faria JL, Pereira MFR, Castro-Silva S, Segundo MA, Manaia CM, Nunes OC, Silva AMT (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>
- Moreira FC, Boaventura RAR, Brillias E, Vilar VJP (2017) Electrochemical advanced oxidation processes: a review on their application to synthetic and real wastewaters. *Appl Catal B Environ* 202:217–261. <https://doi.org/10.1016/j.apcatb.2016.08.037>
- Morin-Crini N, Crini G (2013) Environmental applications of water-insoluble β -cyclodextrin-epichlorohydrin polymers. *Progr Polym Sci* 38:344–368. <https://doi.org/10.1016/j.progpolymsci.2012.06.005>
- Morin-Crini N, Crini G (eds) (2017) *Eaux industrielles contaminées* (in French). PUFC, Besançon, 513 p
- Morin-Crini N, Winterton P, Fourmentin S, Wilson LD, Fenyvesi É, Crini G (2018) Water-insoluble β -cyclodextrin-epichlorohydrin polymers for removal of pollutants from aqueous solutions by sorption processes using batch studies: a review of inclusion mechanisms. *Progr Polym Sci* 78:1–23. <https://doi.org/10.1016/j.progpolymsci.2017.07.004>
- Morin-Crini N, Lichtfouse E, Torri G, Crini G (2019) Applications of chitosan in food, pharmaceuticals, medicine, cosmetics, agriculture, textiles, pulp and paper, biotechnology,

- and environmental chemistry. *Environ Chem Lett* 17:1667–1692. <https://doi.org/10.1007/s10311-019-00904-x>
- Moussa D, Doubla A, Kamgang-Youbi G, Brisset JL (2007) Postdischarge long life reactive intermediates involved in the plasma chemical degradation of an azoic dye. *IEEE Trans Plasma Sci* 35:444–453. <https://doi.org/10.1109/TPS.2007.892578>
- Murray A, Örmeci B (2012) Application of molecularly imprinted and non-imprinted polymers for removal of emerging contaminants in water and wastewater treatment: a review. *Environ Sci Pollut Res* 19:3820–3830. <https://doi.org/10.1007/s11356-012-1119-2>
- Nagy ZM, Molnár M, Fekete-Kertész I, Molnár Perl I, Fenyvesi E, Gruiz K (2014) Removal of emerging micropollutants from water using cyclodextrin. *Sci Total Environ* 485-486:711–719. <https://doi.org/10.1016/j.scitotenv.2014.04.003>
- Nakamura H, Kuruto-Niwa R, Uchida M, Terao Y (2007) Formation of chlorinated estrones *via* hypochlorous disinfection of wastewater effluent containing estrone. *Chemosphere* 66:1441–1448. <https://doi.org/10.1016/j.chemosphere.2006.09.011>
- Nakashima Y, Ikawa S, Tani A, Kitano K (2016) Ion-exchange chromatographic analysis of peroxynitric acid. *J Chromatogr A* 1431:89–93. <https://doi.org/10.1016/j.chroma.2015.12.054>
- Nam S, Choi D, Kim S, Her N, Zoh K (2014) Adsorption characteristics of selected hydrophilic and hydrophobic micropollutants in water using activated carbon. *J Hazard Mater* 270:144–152
- Nasuhoglu D, Isazadeh S, Westlund P, Neamatallah S, Yargeau V (2018) Chemical, microbial and toxicological assessment of wastewater treatment plant effluents during disinfection by ozonation. *Chem Eng J* 346:466–476. <https://doi.org/10.1016/j.cej.2018.04.037>
- Navalon S, Alvaro M, Garcia H (2008) Reaction of chlorine dioxide with emergent water pollutants: product study of the reaction of three β -lactam antibiotics with ClO_2 . *Water Res* 42:1935–1942
- Neamtu M, Frimmel F (2006) Photodegradation of endocrine disrupting chemical nonylphenol by simulated solar UV-irradiation. *Sci Total Environ* 369:295–306. <https://doi.org/10.1016/j.scitotenv.2006.05.002>
- Nemoto J, Saito T, Isogai A (2015) Simple freeze-drying procedure for producing nanocellulose aerogel-containing, high performance air filters. *ACS Appl Mater Interfaces* 7:19809–19815
- Nika MC, Bletsou A, Koumaki E, Noutsopoulos C, Mamais D, Stasinakis AS, Thomaidis NS (2016) Chlorination of benzothiazoles and benzotriazoles and transformation products identification by LC-HR-MS/MS. *J Hazard Mater* 323:400–413. <https://doi.org/10.1016/j.jhazmat.2016.03.035>
- Norvill ZN, Toledo-Cervantes A, Blanco S, Shilton A, Guieysse B, Muñoz R (2017) Photodegradation and sorption govern tetracycline removal during wastewater treatment in algal ponds. *Bioresour Technol* 232:35–43. <https://doi.org/10.1016/j.biortech.2017.02.011>
- Noutsopoulos C, Mamais D, Thomaidis N, Koumaki E, Nika M, Bletsou A, Stasinakis A (2013a) Removal of emerging pollutants through wastewater disinfection. Proceedings of the 13th international conference on environmental science and technology. Athens, Greece, 5–7 September 2013
- Noutsopoulos C, Mamais D, Bouras A, Kokkinidou D, Samaras V, Antoniou K, Gioldasi M (2013b) The role of activated carbon and disinfection on the removal of endocrine disrupting chemicals and non-steroidal anti-inflammatory drugs from wastewater. *Environ Technol* 35:698–708. <https://doi.org/10.1080/09593330.2013.846923>
- Noutsopoulos C, Mamais D, Samaras V, Bouras T, Marneri M, Antoniou K (2013c) Effect of wastewater chlorination on endocrine disruptor removal. *Water Sci Technol* 67:1551–1556. <https://doi.org/10.2166/wst.2013.025>
- Noutsopoulos C, Koumaki E, Mamais D, Nika MC, Bletsou A, Thomaidis N (2015) Removal of endocrine disruptors and non-steroidal anti-inflammatory drugs through wastewater chlorination: the effect of pH, total suspended solids and humic acids and identification of degradation by-products. *Chemosphere* 119:S109–S114. <https://doi.org/10.1016/j.chemosphere.2014.04.107>
- Oishi K, Moriuchi A (2010) Removal of dissolved estrogen in sewage effluents by beta-cyclodextrin polymer. *Sci Total Environ* 409:112–115. <https://doi.org/10.1016/j.scitotenv.2010.09.031>

- Ojajuni O, Saroj D, Cavalli G (2015) Removal of organic micropollutants using membrane-assisted processes: a review of recent progress. *Environ Technol Rev* 4:17–37. <https://doi.org/10.1080/21622515.2015.1036788>
- Oliveira MF, Souza VM, da Silva MGC, Vieira MGA (2018) Fixed-bed adsorption of caffeine onto thermally modified Verdelodo bentonite. *Ind Eng Chem Res* 57:17480–17487. <https://doi.org/10.1021/acs.iecr.8b03734>
- Oliveira MF, da Silva MGC, Vieira MGA (2019) Equilibrium and kinetic studies of caffeine adsorption from aqueous solutions on thermally modified Verde-Iodo bentonite. *Appl Clay Sci* 168:366–373. <https://doi.org/10.1016/j.clay.2018.12.011>
- Omtvedt LA, Dalheim MØ, Nielsen TT, Larsen KL, Strand BL, Aachmann FL (2019) Efficient grafting of cyclodextrin to alginate and performance of the hydrogel for release of model drug. *Sci Rep* 9:9325. <https://doi.org/10.1038/s41598-019-45761-4>
- Ono R, Oda (2002) Dynamics and density estimation of hydroxyl radicals in a pulsed corona discharge. *J Phys D* 35:2133. <https://doi.org/10.1088/0022-3727/35/17/309>
- Orprecio R, Evans CH (2003) Polymer-immobilized cyclodextrin trapping of model organic pollutants in flowing water streams. *J Appl Polym Sci* 90:2103–2110. <https://doi.org/10.1002/app.12818>
- Osei AR, Konate Y, Abagale FK (2019) Pollutant removal and growth dynamics of macrophyte species for faecal sludge treatment with constructed wetland technology. *Water Sci Technol* 80:1145–1154. <https://doi.org/10.2166/wst.2019.354>
- Oturan MA, Aaron JJ (2014) Advanced oxidation processes in water/wastewater treatment: principles and applications: a review. *Critical Rev Environ Sci Technol* 44:2577–2641. <https://doi.org/10.1080/10643389.2013.829765>
- Pablos C, Marugán J, van Grieken R, Serrano E (2013) Emerging micropollutant oxidation during disinfection processes using UV-C, UV-C/H₂O₂, UV-A/TiO₂ and UV-A/TiO₂/H₂O₂. *Water Res* 47:1237–1245. <https://doi.org/10.1016/j.watres.2012.11.041>
- Panorel I, Preis S, Kornev I, Hatakka H, Louhi-Kultanen M (2013) Oxidation of aqueous pharmaceuticals by pulsed corona discharge. *Environ Technol* 34:923–930. <https://doi.org/10.1080/09593330.2012.722691>
- Park JY, Kostyuk PV, Han SB, Kim JS, Vu CN, Lee HW (2006) Study on optical emission analysis of AC air-water discharges under He, Ar and N₂ environments. *J Phys D Appl Phys* 39:3805e3813. <https://doi.org/10.1088/0022-3727/39/17/015>
- Park DP, Davis K, Gilani S, Alonzo C, Dobrynin D, Fridman G, Fridman A, Rabinovich A, Fridman G (2013) Reactive nitrogen species produced in water by non-equilibrium plasma increase plant growth rate and nutritional yield. *Curr Appl Phys* 13:S19–S29. <https://doi.org/10.1016/j.cap.2012.12.019>
- Parlade E, Hom-Díaz A, Blázquez P, Martínez-Alonso M, Vicent T, Gaju N (2018) Effect of cultivation conditions on β -estradiol removal in laboratory and pilot-plant photobioreactors by an algal-bacterial consortium treating urban wastewater. *Water Res* 137:86–96. <https://doi.org/10.1016/j.watres.2018.02.060>
- Parolo ME, Savini M, Valles J, Baschini M, Avena M (2008) Tetracycline adsorption on montmorillonite: effects of pH and ionic strength. *Appl Clay Sci* 40:179–186. <https://doi.org/10.1016/j.clay.2007.08.003>
- Parvulescu VI, Magureanu M, Lukes P (2012) Plasma chemistry and catalysis in gases and liquids. Wiley-VCH, Weinheim. <https://doi.org/10.1002/9783527649525>
- Patel M, Kumar R, Kishor K, Mlsna T, Pittman CU Jr, Mohan D (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>
- Pathak N, Tran VH, Phuntsho S, Shon HY (2020) Chapter 10: Membrane reactors for the removal of organic micro-pollutants. In: Varjani S, Pandey A, Tyagi RD, Ngo HH, Larroche C (eds) Current developments in biotechnology and bioengineering. Emerging organic micro-pollutants. Elsevier, Amsterdam, pp 231–252

- Patiño Y, DíazE OS, Gallegos-Suarez E, Guerrero-Ruiz A, Rodríguez-Ramos I (2015) Adsorption of emerging pollutants on functionalized multiwall carbon nanotubes. *Chemosphere* 136:174–180. <https://doi.org/10.1016/j.chemosphere.2015.04.089>
- Paucar NE, Kim I, Tanaka H, Sato C (2018) Ozone treatment process for the removal of pharmaceuticals and personal care products in wastewater. *Ozone Sci Eng* 41:3–16. <https://doi.org/10.1080/01919512.2018.1482456>
- Pereira VJ, Linden KG, Weinberg HS (2007a) Evaluation of UV irradiation for photolytic and oxidative degradation of pharmaceutical compounds in water. *Water Res* 41:4413–4423. <https://doi.org/10.1016/j.watres.2007.05.056>
- Pereira VJ, Weinberg HS, Linden KG, Singer PC (2007b) UV degradation of pharmaceutical compounds in surface water *via* direct and indirect photolysis at 254 nm. *Environ Sci Technol* 41:1682–1688. <https://doi.org/10.1021/es061491b>
- Petrie B, Barden R, Kasprzk-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. <https://doi.org/10.1016/j.watres.2014.08.053>
- Petrovic M, Diaz A, Ventura F, Barceló D (2003) Occurrence and removal of estrogenic short-chain ethoxy nonylphenolic compounds and their halogenated derivatives during drinking water production. *Environ Sci Technol* 37:4442–4448
- Phan HV, Hai FI, McDonald JA, Khan SJ, Van De Merwe JP, Leusch FD, Zhang R, Price WE, Broeckmann A, Nghiem LD (2015) Impact of hazardous events on the removal of nutrients and trace organic contaminants by an anoxic-aerobic membrane bioreactor receiving real wastewater. *Bioresour Technol* 192:192–201
- Pichon V, Chapuis-Hugon F (2008) Role of molecularly imprinted polymers for selective determination of environmental pollutants – a review. *Anal Chim Acta* 622:48–61
- Picos-Corrales LA, Sarmiento-Sánchez JI, Ruelas-Leyva JP, Crini G, Hermsillo-Ochoa E, Gutierrez-Montes JA (2020) Environment-friendly approach toward the treatment of raw agricultural wastewater and river water *via* flocculation using chitosan and bean straw flour as bioflocculants. *ACS Omega* 5:3943–3951. <https://doi.org/10.1021/acsomega.9b03419>
- Pinkston KE, Sedlak DL (2004) Transformation of aromatic ether- and amine-containing pharmaceuticals during chlorine disinfection. *Environ Sci Technol* 38:4019–4025. <https://doi.org/10.1021/es0353681>
- Polatti S, Angioi S, Gianotti V, Gosetti F, Gennaro M (2006) Sorption of pesticides on kaolinite and montmorillonite as a function of hydrophilicity. *J Environ Sci Health B* 41:333–344
- Polo-López MI, Castro-Alfárez M, Oller I, Fernández-Ibáñez P (2014) Assessment of solar photo-Fenton, photocatalysis, and H₂O₂ for removal of phytopathogen fungi spores in synthetic and real effluents of urban wastewater. *Chem Eng J* 257:122–130. <https://doi.org/10.1016/j.cej.2014.07.016>
- Portinho R, Zanella O, Féris LA (2017) Grape stalk application for caffeine removal through adsorption. *J Environ Manag* 202:178–187. <https://doi.org/10.1016/j.jenvman.2017.07.033>
- Preis S, Panorel IC, Kornev I, Hatakka H, Kallas J (2013) Pulsed corona discharge: the role of ozone and hydroxyl radical in aqueous pollutants oxidation. *Water Sci Technol* 68:1536–1542. <https://doi.org/10.2166/wst.2013.399>
- Priac A, Morin-Crini N, Druart C, Gavoille S, Bradu C, Lagarrigue C, Torri G, Winterton P, Crini G (2017) Alkylphenol and alkylphenol polyethoxylates in water and wastewater: a review of options for their elimination. *Arab J Chem* 10:S3749–S3773. <https://doi.org/10.1016/j.arabjc.2014.05.011>
- Putra EK, Pranowo R, Sunarso J, Indraswati N, Ismadji S (2009) Performance of activated carbon and bentonite for adsorption of amoxicillin from wastewater: mechanisms, isotherms and kinetics. *Water Res* 43:2419–2430. <https://doi.org/10.1016/j.watres.2009.02.039>
- Putro JN, Kurniawan A, Ismadji S, Ju YH (2017) Nanocellulose based biosorbents for wastewater treatment: study of isotherm, kinetic, thermodynamic and reusability. *Environ Nanotechnol Monitoring Manage* 8:134–149. <https://doi.org/10.1016/j.enmm.2017.07.002>

- Qin S, Su L, Wang P, Gao Y (2015) Rapid and selective extraction of multiple sulfonamides from aqueous samples based on Fe₃O₄-chitosan molecularly imprinted polymers. *Anal Methods* 7:874–8713
- Qu RJ, Xu BG, Meng LJ, Wang LS, Wang ZY (2015) Ozonation of indigo enhanced by carboxylated carbon nanotubes: performance optimization, degradation products, reaction mechanism and toxicity evaluation. *Water Res* 68:316–327. <https://doi.org/10.1016/j.watres.2014.10.017>
- Quintana JB, Rodil R, Lopez-Mahia P, Muniategui-Lorenzo S, Prada-Rodriguez P (2010) Investigating the chlorination of acidic pharmaceuticals and by-product formation aided by an experimental design methodology. *Water Res* 44:243–255
- Quintana JB, Rodil R, Cela R (2012) Reaction of β -blockers and β -agonist pharmaceuticals with aqueous chlorine. Investigation of kinetics and by-products by liquid chromatography quadrupole time-of-flight mass spectrometry. *Anal Bioanal Chem* 403:2385–2395. <https://doi.org/10.1007/s00216-011-5707-7>
- Racar M, Dolar D, Karadakić K, Čavarović N, Glumac N, Ašperger D, Košutić K (2020) Challenges of municipal wastewater reclamation for irrigation by MBR and NF/RO: physicochemical and microbiological parameters, and emerging contaminants. *Sci Total Environ* 722:137959. <https://doi.org/10.1016/j.scitotenv.2020.137959>
- Radha KV, Sirisha K (2018) Chapter 11: Electrochemical oxidation processes. In: *Advanced oxidation processes for waste water treatment*, pp 359–373. <https://doi.org/10.1016/B978-0-12-810499-6.00011-5>
- Radjenovic J, Petrovic M, Barceló D (2007) Analysis of pharmaceuticals in wastewater and removal using a membrane bioreactor. *Anal Bioanal Chem* 387:1365–1377. <https://doi.org/10.1007/s00216-006-0883-6>
- Radich JG, Krenselewski AL, Zhu JD, Kamat PV (2014) Is graphene a stable platform for photocatalysis? Mineralization of reduced graphene oxide with UV-irradiated TiO₂ nanoparticles. *Chem Mater* 26:4662–4668. <https://doi.org/10.1021/cm5026552>
- Real FJ, Benitez FJ, Acero JL, Sagasti JJP, Casas F (2009) Kinetics of the chemical oxidation of the pharmaceuticals primidone, ketoprofen, and diatrizoate in ultrapure and natural waters. *Ind Eng Chem Research* 48:3380–3388
- Rehman MSU, Munir M, Asfaq M, Rashis N, Nazar MF, Danish M, Han JI (2013) Adsorption of Brilliant Green dye from aqueous solution onto red clay. *Chem Eng J* 228:54–62. <https://doi.org/10.1016/j.cej.2013.04.094>
- Ren YM, Zhang HY, An HG, Zhao Y, Feng J, Xue L, Luan TZ, Fan ZG (2018) Catalytic ozonation of di-n-butyl phthalate degradation using manganese ferrite/reduced graphene oxide nanofiber as catalyst in the water. *J Colloid Interface Sci* 526:347–355. <https://doi.org/10.1016/j.jcis.2018.04.073>
- Renew JE, Huang CH (2004) Simultaneous determination of fluroquinolone, sulfonamide, and trimethoprim antibiotics in wastewater using tandem solid phase extraction and liquid chromatography-electrospray mass spectrometry. *J Chromatogr A* 1042:113–121. <https://doi.org/10.1016/j.chroma.2004.05.056>
- Restivo J, Órfão JJM, Armenise S, Garcia-Bordejé E, Pereira MFR (2012) Catalytic ozonation of metolachlor under continuous operation using nanocarbon materials grown on a ceramic monolith. *J Hazard Mater* 239-240:249–256
- Restivo J, Órfão JJM, Pereira MFR, Garcia-bordejé E, Roche P, Bourdin D, Houssais B, Coste M, Derrouiche S (2013) Catalytic ozonation of organic micropollutants using carbon nanofibers supported on monoliths. *Chem Eng J* 230:115–123. <https://doi.org/10.1016/j.cej.2013.06.064>
- Restivo J, Garcia-bordejé E, Órfão JJM, Pereira MFR (2016) Carbon nanofibers doped with nitrogen for the continuous catalytic ozonation of organic pollutants. *Chem Eng J* 293:102–111. <https://doi.org/10.1016/j.cej.2016.02.055>
- Reungoat J, Escher BI, Macova M, Argaud FX, Gernjak W, Keller J (2012) Ozonation and biological activated carbon filtration of wastewater treatment plant effluents. *Water Res* 46:863–872

- Ribeiro AR, Nunes OC, Pereira MFR, Silva AMT (2015) An overview on the advanced oxidation processes applied for the treatment of water pollutants defined in the recently launched Directive 2013/39/EU. *Environ Int* 75:33–51. <https://doi.org/10.1016/j.envint.2014.10.027>
- Riva V, Mapelli F, Syranidou E, Crotti E, Choukrallah R, Kalogerakis N, Borin S (2019) Root bacteria recruited by *Phragmites australis* in constructed wetlands have the potential to enhance azo-dye phytodepuration. *Microorganisms* 7:384. <https://doi.org/10.3390/microorganisms7100384>
- Riva V, Riva F, Vergani L, Crotti E, Borin S, Mapelli F (2020) Microbial assisted phytodepuration for water reclamation: environmental benefits and threats. *Chemosphere* 241:124843. <https://doi.org/10.1016/j.chemosphere.2019.124843>
- Rivera-Utrilla J, Gómez-Pacheco CV, Sánchez-Polo M, López-Peñalver JJ, Ocampo-Pérez R (2013) Tetracycline removal from water by adsorption/bioadsorption on activated carbons and sludgederived adsorbents. *J Environ Manag* 131:16–24
- Rizzi V, Romanazzi F, Gubitosa J, Fini P, Romita R, Agostiano A, Petrella A, Cosma P (2019) Chitosan film as eco-friendly and recyclable bio-adsorbent to remove/recover diclofenac, ketoprofen, and their mixture from wastewater. *Biomol Ther* 9:571. <https://doi.org/10.3390/biom9100571>
- Roca Jalil ME, Vieira R, Azevedo D, Baschini M, Sapag K (2013) Improvement in the adsorption of thiabendazole by using aluminum pillared clays. *Appl Clay Sci* 71:55–63. <https://doi.org/10.1016/j.clay.2012.11.005>
- Roca Jalil ME, Baschini M, Sapag K (2015) Influence of pH and antibiotic solubility on the removal of ciprofloxacin from aqueous media using montmorillonite. *Appl Clay Sci* 114:69–76. <https://doi.org/10.1016/j.clay.2015.05.010>
- Rocha RP, Gonçalves AG, Pastrana-Martínez LM, Bordoni BC, Soares OSGP, Órfão JJM, Faria JL, Figueiredo JL, Silva AMT, Pereira MFR (2015) Nitrogen-doped graphene-based materials for advanced oxidation processes. *Catal Today* 249:192–198. <https://doi.org/10.1016/j.cattod.2014.10.046>
- Rodríguez-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>
- Rodríguez-Rodríguez CE, Cambronero JC, Beita-Sandi W, Duran JE (2019) Chapter 7: Removal of emerging pollutants by fungi. In: *Fungal bioremediation: fundamentals and applications*. CRC Press, Taylor & Francis Group, pp 186–237. <https://doi.org/10.1201/9781315205984-7>
- Rojas S, Horcajada P (2020) Metal-organic frameworks for the removal of emerging organic contaminants in water. *Chem Rev*. <https://doi.org/10.1021/acs.chemrev.9b00797>
- Romo A, Penas FJ, Sevillano X, Isasi JR (2006) Application of factorial experimental design to the study of the suspension polymerization of beta-cyclodextrin and epichlorohydrin. *J Appl Polym Sci* 100:3393–3402. <https://doi.org/10.1002/app.23778>
- Rong S, Sun Y (2014) Wetted-wall corona discharge induced degradation of sulfadiazine antibiotics in aqueous solution. *J Chem Technol Biotechnol* 89:1351–1359. <https://doi.org/10.1002/jctb.4211>
- Rong SP, Sun YB, Zhao ZH (2014) Degradation of sulfadiazine antibiotics by water falling film dielectric barrier discharge. *Chinese Chem Lett* 25:187–192. <https://doi.org/10.1016/j.cclet.2013.11.003>
- Rosal R, Rodríguez A, Perdígón-Melón JA, Petre A, Garcia-Calvo E, Gomez MJ, Aguera A, Fernandez-Alba A (2010a) Occurrence of emerging pollutants in urban wastewater and their removal through biological treatment followed by ozonation. *Water Res* 44:578–588. <https://doi.org/10.1016/j.watres.2009.07.004>
- Rosal R, Gonzalo M, Rodríguez A, García-Calvo E (2010b) Catalytic ozonation of fenofibric acid over alumina-supported manganese oxide. *J Hazard Mater* 183:271–278
- Rosario-Ortiz FL, Wert EC, Snyder SA (2010) Evaluation of UV/H₂O₂ treatment for the oxidation of pharmaceuticals in wastewater. *Water Res* 44:1440–1448. <https://doi.org/10.1016/j.watres.2009.10.031>

- Rosenfeldt EJ, Linden KG (2004) Degradation of endocrine disrupting chemicals bisphenol A, ethinyl estradiol, and estradiol during UV photolysis and advanced oxidation. *Environ Sci Technol* 38:5476–5483. <https://doi.org/10.1021/es035413p>
- Rossner A, Snyder SA, Knappe DR (2009) Removal of emerging contaminants of concern by alternative adsorbents. *J Water Res* 43:3787–3796. <https://doi.org/10.1016/j.watres.2009.06.009>
- Sakairi N, Nishi N, Tokura S (1999) Cyclodextrin-linked chitosan: synthesis and inclusion complexation abilities. *ACS Symp Ser* 737:68–84. <https://doi.org/10.1021/bk-1999-0737.ch005>
- Salgado R, Marques R, Noronha JP, Carvalho G, Oehmen A, Reis MAM (2011) Assessing the removal of pharmaceuticals and personal care products in a full-scale activated sludge plant. *Environ Sci Pollut Res*. <https://doi.org/10.1007/s11356-011-0693-z>
- Salgado R, Marques R, Noronha JP, Carvalho G, Oehmen A, Reis MAM (2012) Assessing the removal of pharmaceuticals and personal care products in a full-scale activated sludge plant. *Environ Sci Pollut Res Int* 19:1818–1827. <https://doi.org/10.1007/s11356-011-0693-z>
- Salgado R, Pereira VJ, Carvalho G, Soeiro R, Gaffney V, Almeida C, Vale Cardoso V, Ferreira E, Benoliel MJ, Ternes TA, Oehmen A, Reis MAM, Noronha JP (2013) Photodegradation kinetics and transformation products of ketoprofen, diclofenac and atenolol in pure water and treated wastewater. *J Hazard Mater* 244-245:516–527
- Sampaio MJ, Bacsá RR, Benyounes A, Axet R, Serp P, Silva CG, Silva AMT, Faria JL (2015) Synergistic effect between carbon nanomaterials and ZnO for photocatalytic water decontamination. *J Catalysis* 331:172–180. <https://doi.org/10.1016/j.jcat.2015.08.011>
- Sanford S, Singh KS, Chai S, LeClair G (2012) Study of natural adsorbent chitosan and derivatives for the removal of caffeine from water. *Water Quality Res J* 47:80–90. <https://doi.org/10.2166/wqrj.2012.021>
- Sanguanpak S, Chiemchaisri C, Chiemchaisri W, Yamamoto K (2015) Effects of mixed liquor pH on membrane fouling and micro-pollutant removals in membrane bioreactors for municipal landfill leachate treatment. *Water Sci Technol* 72:770–778
- Santos-Silva TG, Montagner CC, Martínez CBR (2018) Evaluation of caffeine effects on biochemical and genotoxic biomarkers in the neotropical freshwater teleost *Prochilodus lineatus*. *Environ Toxicol Pharmacol* 58:237–242. <https://doi.org/10.1016/j.etap.2018.02.002>
- Sarangapani C, Ziuzina D, Behan P, Boehm D, Gilmore BF, Cullen PJ, Bourke P (2019) Degradation kinetics of cold plasma-treated antibiotics and their antimicrobial activity. *Sci Rep* 9:3955. <https://doi.org/10.1038/s41598-019-40352-9>
- Sauvêtre A, Schröder P (2015) Uptake of carbamazepine by rhizomes and endophytic bacteria of *Phragmites australis*. *Frontiers Plant Sci* 6:83. <https://doi.org/10.3389/fpls.2015.00083>
- Schaar H, Clara M, Gans O, Kreuzinger N (2010) Micropollutant removal during biological wastewater treatment and a subsequent ozonation step. *Environ Pollut* 158:1399–1404. <https://doi.org/10.1016/j.envpol.2009.12.038>
- Secundes MFN, Naddeo V, Belgiorno V, Ballesteros F Jr (2014) Removal of emerging contaminants by simultaneous applications of membrane ultrafiltration, activated carbon adsorption, and ultrasound irradiation. *J Hazard Mater* 264:342–349. <https://doi.org/10.1016/j.jhazmat.2013.11.039>
- Serna-Galvis EA, Silva-Agredo J, Giraldo-Aguirre AL, Flórez-Acosta OA, Torres-Palma RA (2016) High frequency ultrasound as a selective advanced oxidation process to remove penicillinic antibiotics and eliminate its antimicrobial activity from water. *Ultrasonics Sonochem* 31:276–283. <https://doi.org/10.1016/j.ultsonch.2016.01.007>
- Serna-Galvis EA, Botero-Coy AM, Martínez-Pachón D, Moncayo-Lasso A, Ibáñez M, Hernández F, Torres-Palma RA (2019) Degradation of seventeen contaminants of emerging concern in municipal wastewater effluents by sonochemical advanced oxidation processes. *Water Res* 154:349–360. <https://doi.org/10.1016/j.watres.2019.01.045>
- Shak KPY, Pang YL, Mah SK (2018) Nanocellulose: recent advances and its prospects in environmental remediation. *Beilstein J Nanotechnol* 9:2479–2498. <https://doi.org/10.3762/bjnano.9.232>

- Sharma VK (2008) Oxidative transformations of environmental pharmaceuticals by Cl₂, ClO₂, O₃ and Fe(VI): kinetics assessment. *Chemosphere* 73:1379–1386. <https://doi.org/10.1016/j.chemosphere.2008.08.033>
- Shen X, Xu C, Ye L (2013) Molecularly imprinted polymers for clean water: analysis and purification. *Ind Eng Chem Res* 52:13890–13899
- Shiono T, Yamamoto K, Yotsumoto Y, Yoshida A (2017) Caffeine adsorption of montmorillonite in coffee extracts. *Biosci Biotechnol Biochem* 81:1591–1597. <https://doi.org/10.1080/09168451.2017.1340087>
- Shreve MJ, Brockman A, Hartleb M, Prebhalo S, Dorman FL, Brennan RA (2016) The white-rot fungus *Trametes versicolor* reduces the estrogenic activity of a mixture of emerging contaminants in wastewater treatment plant effluent. *Int Biodeterior Biodegrad* 109:132–140. <https://doi.org/10.1016/j.ibiod.2016.01.018>
- Silva A, Delerue-Matos C, Figueiredo SA, Freitas OM (2019) The use of algae and fungi for removal of pharmaceuticals by bioremediation and biosorption processes: a review. *Water* 11:1555. <https://doi.org/10.3390/w11081555>
- Simazaki D, Fujiwara J, Manabe S, Matsuda M, Asami M, Kunikane S (2008) Removal of selected pharmaceuticals by chlorination, coagulation-sedimentation and powdered activated carbon treatment. *Water Sci Technol* 58:1129–1135
- Singh RN, Sharma S (2012) Development of suitable photobioreactor for algae production - a review. *Renew Sust Energ Rev* 16:2347–2353. <https://doi.org/10.1016/j.rser.2012.01.026>
- Singh RK, Philip L, Ramanujam S (2016) Rapid removal of carbofuran from aqueous solution by pulsed corona discharge treatment: kinetic study, oxidative, reductive degradation pathway, and toxicity assay. *Ind Eng Chem Res* 55:7201–7209. <https://doi.org/10.1021/acs.iecr.6b01191>
- Singh RK, Philip L, Ramanujam S (2017) Removal of 2,4-dichlorophenoxyacetic acid in aqueous solution by pulsed corona discharge treatment: effect of different water constituents, degradation pathway and toxicity assay. *Chemosphere* 184:207–214. <https://doi.org/10.1016/j.chemosphere.2017.05.134>
- Singhal N, Perez-Garcia O (2016) Degrading organic micropollutants: the next challenge in the evolution of biological wastewater treatment processes. *Front Environ Sci* 4:36. <https://doi.org/10.3389/fenvs.2016.00036>
- Slade R, Bauen A (2013) Micro-algae cultivation for biofuels: cost, energy balance, environmental impacts and future prospects. *Biomass Bioenergy* 53:29–38. <https://doi.org/10.1016/j.biombioe.2012.12.019>
- Smith JB, Adams I, Ji H-F (2018) Mechanism of ampicillin degradation by non-thermal plasma treatment with FE-DBD. *Plasma* 1:1–11. <https://doi.org/10.3390/plasma1010001>
- Snyder SA, Wert EC, Rexing DJ, Zegers RE, Drury DD (2006) Ozone oxidation of endocrine disruptors and pharmaceuticals in surface water and wastewater. *Ozone Sci Eng* 28:445–460. <https://doi-org.inec.bib.cnrs.fr/10.1080/01919510601039726>
- Snyder SA, Adham S, Redding AM, Cannon FS, DeCarolis J, Oppenheimer J, Wert EC, Yoon Y (2007) Role of membranes and activated carbon in the removal of endocrine disruptors and pharmaceuticals. *Des* 202:156–181
- Soares OSGP, Gonçalves AG, Delgado JJ, Órfão JJM, Pereira MFR (2015) Modification of carbon nanotubes by ball-milling to be used as ozonation catalysts. *Catal Today* 249:199–203
- Sole M, Lopez de Alda MJ, Castillo M, Porte C, Ladegaard-Pedersen K, Barceló D (2000) Estrogenicity determination in sewage treatment plants and surface waters from the Catalanian area (NE Spain). *Environ Sci Technol* 34:5076–5083
- Song Z, Wang MG, Wang Z, Wang YF, Li RY, Zhang YT, Liu C, Liu Y, Xu BB, Qi F (2019a) Insights into heteroatom-doped graphene for catalytic ozonation: active centers, reactive oxygen species evolution, and catalytic mechanism. *Environ Sci Technol* 53:5337–4538
- Song Z, Zhanf Y, Liu C, Xu BB, Qi F, Yuan DG, Pu SG (2019b) Insight into OH and O₂-formation in heterogeneous catalytic ozonation by delocalized electrons and surface oxygen-containing functional groups in layered-structure nanocarbons. *Cheml Eng J* 357:655–666

- Soufan M, Deborde M, Legube B (2012) Aqueous chlorination of diclofenac: kinetic study and transformation products identification. *Water Res* 46:3377–3386. <https://doi.org/10.1016/j.watres.2012.03.056>
- Spina F, Anastasi A, Prigione V, Tigini V, Varese GC (2012) Biological treatment of industrial wastewaters: a fungal approach. *Chem Eng Trans* 27:175–180. <https://doi.org/10.33031/CET1227030>
- Stackelberg PE, Gibs J, Furlong ET, Meyer MT, Zaugg SD, Lippincott RL (2007) Efficiency of conventional drinking-water-treatment processes in removal of pharmaceuticals and other organic compounds. *Sci Total Environ* 377:255–272. <https://doi.org/10.1016/j.scitotenv.2007.01.095>
- Stadlmair LF, Letzel T, Graßmann J (2018) Monitoring enzymatic degradation of emerging contaminants using a chip-based robotic nano-ESI-MS tool. *Anal Bioanal Chem* 410:7–32. <https://doi.org/10.1007/s00216-017-0729-4>
- Stalter D, Magdeburg A, Oehlmann J (2010a) Comparative toxicity assessment of ozone and activated carbon treated sewage effluents using an in vivo test battery. *Water Res* 44:2610–2620. <https://doi.org/10.1016/j.watres.2010.01.023>
- Stalter D, Magdeburg A, Weil M, Knacker T, Oehlmann J (2010b) Toxication or detoxication? In vivo toxicity assessment of ozonation as advanced wastewater treatment with the rainbow trout. *Water Res* 44:439–448. <https://doi.org/10.1016/j.watres.2009.07.025>
- Stalter D, Magdeburg A, Wagner M, Oehlmann J (2011) Ozonation and activated carbon treatment of sewage effluents: removal of endocrine activity and cytotoxicity. *Water Res* 45:1015–1024. <https://doi.org/10.1016/j.watres.2010.10.008>
- Stará Z, Krčma F, Nejezchleb M, Skalný JD (2009) Organic dye decomposition by DC diaphragm discharge in water: effect of solution properties on dye removal. *Des* 239:283–294. <https://doi.org/10.1016/j.desal.2008.03.025>
- Stofela SKF, de Andrade JR, Vieira MGA (2017) Adsorption of benzene, toluene, and xylene (BTX) from binary aqueous solutions using commercial organoclay. *Can J Chem Eng* 95:1034–1044. <https://doi.org/10.1002/cjce.22748>
- Suárez S, Reif R, Lema JM, Omil F (2012) Mass balance of pharmaceutical and personal care products in a pilot-scale single-sludge system: influence of T SRT and recirculation ratio. *Chemosphere* 89:164–171
- 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* 227–228:227–236
- Sugiarto AT, Ito S, Ohshima SM, Skalny JD (2003) Oxidative decoloration of dyes by pulsed discharge plasma in water. *J Electroanal Chem* 58:135–145. [https://doi.org/10.1016/S0304-3886\(02\)00203-6](https://doi.org/10.1016/S0304-3886(02)00203-6)
- Sun J, Wang J, Zhang R, Wei D, Long Q, Huang Y, Xie X, Li A (2017) Comparison of different advanced treatment processes in removing endocrine disruption effects from municipal wastewater secondary effluent. *Chemosphere* 168:1–9. <https://doi.org/10.1016/j.chemosphere.2016.10.031>
- Syam Babu D, Srivastava V, Nidheesh PV, Suresh Kumar M (2019) Detoxification of water and wastewater by advanced oxidation processes. *Sci Total Environ* 696:133961. <https://doi.org/10.1016/j.scitotenv.2019.133961>
- Syranidou E, Christofilopoulos S, Politi M, Weyens N, Venieri D, Vangronsveld J, Kalogerakis N (2017) Bisphenol-A removal by the halophyte *Juncus acutus* in a phytoremediation pilot, characterization and potential role of the endophytic community. *J Hazard Mater* 323:350–358. <https://doi.org/10.1016/j.jhazmat.2016.05.034>
- Szejtli J (1998) Introduction and general overview of cyclodextrin chemistry. *Chem Rev* 98:1743–1753. <https://doi.org/10.1021/cr970022c>
- Szejtli J, Szenté L (2005) Elimination of bitter, disgusting tastes of drugs and foods by cyclodextrins. *Eur J Pharm Biopharm* 61:115–125. <https://doi.org/10.1016/j.ejpb.2005.05.006>
- Tang S, Yuan D, Rao Y, Li N, Qi J, Cheng T, Sun Z, Gu J (2018a) Huang H Persulfate activation in gas phase surface discharge plasma for synergetic removal of antibiotic in water. *Chem Eng J* 337:446–454. <https://doi.org/10.1016/j.cej.2017.12.117>

- Tang S, Yuan D, Rao Y, Zhang J, QumY GJ (2018b) Evaluation of antibiotic oxytetracycline removal in water using a gas phase dielectric barrier discharge plasma. *J Environ Manag* 226:22–29. <https://doi.org/10.1016/j.jenvman.2018.08.022>
- Tang S, Yuan D, Rao Y, Li M, Shi G, Gu J, Zhang T (2019) Percarbonate promoted antibiotic decomposition in dielectric barrier discharge plasma. *J Hazard Mater* 366:669–676. <https://doi.org/10.1016/j.jhazmat.2018.12.056>
- Tay K, Rahman N, Abas M (2010) Ozonation of parabens in aqueous solution: kinetics and mechanism of degradation. *Chemosphere* 81:1446–1453. <https://doi.org/10.1016/j.chemosphere.2010.09.004>
- Teijón G, Candela L, Tamoh K, Molina-Díaz A, Fernández-Alba AR (2010) Occurrence of emerging contaminants, priority substances (2008/105/EC) and heavy metals in treated wastewater and groundwater at Depurbaix facility (Barcelona, Spain). *Sci Total Environ* 408:3584–3595. <https://doi.org/10.1016/j.scitotenv.2010.04.041>
- Ternes TA, Stuber J, Herrmann N, McDowell D, Ried A, Kampmann M, Teiser B (2003) Ozonation: a tool for removal of pharmaceuticals, contrast media and musk fragrances from wastewater? *Water Res* 37:1976–1982. [https://doi.org/10.1016/S0043-1354\(02\)00570-5](https://doi.org/10.1016/S0043-1354(02)00570-5)
- Thanekar P, Murugesan P, Gogate PR (2018) Improvement in biological oxidation process for the removal of dichlorvos from aqueous solutions using pretreatment based on hydrodynamic cavitation. *J Water Proc Eng* 23:20–26. <https://doi.org/10.1016/j.jwpe.2018.03.004>
- Thomas B, Raj MC, Athira KB, Rubiyah MH, Joy J, Moores A, Drisko GL, Sanchez C (2018) Nanocellulose, a versatile green platform: from biosources to materials and their applications. *Chem Rev* 118:11575–11625. <https://doi.org/10.1021/acs.chemrev.7b00627>
- Thompson J, Eaglesham G, Reungoat J, Poussade Y, Bartkow M, Lawrence M, Mueller JF (2011) Removal of PFOS, PFOA and other perfluoroalkyl acids at water reclamation plants in South East Queensland Australia. *Chemosphere* 82:9–17. <https://doi.org/10.1016/j.chemosphere.2010.10.040>
- Thurman M (2006) Accurate-mass identification of chlorinated and brominated products of 4-nonylphenol, nonylphenol dimers, and other endocrine disrupters. *J Mass Spectrom* 41:1287–1297
- Tian W, Kushner MJ (2014) Atmospheric pressure dielectric barrier discharges interacting with liquid covered tissue. *J Phys D Appl Phys* 47:165201. <https://doi.org/10.1088/0022-3727/47/16/165201>
- Tolboom SN, Carrillo-Nieves D, de Jesús R-AM, de la Cruz QR, Barceló D, Iqbal HMN, Parra-Saldivar R (2019) Algal-based removal strategies for hazardous contaminants from the environment – a review. *Sci Total Environ* 665:358–366. <https://doi.org/10.1016/j.scitotenv.2019.02.129>
- Tomasini A, León-Santesteban HH (2019) Fungal bioremediation. Fundamentals and applications. CRC Press Taylor & Francis Group. ISBN: 9781138636408
- Torres-Palma RA, Serna-Galvis EA (2018) Chapter 7: Sonolysis. In: Advanced oxidation processes for waste water treatment, pp 117–213. <https://doi.org/10.1016/B978-0-12-810499-6.00007-3>
- Uekama K, Hirayama F, Arima H (2006) Recent aspect of cyclodextrin-based drug delivery system. *J Incl Phenom Macrocycl Chem* 56:3–8. <https://doi.org/10.1007/s10847-006-9052-y>
- Valero P, Verbel M, Silva-Agredo J, Mosteiro R, Ormad MP, Torres-Palma RA (2017) Electrochemical advanced oxidation processes for *Staphylococcus aureus* disinfection in municipal WWTP effluents. *J Environ Manag* 198:256–265. <https://doi.org/10.1016/j.jenvman.2017.04.070>
- Vandenkoornhuyse P, Quaiser A, Duhamel M, Le Van A, Dufresne A (2015) The importance of the microbiome of the plant holobiont. *New Phytol* 206:1196–1206. <https://doi.org/10.1111/nph.13312>
- Vanraes P, Willems G, Nikiforov A, Surmont P, Lynen F, Vandamme J, Van Durme J, Verheust YP, Van Hulle SWH, Dumoulin A, Leys C (2015) Removal of atrazine in water by combination of activated carbon and dielectric barrier discharge. *J Hazard Mater* 299:647–655. <https://doi.org/10.1016/j.jhazmat.2015.07.075>
- Vanraes P, Ghodbane H, Davister D, Wardenier N, Nikiforov A, Verheust YP, Van Hulle SWH, Hamdaoui O, Vandamme J, Van Durme J, Surmont P, Lynen F, Leys C (2017) Removal of

- several pesticides in a falling water film DBD reactor with activated carbon textile: energy efficiency. *Water Res* 116:1–12. <https://doi.org/10.1016/j.watres.2017.03.004>
- Vasiliadou IA, Sánchez-Vázquez R, Molina R, Martínez F, Melero JA, Bautista LF, Iglesias J, Morales G (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>
- Vergani L, Mapelli F, Zanardini E, Terzaghi E, Di Guardo A, Morosini C, Raspa G, Borin S (2017) Phyto-rhizoremediation of polychlorinated biphenyl contaminated soils: an outlook on plant-microbe beneficial interactions. *Sci Total Environ* 575:1395–1406. <https://doi.org/10.1016/j.scitotenv.2016.09.218>
- Verlicchi P, Al Aukidy M, Zambelle E (2012) Occurrence of pharmaceutical compounds in urban wastewater: removal, mass load and environmental risk after a secondary treatment – a review. *Sci Total Environ* 429:123–155. <https://doi.org/10.1016/j.scitotenv.2012.04.028>
- Vieira WT, de Farias MB, Spaolonzi MP, da Silva MGC, MGA V (2020) Removal of endocrine disruptors in waters by adsorption, membrane filtration and biodegradation. A review. *Environ Chem Lett* 2020. <https://doi.org/10.1007/s10311-020-01000-1>
- Vijayaraghavan K, Yun YS (2008) Bacterial biosorbents and biosorption. *Biotechnol Adv* 26:266–291. <https://doi.org/10.1016/j.biotechadv.2008.02.002>
- Villegas-Guzman P, Silva-Agredo J, Florez O, Giraldo-Aguirre AL, Pulgarin C, Torres-Palma RA (2017) Selecting the best AOP for isoxazolyl penicillins degradation as a function of water characteristics: effects of pH, chemical nature of additives and pollutant concentration. *J Environ Manag* 190:72–79. <https://doi.org/10.1016/j.jenvman.2016.12.056>
- Vogna D, Marotta R, Andreozzi R, Napolitano A, d'Ischia M (2004) Kinetic and chemical assessment of the UV/H₂O₂ treatment of antiepileptic drug carbamazepine. *Chemosphere* 54:497–505. [https://doi.org/10.1016/S0045-6535\(03\)00757-4](https://doi.org/10.1016/S0045-6535(03)00757-4)
- Voisin H, Bergström L, Liu P, Mathew AP (2017) Nanocellulose-based materials for water purification. *Nano* 7:57. <https://doi.org/10.3390/nano7030057>
- von Sonntag C, von Gunten U (2012) Chemistry of ozone in water and wastewater treatment – from basic principles to applications. IWA Publishing, London. <https://doi.org/10.2166/9781780400839>
- Vyas A, Saraf S, Saraf S (2008) Cyclodextrin based novel drug delivery systems. *J Incl Phenom Macrocycl Chem* 62:23–42. <https://doi.org/10.1007/s10847-008-9456-y>
- Wang D (2019) A critical review of cellulose-based nanomaterials for water purification in industrial processes. *Cellulose* 26:687–701. <https://doi.org/10.1007/s10570-018-2143-2>
- Wang JL, Wang SZ (2016) Removal of pharmaceuticals and personal care products (PPCPs) from wastewater: a review. *J Environ Manag* 182:620–640. <https://doi.org/10.1016/j.jenvman.2016.07.049>
- Wang JH, Zhuan R (2020) Degradation of antibiotics by advanced oxidation processes: an overview. *Sci Total Environ* 701:135023. <https://doi.org/10.1016/j.scitotenv.2019.135023>
- Wang CJ, Li Z, Jiang WT (2011) Adsorption of ciprofloxacin on 2:1 dioctahedral clay minerals. *Appl Clay Sci* 53:723–728. <https://doi.org/10.1016/j.clay.2011.06.014>
- Wang CL, Zou XQ, Zhao YF, Li BJ, Song QC, Li YL, Yu WW (2016a) Distribution, sources, and ecological risk assessment of polycyclic aromatic hydrocarbons in the water and suspended sediments from the middle and lower reaches of the Yangtze River, China. *Environ Sci Pollut Res* 23:17158–17170
- Wang Y, Xie Y, Sun H, Xiao J, Cao H, Wang S (2016b) 2D/2D Nano-hybrids of γ -MnO₂ on reduced graphene oxide for catalytic ozonation and coupling peroxydisulfate activation. *J Hazard Mater* 301:56–64. <https://doi.org/10.1016/j.jhazmat.2015.08.031>
- Wang Y, Xie Y, Sun H, Xiao J, Cao H, Wang S (2016c) Efficient catalytic ozonation over reduced graphene oxide for p-hydroxybenzoic acid (PHBA) destruction: active site and mechanism. *Appl Mater Interfaces* 8:9710–9720. <https://doi.org/10.1021/acsami.6b01175>

- Wang T, Huang ZX, Miao HF, Ruan WQ, Ji XP, Sun FB, Ren HY (2018a) Insights into influencing factor, degradation mechanism and potential toxicity involved in aqueous ozonation of oxcarbazepine. *Chemosphere* 201:189–196. <https://doi.org/10.1016/j.chemosphere.2018.02.062>
- Wang J, Chen S, Quan X, Yu HG (2018b) Fluorine-doped carbon nanotubes as an efficient metal-free catalyst for destruction of organic pollutants in catalytic ozonation. *Chemosphere* 190:135–143. <https://doi.org/10.1016/j.chemosphere.2017.09.119>
- Wang Y, Cao H, Chen L, Chen C, Duan X, Xie Y, Song W, Sun H, Wang S (2018c) Tailored synthesis of active reduced graphene oxides from waste graphite: structural defects and pollutant-dependent reactive radicals in aqueous organics decontamination. *Appl Catal B Environ* 229:71–80. <https://doi.org/10.1016/j.apcatb.2018.02.010>
- Wang C, Qu G, Wang T, Deng F, Liang D (2018d) Removal of tetracycline antibiotics from wastewater by pulsed corona discharge plasma coupled with natural soil particles. *Chem Eng J* 346:159–170. <https://doi.org/10.1016/j.cej.2018.03.149>
- Wang J, Quan X, Chen S, Yu H, Liu G (2019a) Enhanced catalytic ozonation by highly dispersed CeO₂ on carbon nanotubes for mineralization of organic pollutants. *J Hazard Mater* 368:621–629. <https://doi.org/10.1016/j.jhazmat.2019.01.095>
- Wang Y, Cao H, Chen C, Xie Y, Sun H, Duan X, Wang S (2019b) Metal-free catalytic ozonation on surface-engineered graphene: microwave reduction and heteroatom doping. *Chem Eng J* 355:118–129. <https://doi.org/10.1016/j.cej.2018.08.134>
- Wang B, Wang C, Yao S, Peng Y, Xu Y (2019c) Plasma-catalytic degradation of tetracycline hydrochloride over Mn/γ-Al₂O₃ catalysts in a dielectric barrier discharge reactor. *Plasma Sci Technol* 21:065503. <https://doi.org/10.1088/2058-6272/ab079c>
- Warsinger DM, Chakraborty S, Tow EW, Plumlee MH, Bellona C, Loutatidou S, Karimi L, Mikelonis AM, Achilli A, Ghassemi A, Padhye LP, Snyder SA, Curcio S, Vecitis CD, Arafat HA, Lienhard VJH (2018) A review of polymeric membranes and processes for potable water reuse. *Prog Polym Sci* 81:209–237. <https://doi.org/10.1016/j.progpolymsci.2018.01.004>
- Watkinson AJ, Murby EJ, Kolpin DW, Costanzo SD (2009) The occurrence of antibiotics in an urban watershed: from wastewater to drinking water. *Sci Total Environ* 407:2711–2723
- Wert EC, Rosario-Ortiz FL, Drury DD, Snyder SA (2007) Formation of oxidation byproducts from ozonation of wastewater. *Water Res* 41:1481–1490. <https://doi.org/10.1016/j.watres.2007.01.020>
- 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. <https://doi.org/10.1021/es0484799>
- Wiedenhof N, Lammers JNJJ, Van Panthaleon Van Eck CL (1969) Properties of cyclodextrins. III Cyclodextrin-epichlorohydrin resins Preparation and analysis *Stärke* 21:119–123. <https://doi.org/10.1002/star.19690210504>
- Wimmer T, Kreuzer FH, Staudinger G, Nussstein P (1992) Synthesis of novel insoluble cyclodextrin polymers. In: Hedges AR (ed) *Minutes Int. Symp. Cyclodextrins*, 6th (1992), 106–9. Editions de Santé, Paris, France
- Xiang Y, Fang J, Shang C (2016) Kinetics and pathways of ibuprofen degradation by the UV/chlorine advanced oxidation process. *Water Res* 90:301–308
- Xie M, Chen W, Xu Z, Zheng S, Zhu D (2014) Adsorption of sulfonamides to demineralized pine wood biochars prepared under different thermochemical conditions. *Environ Pollut* 186:187–194. <https://doi.org/10.1016/j.envpol.2013.11.022>
- Xin L, Sun Y, Feng J, Wang J, He D (2016) Degradation of triclosan in aqueous solution by dielectric barrier discharge plasma combined with activated carbon fibers. *Chemosphere* 144:855–863. <https://doi.org/10.1016/j.chemosphere.2015.09.054>
- Xiong Q, Yang Z, Bruggeman PJ (2015) Absolute OH density measurements in an atmospheric pressure dc glow discharge in air with water electrode by broadband UV absorption spectroscopy. *J Phys D Appl Phys* 48:424008. <https://doi.org/10.1088/0022-3727/48/4/424008>

- Xiong JQ, Kurade MB, Abou-Shanab RAI, Ji MK, Choi JJO, Jeon BH (2016) Biodegradation of carbamazepine using freshwater microalgae *Chlamydomonas mexicana* and *Scenedesmus obliquus* and the determination of its metabolic fate. *Bioresour Technol* 205:183–190
- Xu P, Janex ML, Savoye P, Cockx A, Lazarova V (2002) Wastewater disinfection by ozone: main parameters for process design. *Water Res* 36:1043–1055. [https://doi.org/10.1016/S0043-1354\(01\)00298-6](https://doi.org/10.1016/S0043-1354(01)00298-6)
- Xu G, Xie X, Qin L, Hu X, Zhang D, Xu J, Li D, Ji X, Huang Y, Tu Y, Jiang L, Wei D (2019) Simple synthesis of a swellable porous β -cyclodextrin-based polymer in the aqueous phase for the rapid removal of organic micro-pollutants from water. *Green Chem* 21:6062–6072. <https://doi.org/10.1039/C9GC02422K>
- Xu Z, Xue X, Hu S, Li Y, Shen J, Lan Y, Zhou R, Yang F, Cheng C (2020) Degradation effect and mechanism of gas-liquid phase dielectric barrier discharge on norfloxacin combined with H_2O_2 or Fe^{2+} . *Sep Purif Technol* 230:115862. <https://doi.org/10.1016/j.seppur.2019.115862>
- Yadav AN, Mishra S, Singh S, Gupta (2019) Recent advancement in white biotechnology through fungi. Springer, Cham. <https://doi.org/10.1007/978-3-030-10480-1>
- Yamasaki H, Makihata Y, Fukunaga K (2008) Preparation of crosslinked β -cyclodextrin polymer beads and their application as a sorbent for removal of phenol from wastewater. *J Chem Technol Biotechnol* 83:991–997. <https://doi.org/10.1002/jctb.1904>
- Yamasaki H, Odamura A, Makihata Y, Fukunaga K (2017) Preparation of new photo-crosslinked β -cyclodextrin polymer beads. *Polym J* 49:377–383. <https://doi.org/10.1038/pj.2016.127>
- Yang TR (2003) Adsorbents: fundamentals and applications. Wiley-Interscience, Hoboken, 424 p
- Yang W, Zhou H, Cicek N (2013) Treatment of organic micropollutants in water and wastewater by UV-based processes: a literature review. *Critical Rev Environ Sci Technol* 44:1443–1476. <https://doi-org.ineec.bib.cnrs.fr/10.1080/10643389.2013.790745>
- Yang Z, Wu G, Lim Q AH, Yao X, Ji H (2020) Removal of various pollutants from wastewaters using an efficient and degradable hypercrosslinked polymer. *Sep Sci Technol*. <https://doi.org/10.1080/01496395.2020.1745239>
- Yin RL, Guo WQ, Du JS, Zhou XJ, Zheng H, Wu QL, Chang J, Ren NQ (2017) Heteroatoms doped graphene for catalytic ozonation of sulfamethoxazole by metal-free catalysis: performances and mechanisms. *Chem Eng J* 317:632–639. <https://doi.org/10.1016/j.cej.2017.01.038>
- Ying GG, Kookana RS, Kolpin DW (2009) Occurrence and removal of pharmaceutically active compounds in sewage treatment plants with different technologies. *J Environ Monitoring* 11:1498–1505. <https://doi.org/10.1039/B904548A>
- Yu Z, Peldszus S, Huck PM (2009) Adsorption of selected pharmaceuticals and an endocrine disrupting compound by granular activated carbon. I. Adsorption capacity and kinetics. *Environ Sci Technol* 43:–1467, 1473
- Yu X, Tong S, Ge M, Wu L, Zuo J, Cao C, Song W (2013) Adsorption of heavy metal ions from aqueous solution by carboxylated cellulose nanocrystals. *J Environ Sci* 25:933–943
- Yu Z, Sun Y, Zhang G, Zhang C (2017) Degradation of DEET in aqueous solution by water falling film dielectric barrier discharge: effect of three operating modes and analysis of the mechanism and degradation pathway. *Chem Eng J* 317:90–102. <https://doi.org/10.1016/j.cej.2017.02.068>
- Yuan F, Hu C, Hu X, Qu J, Yang M (2009) Degradation of selected pharmaceuticals in aqueous solution with UV and UV/ H_2O_2 . *Water Res* 43:1766–1774. <https://doi.org/10.1016/j.watres.2009.01.008>
- Zha SX, Zhou Y, Jin X, Chen Z (2013) The removal of amoxicillin from wastewater using organo-bentonite. *J Environ Manag* 129:569–576. <https://doi.org/10.1016/j.jenvman.2013.08.032>
- Zhang S, Grimm D (2005) Naproxen removal from water by chlorination and biofilm processes. *Water Res* 39:668–676
- Zhang Y, Geißen SU (2012) Elimination of carbamazepine in a non-sterile fungal bioreactor. *Bioresour Technol* 112:221–227
- Zhang Z, Feng Y, Liu Y, Sun Q, Gao P, Ren N (2010) Kinetic degradation model and estrogenicity changes of EE2 (17 α -ethinylestradiol) in aqueous solution by UV and UV/ H_2O_2 technology. *J Hazard Mater* 181:1127–1133. <https://doi.org/10.1016/j.jhazmat.2010.05.132>

- 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* 102:2265–2271
- Zhang Y, Xie J, Liu M, Tian Z, He Z, van Nostrand JD, Ren L, Zhou J, Yang M (2013) Microbial community functional structure in response to antibiotics in pharmaceutical wastewater treatment systems. *Water Res* 47:6298–6308
- Zhang X, Guo W, Ngo HH, Wen H, Li N, Wu W (2016a) Performance evaluation of powdered activated carbon for removing 28 types of antibiotics from water. *J Environ Manag* 172:193–200. <https://doi.org/10.1016/j.jenvman.2016.02.038>
- Zhang Y, Lv T, Carvalho PN, Arias CA, Chen Z, Brix H (2016b) Removal of the pharmaceuticals ibuprofen and iohexol by four wetland plant species in hydroponic culture: plant uptake and microbial degradation. *Environ Sci Pollut Res* 23:2890–2898. <https://doi.org/10.1007/s11356-015-5552-x>
- Zhang Q, Zhang H, Zhang Q, Huang Q (2018) Degradation of norfloxacin in aqueous solution by atmospheric pressure non-thermal plasma: mechanism and degradation pathways. *Chemosphere* 210:433–439. <https://doi.org/10.1016/j.chemosphere.2018.07.035>
- Zhao D, Zhao L, Zhu CS, Huang WQ, Hu JL (2009) Water-insoluble beta-cyclodextrin polymer crosslinked by citric acid: synthesis and adsorption properties toward phenol and methylene blue. *J Incl Phenom Macrocylic Chem* 63:195–201. <https://doi.org/10.1007/s10847-008-9507-4>
- Zhongbo Z, Hu J (2008) Selective removal of estrogenic compounds by molecular imprinted polymer (MIP). *Water Res* 42:4101–4108
- Zhou AJ, Chen WG, Liao L, Xie PC, Zhang TC, Wu XM, Feng XN (2019) Comparative adsorption of emerging contaminants in water by functional designed magnetic poly(*N*-isopropylacrylamide)/chitosan hydrogels. *Sci Total Environ* 671:377–387. <https://doi.org/10.1016/j.scitotenv.2019.03.183>
- Zhu XX, Brizard F, Wen CC, Brown GR (1997) Binding of bile acids by polymerized cyclodextrin. *J Macromol Sci Pure Appl Chem* A34:335–347. <https://doi.org/10.1080/10601329708014959>
- Zhu R, Chen Q, Zhou Q, Xi Y, Zhu J, He H (2016) Adsorbents based on montmorillonite for contaminant removal from water: a review. *Appl Clay Sci* 123:239–258. <https://doi.org/10.1016/j.clay.2015.12.024>
- Zimmermann SG, Wittenwiler M, Hollender J, Krauss M, Ort C, Siegrist H, von Gunten U (2011) Kinetic assessment and modeling of an ozonation step for full-scale municipal wastewater treatment: micropollutant oxidation, by-product formation and disinfection. *Water Res* 45:605–617. <https://doi.org/10.1016/j.watres.2010.07.080>
- Zraunig A, Estelrich M, Gattringer H, Kissler J, Langergraber G, Radtke M, Rodriguez-Roda I, Buttiglieri G (2019) Long term decentralized greywater treatment for water reuse purposes in a tourist facility by vertical ecosystem. *Ecol Eng* 138:138–147. <https://doi.org/10.1016/j.ecoleng.2019.07.003>