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Removal of emerging contaminants from wastewater using advanced treatments. A review

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Abstract

The rise of emerging contaminants in waters challenges the scientific community and water treatment stakeholders to design remediation techniques that are simple, practical, inexpensive, effective, and environmentally friendly. Emerging contaminants include antibiotics, hormones, illicit drugs, endocrine disruptors, cosmetics, personal care products, pesticides, surfactants, industrial products, microplastics, nanoparticles, and nanomaterials. Removing those contaminants is not easy because classical wastewater treatment systems are not designed to handle emerging contaminants, and contaminants often occur as traces in complex organo-mineral mixtures. Here, we review advanced treatments for the removal of emerging contaminants in wastewater, with focus on adsorption-oriented processes using non-conventional adsorbents such as cyclo-dextrin polymers, metal-organic frameworks, molecularly imprinted polymers, chitosan, and nanocellulose. We describe biological-based technologies for the degradation and removal of emerging contaminants. Then, we present advanced oxidation processes as the most promising strategies because of their simplicity and efficiency.

Keywords Emerging contaminants · Wastewater · Advanced treatments · Adsorption · Biological technology · Oxidation processes

Introduction

Emerging contaminants are a group of natural and synthetic chemicals, and biological agents that are not or poorly regulated. These substances are currently of concern because they have known or suspected adverse impacts on the environment and the human health. Indeed, emerging contaminants are not necessarily of new use, but newly identified and for which data on their presence and fate in the environment, and their effects on organisms is not completely understood. The list of these substances is particularly long and includes pharmaceuticals such as antibiotics, anti-inflammatory drugs, anti-diabetics, analgesics, antidepressants,

antisiolitics, lipid regulators, natural and synthetic hormones, illicit drugs and endocrine disruptors; cosmetics and personal care products including fragrances, fats, oils, detergents, disinfectants, sunscreens and insect repellants; pesticides; industrial products such as surfactants, additives, solvents, flame retardants and nanomaterials; microplastics and pathogens. The number of chemical substances concerned is constantly changing both in terms of parent substances and their degradation products, for example resulting from biological treatment. Due to advantages offered by these products in everyday life, many of them are employed and released continuously into the environment, even at very low concentrations, and some can cause chronic toxicity, endocrine disruption in humans and aquatic organisms, and the development of antibiotic resistant bacteria. It is therefore necessary to mobilize efforts to protect human health and biodiversity (Patle et al. 2020; Hube and Wu 2021; Karpińska and Kotowska 2021).

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Nowadays, it is recognized that the presence of many emerging contaminants can be correlated with the discharge of wastewater effluents, mainly from wastewater treatment plants located in highly industrialized and urban areas (Fig. 1) (Morin-Crini and Crini 2017; Priac et al. 2017; Gilbert-Alarcón et al. 2018; Mezzelani et al. 2018; Picos-Corales et al. 2020). Indeed, conventional domestic wastewater treatment plants, often stabilization ponds and activated sludge systems, have not been designed to treat recalcitrant organic pollutants including emerging substances (Botero-Coy et al. 2018; Gogoi et al. 2018; Crini and Lichtfouse 2019; Tolboom et al. 2019; Patel et al. 2019). As a result, the discharged effluents always contain a heterogeneous mixture of substances. There are complementary solutions to existing treatments to deal with this residual contamination, such as the use of activated carbon coupled with oxidation steps and membrane filtration. Other advanced treatments have been studied in recent years as well (Rodríguez-Narvaez et al. 2017; Bourgin et al. 2018; Collivignarelli et al. 2018; Miklos et al. 2018; Liu et al. 2019; Khan et al. 2020).

This review presents advanced treatment methods such as adsorption-oriented processes using biosorbents, biological-based technologies, and advanced oxidation processes. Biosorbents such as cyclodextrin bead polymers have great potential in environmental applications although they are still at laboratory stage. Selected



Fig. 1 Over-consumption of pharmaceuticals and personal care products leads to contamination of rivers via wastewater from sewage treatment plants. Sinaloa, Mexico. source: Lorenzo A. Picos-Corales, Sinaloa, Mexico

biological approaches include constructed wetlands, biomembrane reactors, strategies based on the use of algae, fungi or bacteria, and enzymatic degradation. Advanced oxidation processes such as electrochemical technologies, catalytic ozonation and plasma also represent the most promising approaches. This article is an abridged version of the chapter published by Morin-Crini et al. (2021) in the series Environmental Chemistry for a Sustainable World.

Adsorption-oriented processes for the removal of emerging contaminants

Liquid–solid adsorption using commercial activated carbons is a key method for removing contaminants from wastewaters or drinking water sources. Indeed, this industrial technique of contaminant removal can produce high quality water, while also being a process that is both technologically simple and economically feasible (Crini 2010). It is known that commercial activated carbons in granular or powder form are effective adsorbents for treating a wide range of contaminants, including pesticides and pharmaceuticals, for adsorbing organic matter to reduce chemical oxygen demand and biochemical oxygen demand, for decoloring water, or for treating substances that cause a specific taste or odor (Crini and Badot 2007, 2010; Couto et al. 2015; Ferreira et al. 2015; Crini et al. 2019; Khan et al. 2020). However, even though the high adsorption capacity of active carbons is widely recognized, there are some drawbacks, namely their rapid saturation and regeneration. This regeneration step of saturated carbon is costly, not straightforward, and leads to a loss of the adsorbent. However, even though the high adsorption capacity of active carbons is widely recognized, active carbon technology has several drawbacks. Active carbons are quite expensive, the higher the quality, the greater the cost. The different qualities of carbon are strongly related to the raw material used, as well as dependent on the carbonization conditions and the way in which activation is carried out (physical or chemical). There are also two shortcomings, the rapid saturation and the need of regeneration of saturated carbon, which is also expensive, not straightforward, and results in adsorbent loss. It is therefore interesting to find new materials capable of having the same performance as carbon without its disadvantages. For more than 30 years, numerous studies have been published to meet this challenge. The research is divided into two directions: the use of natural, cheap, and abundant non-conventional materials in raw or modified form and the development of new synthetic materials. The materials proposed include cyclodextrin beads, metal–organic frameworks, molecularly imprinted polymers, chitosan-based materials, and nanocellulose.

Removal of pharmaceuticals using cyclodextrin bead polymers

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 (Morin-Crini et al. 2018; Fenyvesi et al. 2019; Cova et al. 2021; Yadav et al. 2021). 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, such as the use of cyclodextrin bead polymers.

Cyclodextrins are carbohydrates produced from starch and characterized by cyclic structure with hydrophilic surface and moderately hydrophobic inner cavity; cyclodextrins are able to encapsulate compounds in their cavity (Szejtli 1998). 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, with numerous pharmaceuticals among them (Crini 2014). Within the cavity of cyclodextrins, the water molecules are readily replaced by less hydrophilic guest compounds such as low water-soluble drugs (Fig. 2). 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 and van der Waals forces; 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

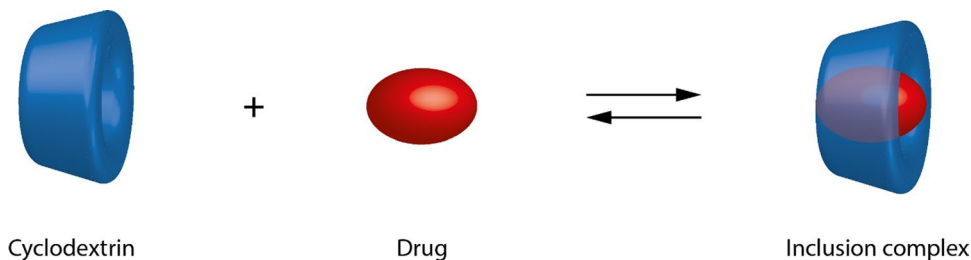
et al. 2005; Szejtli and Szenté 2005; Uekama et al. 2006). The number of active ingredients marketed in the form of cyclodextrin complexes is above 100 at the end of 2021 and is continuously increasing (CycloLab archive). Among the three natural cyclodextrins, α -cyclodextrin, β -cyclodextrin and γ -cyclodextrin 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).

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 adsorption/sorption/biosorption, both terms being used in the 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, and fluoroterphthalonitriles (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. 3 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, or 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

Fig. 2 Formation of an inclusion complex of cyclodextrin with a drug. *Source* Éva Fenyvesi, Budapest, Hungary; Marc Fourmentin, Dunkerque, France



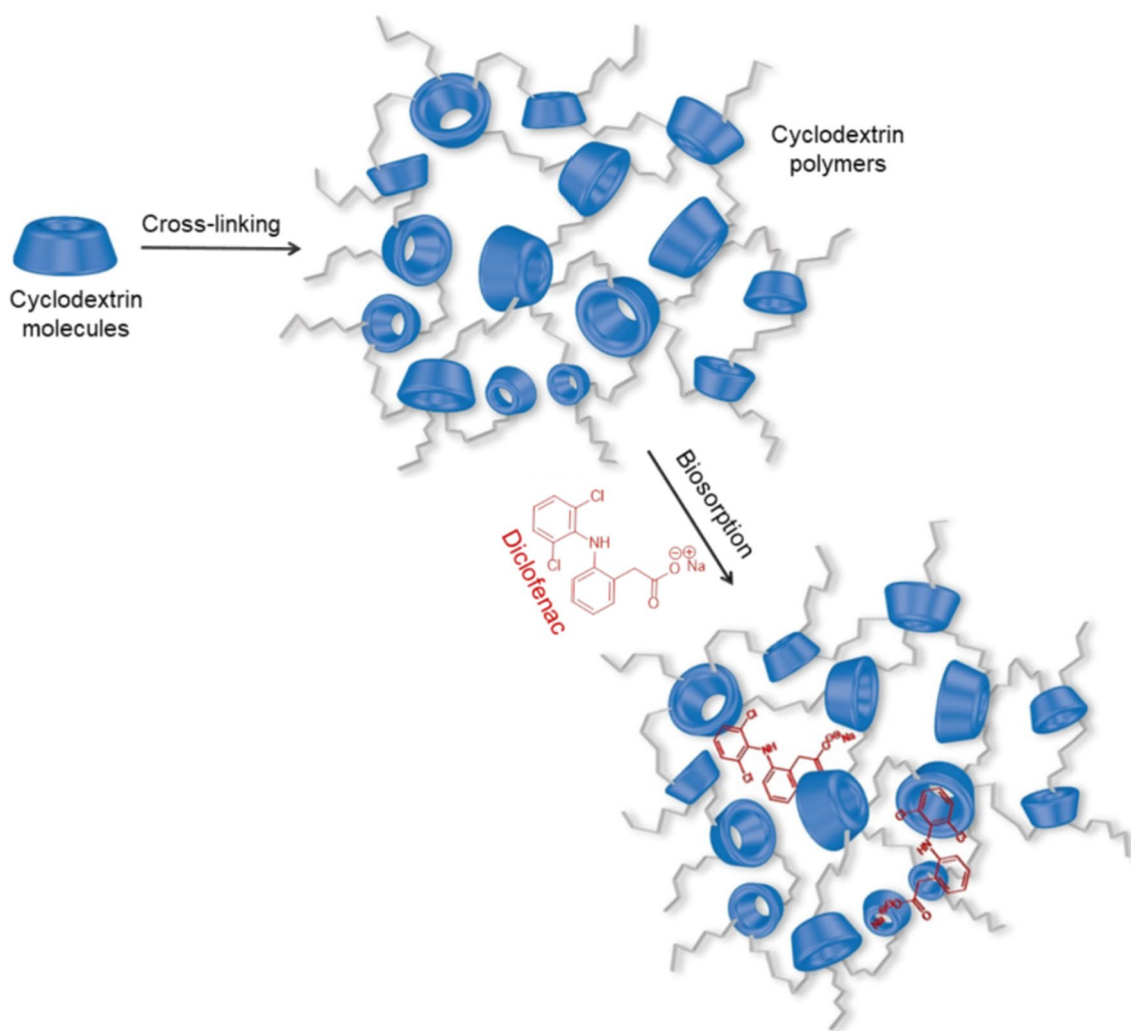


Fig. 3 Cyclodextrin polymer obtained by a cross-linking reaction between cyclodextrin molecules and a cross-linking agent followed by the diclofenac sorption onto the cyclodextrin polymer. *Source*

Marc Fourmentin, Dunkerque, France; Éva Fenyvesi, Budapest, Hungary; Grégorio Crini, Besançon, France

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, and reaction time. (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 bead polymer is higher in case of lower degree of cross-linking and reduced temperature (Zhu et al. 1997; Baille et al. 2000). For 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, and chelation. (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).

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 et al. 2013; Fenyvesi et al. 2019; Cova et al. 2021; Yadav et al. 2021). The early sorption/biosorption experiments with cyclodextrin bead polymers aimed at the removal of various organic contaminants such as phenols and dyes. Although these beads usually outperformed activated charcoal, it became clear that cyclodextrin polymers 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 persists the traditional wastewater treatment and are usually detected in treated 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–>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 cyclodextrins 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 primavanserin from single solutions (93% and 80% removal rates, respectively) and from post-reaction 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 the 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, including estrogen hormones, from water (Bhattarai et al. 2012). More than 95% of 17- β -estradiol was removed from a single component solution and more than 90% of most estrogens from a multicomponent system, even after 4 regeneration cycles. Also magnetic graphene oxide modified with β -cyclodextrins/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/L of 17- β -estradiol. 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 (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, codeine, diclofenac, estrone, famotidine, fluoxetine, gemfibrozil, ibuprofen, testosterone, triclosan to mention only a few and several pesticides (Ling et al. 2017). Figure 3 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 (Xu et al. 2019). A further possibility for preparing filters of good mechanical stability is sintering cyclodextrin bead polymers 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 (87–99%) from the spiked test solution (800 mL) containing some other emerging contaminants. 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. 4). 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 (among other drugs, e.g., diclofenac, 17- α -ethinylestradiol 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%), 17- α -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 and 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 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 cyclodextrin polymer was successful, with most

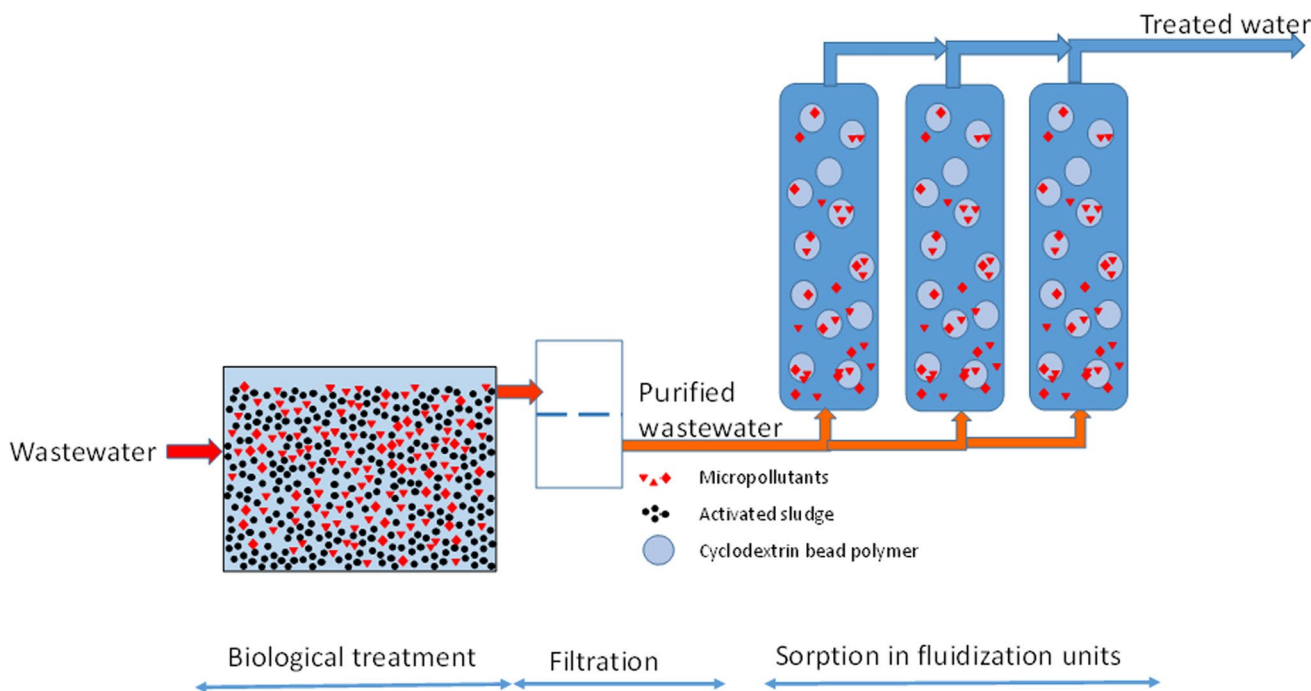


Fig. 4 Wastewater purification by applying cyclodextrin polymer beads for sorption of emerging pollutants and micropollutants such as residual pharmaceuticals. *Source* Éva Fenyvesi, Budapest, Hungary

of the pharmaceuticals as emerging contaminants, especially those on the European watch list, being 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 bead polymer 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 Dexasorb® 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 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.

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, catalytic degradation and/or membrane processes (Dias and Petit 2015; de Andrade et al. 2018; Mon et al. 2018; Bedia et al. 2019; Li et al. 2019, 2020b; Dhaka et al. 2019; Rojas and Horcajada 2020; Russo et al. 2020; Zango et al. 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 multifunctional 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/or degrade pollutants. In addition to superhigh pore volume, metal–organic frameworks also have values of surface area, between 1000 and 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, higher than $> 30 \text{ \AA}$, high surface area, higher than $3,000 \text{ m}^2/\text{g}$, and a huge cell volume, e.g., $702,000 \text{ \AA}^3$.

Because of their distinctive characteristics, metal–organic frameworks are very useful in chemistry and supramolecular chemistry including gas separation, adsorbent for carbon capture, and hydrogen for energy storage, nanotechnology for electrocatalysis, photocatalysis, and 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 render them interesting for 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.

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, these organic–inorganic hybrid crystalline porous materials 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, benzene, toluene, ethylbenzene and xylene 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. (2019), 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/or catalytic degradation such as photocatalysis and could also find applications in other advanced oxidation processes such as photo-Fenton and 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. 2019). 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.

Application of molecularly imprinted polymers for the 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 these synthetic 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. Non-imprinted polymers 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. However, while their specificity 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/or destroy, in combination with other technologies, such as 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 UV light (Fernández-Alvarez et al. 2009). This method was able to regenerate and reuse both the polymeric material and the solvent, while simultaneously degrading 17- β -estradiol. For that, acetone was used as a solvent under both UV-C and UV-visible light. After a 10-h cycle, the molecularly imprinted polymer was completely regenerated, and no residual 17- β -estradiol was found in acetone.

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 the material with a 3 mL methanol/acetic acid solution for 2 min. The performance remained the same after at least four adsorption/regeneration cycles. The proposed 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 ~90% of diclofenac from an aqueous solution at a concentration of 1×10^{-4} mol/L, while only 8% being removed by the corresponding non-imprinted polymer. The adsorption capacity was 110 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 to best integrate this technology into treatment plants. In addition, their potential toxicity and possible health effects are subject to discussion (Murray and Örmeci 2012).

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 2018; Pakdel and Peighamardoust 2018; Morin-Crini et al. 2019; Vidal and Moraes 2019; Brião et al., 2020). Chitosan is a biopolymer derived from chitin, the second most abundant

polysaccharide (after cellulose) on Earth. This aminopolysaccharide can interact and adsorb a wide range of pollutants such as metals, dyes, organics, including emerging substances. In water and wastewater treatment, it 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: exceptional pollutant binding capacities, excellent selectivity, and versatility (Crini and Lichtfouse 2018; Morin-Crini et al. 2019). Chitosan-based materials can be used in solid form for the removal of pollutants 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 such as 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 the beta-lactamic antibiotic amoxicillin on chitosan beads. This highly excreted antibiotic is difficult to eliminate in conventional wastewater treatment systems due to its structure and amphoteric properties resulting from the presence of carboxylic (pKa 2.68), amine (pKa 7.49) and hydroxyl (pKa 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 with an equilibrium time of 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 (Morin-Crini et al. 2019). 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, 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 used to prepare the hydrogels. 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 to best integrate this technology into treatment plants.

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 several 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, including cellulose nanocrystals, cellulose nanofibrils, and 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; Ibrahim et al. 2021; Sayyed et al. 2021; Thakur et al. 2021), 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), gas separation (Ibrahim et al. 2021), 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 obtain 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) and Abou-Zeid et al. (2019) 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 been published (Herrera-Morales et al. 2017, 2019; 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; Ibrahim et al. 2021; Sayyed et al. 2021; Thakur et al. 2021). 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; Thakur et al. 2021).

Biological-based technologies for the degradation and elimination of emerging contaminants

The biological treatment approach, specifically the activated sludge process, is the most used wastewater treatment technology. While it was originally designed to remove organic carbon, it was subsequently extended to remove nitrogen and phosphorous. However, 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 constraint for their further implementation. Other techniques such as constructed wetlands, algal-based technologies and enzymatic degradation, and bioreactors are being developed (Mohsenpour et al. 2021; Parde et al. 2021; Plöhn et al. 2021; Vymazal et al. 2021).

Constructed wetlands for the removal of emerging contaminants

Constructed wetlands are artificial ecosystems that rely on plants activity for water remediation (Kaur et al. 2020) and can be categorized according to different operational parameters, such as the type of flow, e.g., horizontal vs vertical and free water vs sub-surface, the hydraulic regime, and the plant species used for phytodepuration. These systems, likewise natural wetlands, take advantage of the numerous physical, chemical and biological processes that occur at the interface between the root system and the wastewater under treatment, including, for instance, adsorption on soil/sediment, volatilization, uptake, and degradation (Gorito et al. 2017). Constructed wetlands are a suitable technology to remove total suspended solids, ammonia, phosphorous, and to reduce the chemical oxygen demand and biochemical oxygen demand. They offer several advantages in terms of environmental and economic sustainability. Representing a low-cost and easy to maintain technology, constructed wetlands are considered 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). Several studies highlighted the potentiality 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 such as bisphenol A (Syranidou et al. 2017; Meneghetti Campos et al. 2019), and synthetic dyes (Riva et al. 2019). Indeed, phytodepuration has been also proposed as a tertiary treatment downstream of conventional wastewater treatment plants which are not designed to remove these types of contaminants, often present in their effluents (Castiglioni et al. 2006). Within this framework, antibiotic resistance is a hot topic in relation to water reuse, as its determinants (including genes and bacteria) are recognized as contaminants of

emerging concern and are currently being addressed by the first EU regulation (2020/741) on wastewater reuse to be implemented in the coming years.

The contaminant removal in constructed wetlands results from the synergistic effect played by plant roots and their associated microbiome. The plant root system is an environmental niche that provides favorable conditions for microorganisms, which are specifically recruited by the release of root exudates and can help the plants cope with adverse conditions, including pollution (Rolli et al. 2021). Noteworthy, microorganisms can play a direct role in organic contaminant degradation. Constructed wetlands can be designed using single or mixed plant species, which belong mainly to the genera *Typha*, *Phragmites*, *Iris* and *Juncus*. A constructed wetland system realized co-cultivating the halophytes species *Tamarix parviflora*, *Juncus acutus*, *Sarcocornia perrenis*, and *Limoniastrum monopetalum* was able to efficiently decrease organic matter and pathogen concentration in the effluent (Fountoulakis et al. 2017). This is a promising result in the context of bioremediation of wastewater produced by aquaculture, an antropic activity whose environmental impact is increasing, especially 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, and the removal rate varied according to the planting pattern and the target molecule. The tested plants showed the best removal performances in single species. *Iris pseudacorus* removed up to 77.64%, 68.70%, and 58.21% of enrofloxacin, sulfamethoxazole, and total antibiotic resistance genes, while *Phragmites australis* showed removal efficiencies of 81.11%, 64.94%, and 56.26% for the same molecules and genes (Huang et al. 2019). Indeed, several authors showed that the performance of constructed wetland systems strictly depends on both operational parameters and the emerging contaminant to be removed. A microcosm scale study using *Phragmites australis* in a vertical subsurface flow constructed wetland, showed high removal efficiencies for all considered 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 *Phragmites australis* was also demonstrated on the antiepileptic carbamazepine in a study that highlighted how several bacterial species isolated from *Phragmites australis* endosphere (i.e., the internal root tissue) were able to remove and degrade this recalcitrant molecule (Sauvêtre and Schröder 2015). On the opposite, subsurface horizontal flow constructed wetlands planted with *Heliconia zingiberales* and *Cyperus haspan* showed a carbamazepine removal efficiency

lower than 10% although the system successfully reduced the effluent concentrations of the pharmaceutical sildenafil and the personal care product methylparaben (Delgado et al. 2020). A strategy to improve emerging contaminant degradation in constructed wetlands could be the use of substrates endowed with adsorptive ability, such as manganese oxides which were indicated as enhancer of triclosan removal during microcosm experiments (Xie et al. 2018).

In the last decade, the root microbiome of constructed wetland plants has gained increasing attention, given the importance of microbial metabolism for the degradation of pharmaceuticals and other organic molecules. For example, several bacterial endophytes isolated from *Juncus acutus* plants grown in a pilot constructed wetland were able to tolerate and/or use bisphenol A, ciprofloxacin and sulfamethoxazole as sole carbon source (Syranidou et al. 2017). Therefore, selected bacterial strains could be used in the so-called *microbial assisted phytodepuration* given their ability to promote plant growth and, on the other hand, to tolerate and/or degrade emerging contaminants. A study aimed at removing the model azo-dye Reactive Black 5 in constructed wetland microcosms planted using *Juncus acutus* showed the beneficial effect of plant growth promoting bacteria inoculation. Plants were supplemented by two different single inocula and a mixed consortium of previously selected root-associated bacteria and showed a higher removal of Reactive Black 5 in the effluent compared to the non-inoculated control ones, suggesting that '*microbial assisted phytodepuration*' could be successfully exploited for the remediation of textile industry wastewater, an issue in several developing countries (Riva et al. 2019). Finally, phytodepuration represents a wastewater treatment technology of interest also for water reclamation (Petroselli et al. 2017), 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 especially in terms of antibiotic resistance spread into the environment (Riva et al. 2020).

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; Plöhn et al. 2021). 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) 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 can remove 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), Ghosh et al. (2016), 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, 2017b), 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, 2017b), 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 *Tetrademus obliquus* removed both pharmaceutical contaminants better than *Chlorella vulgaris* in batch culture. The removal efficiency of salicylic acid by *Tetrademus 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 such as temperature, seasons, retention time, environmental pH, dissolved oxygen, and 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 include biodegradation, photodegradation and biosorption including cell sorption and/or bioaccumulation to algae. Other mechanisms and interactions are also cited, such as volatilization (stripping), biotransformation, bio-precipitation (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 could open new opportunities for wastewater treatment and to reduce environmental pollution. 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/or biodegradation mechanisms, and the optimization and better control of the operating parameters such as temperature, pH, and dissolved oxygen, 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.

Fungi for the 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. 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 (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 or mycoreactors can be suspended or immobilized growth systems. They can operate under aerobic or anaerobic conditions. This technology requires specific and controlled conditions 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. (2013). 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 concentrations 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 achieved after 2 days. Carbamazepine, a well-known recalcitrant psychiatric drug in activated sludge treatment was also detected in the wastewater at $0.7 \mu\text{g/L}$. Cruz-Morató et al. (2013) showed that carbamazepine and its metabolites were also strongly eliminated by *Trametes versicolor* during batch treatment in a fluidized bed bioreactor under sterile conditions, in agreement with the results published by Zhang and Geißel (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 *Trametes 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/or 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 plants, 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 degrade by the fungus (< 40% removal). Excluding caffeine and iopromide concentrations, the overall elimination of pharmaceuticals and endocrine disruptors was above 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 *Trametes 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 *Trametes 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. (2014a) concluded that fungi-based technologies were a potential alternative to pretreat 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 such as 4-acetamidopyrin, clofibrilic acid, atenolol, caffeine, carbamazepine, hydrochlorothiazide, sulfamethoxazole, and sulpiride, although the combination of the two

strains improved the efficiency of the system. Vasiliadou et al. (2016) also demonstrated efficient production of bio-diesel 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 can degrade 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.

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, such as transferases, hydrolases, and oxidoreductases, 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 et al. 2017a; Bilal et al. 2019a, 2019b). Iqbal's group concluded that laccases are one 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.

Membrane bioreactors

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 and 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 and biodegradation 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), leading 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 such as organic matter, minerals, and metals, and pollution including suspended solids, chemical oxygen demand, and biological oxygen demand (Radjenovic et al. 2007; González et al. 2008; Huang et al. 2010). Membrane bioreactors 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; Beshar et al. 2017; Gurung et al. 2017; Abargues et al. 2018; Jiang et al. 2018; Ma et al. 2018; Mert et al. 2018; Bodzek et al. 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, and estrogens including estrone, estradiol, and 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 (Besha 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, such as ibuprofen, diclofenac, and ketoprofen, under low pH conditions (the optimal pH was about 6), mainly due to the increased lipophilicity and the ionizability of pH-dependent of the 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, with a high concentration in November for acetamiprid, clothianidin, imidacloprid and thiamethoxam, which were found at had significantly lower concentrations in the other months. 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 including parabens, bisphenols, phthalates, estrogens, and nonylphenols, and pesticides. The authors comprehensively discussed the advantages and disadvantages of each process.

Literature data show 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 including aerobic degradation, anaerobic degradation, metabolism and co-metabolism, and 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, and electrostatic interactions. For biological degradation, performance depends also on the biodegradability and bioavailability of the substances, and the conditions 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 such as estrone and estradiol can be well degraded under aerobic and anoxic

conditions, whereas the transformation of ibuprofen, roxithromycin, erythromycin, citalopram, and naproxen occur 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 laboratory studies. 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 nanoproducts 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; Montoliva-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/or 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 fields. Recycling or reusing 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 source of 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.

Advanced oxidation technologies to degrade emerging contaminants

Removal of emerging contaminants by wastewater disinfection

The main objective of disinfection is to either eliminate pathogens from water to produce potable water or to reduce the pathogen content of treated wastewater in wastewater treatment plants. Disinfection is indeed the final treatment step to produce 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 including UV radiation and 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 (UV 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 is that the processes can lead to the formation of organic and inorganic disinfection by-products such as trihalomethanes, chlorite and chlorate, and aldehydes (von Sonntag and von Gunten 2012). Advanced technologies include the combination of ozone and hydrogen peroxide, ozone and UV radiation, hydrogen peroxide and UV radiation, UV radiation with titanium dioxide, alone or combined with other processes, such as land

filtration, membrane technologies, nanotechnology, photo-voltaic method, solar photocatalytic, and sonodisinfection.

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, 2012b; 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/or secondary wastewater treatment. A review of the abundant literature published over the past 20 years highlights that the three main technologies studied for both disinfecting water from pathogens and removing substances are chlorination, ozonation and UV irradiation. These are the technologies used at industrial scale, either alone or in combination with other chemicals.

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. The effect of chlorination on the removal of emerging contaminants has been widely documented (Hu et al. 2002; Petrovic et al. 2003; Boyd et al. 2005; Westerhoff et al. 2005; Zhang and Grimm 2005; Greyshock and Vikesland 2006; Thurman 2006; Korshin et al. 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 in pure water or drinking water rather than in wastewater matrix. On the other 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, 2013b, 2013c, 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, e.g., diclofenac, naproxen, sulfamethoxazole, amitriptyline hydrochloride, and methyl salicylate, endocrine disruptors, e.g., 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, such as organic matter content of the wastewater, presence of total suspended solids and pH, 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 impact 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/or 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 (pKa, chemical structure) of the compounds under different pH conditions may 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 intense for chemicals with high K_{ow} values, e.g., nonylphenol and its ethoxylates, and 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. 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; Nika et al. 2016). In many cases, toxicity measurements show that some of the by-products of chlorination are more toxic than the original compounds.

Chlorine dioxide (ClO₂) has a stronger disinfectant activity than chlorine. Considering its higher cost compared to conventional chlorination, disinfection with ClO₂ is generally adopted in cases where minimizing the production of chlorine-based disinfection by-products is desirable. Because of its instability, ClO₂ is produced on-site by mixing a chlorine solution with a sodium chlorite solution. The literature on the effectiveness of ClO₂ in removing emerging contaminants during wastewater disinfection is rather limited. In their comprehensive review, Hey and colleagues (2012a) investigated the effect of ClO₂ on the removal of a wide range of 56 pharmaceuticals. According to this study,

it was shown that, in addition to the effectiveness of ClO₂ 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, namely naproxen, diclofenac, and mefenamic acid, and a lipid-regulating agent, gemfibrozil, while no elimination was reported for ibuprofen and clofibrac acid. The inability of ClO₂ 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 17 α -ethinyl estradiol. In addition, Huber et al. (2005a, 2005b) showed an effective elimination of estrogenic hormones at very low doses of ClO₂ and a short contact time (5 min). Its ability to remove emerging contaminants has also been demonstrated for a range of antibiotics (Sharma 2008; Navalon et al. 2008; Wang et al. 2019).

The UV radiation process is a well-known disinfection step used to effectively remove bacteria, viruses and protozoa. 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 used for disinfection purposes (Asano et al. 2007). The main germicidal mechanism of UV 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 UV irradiation on the removal of pathogens and organic micropollutants is highly dependent on the applied dose (in mJ/cm² or mWs/cm²), calculated as the product of average UV intensity and contact time. The effectiveness of UV 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 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, 2009b) reported that of the 42 pharmaceuticals studied under real wastewater conditions, only a few showed high removal, e.g., ketoprofen, diclofenac, and antipyrine, while several others and particularly antibiotics such as clarithromycin, erythromycin, and azithromycin, showed very low degradation due to UV irradiation, even at doses above 2700 mJ/cm². Consequently, Noutsopoulos et al. (2013c) concluded that with the application of the low-pressure UV 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 2010; Baeza and Knappe 2011; Salgado et al. 2011; Pablos et al. 2013). The moderate effect of UV 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 UV 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. 2012; Noutsopoulos et al. 2013a), the structure of each chemical as well as its physical characteristics, i.e., decadal molar absorption coefficient at 254 nm, largely govern its sensitivity to degradation. Studies of UV 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 to improve the efficiency of UV irradiation such as the use of medium-pressure lamps (Kim et al. 2009a; Pereira et al. 2007) or the UV-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 UV 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 assimilable organic carbon that can feed microbes in biofilm formed within the water distribution lines.

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 ClO₂. 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 to be 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 (O₃) 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, and nitrites. 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 most of these studies use pure water rather than a wastewater matrix (Ahmed et al. 2017b; Sun et al. 2017; Bourgin et al. 2018; Lacson et al. 2018; Paucar et al. 2018; Thanekar et al. 2018; Wang et al. 2018a).

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, perfluorooctanesulfonic acids and perfluorooctanoic acids.

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, regarding emerging contaminants removal, while UV as stand-alone disinfection method, without being upgraded to UV assisted advanced oxidation processes, exhibit rather moderate performance. To guarantee satisfactory removal capacities for a wide range of compounds, higher doses than those typically used for the removal of pathogens should be applied. These higher doses are important to prevent the regrowth of bacteria after treatment. 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, including streams, rivers, lakes, and 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.

Electrochemical, photochemical and ultrasonic technologies for the removal of emerging contaminants in industrial wastewaters

Advanced oxidation processes represent one of the most promising strategies for the removal of emerging contaminants present in wastewater treatment effluents. Although these processes use different reagent systems, all techniques are based on the generation of reactive radicals. Hydroxyl radical-mediated advanced oxidation processes are based on 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. Other radicals can be involved such as $\text{SO}_4^{\cdot-}$ in sulfate radical-mediated advanced oxidation processes that have gained attention due to its high redox potential comparable with that of HO^\cdot and chlorine radical-mediated advanced oxidation processes (e.g., UV/chlorine) that are based on Cl^\cdot , $\text{Cl}_2^{\cdot-}$, ClO^\cdot . Several types of advanced oxidation processes are presented in Fig. 5. 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/or 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 are detailed in numerous reviews (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). Moreover, their performance can be affected by a wide range of wastewater constituents, including the natural organic matter such as humic and fulvic acids, carbohydrates, and proteins, and inorganic species like carbonate, bicarbonate, nitrite, sulfate, chloride. Both organic and inorganic species can react with radicals, thus competing with emerging contaminants for oxidation or generating other radicals with lower oxidation potential, but promoting effects can also be observed, as recently reviewed by Lado Ribeiro et al. (2019).

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, such as electro-Fenton, photo-electro-Fenton, and sono-electrolysis, in homogeneous (e.g.,

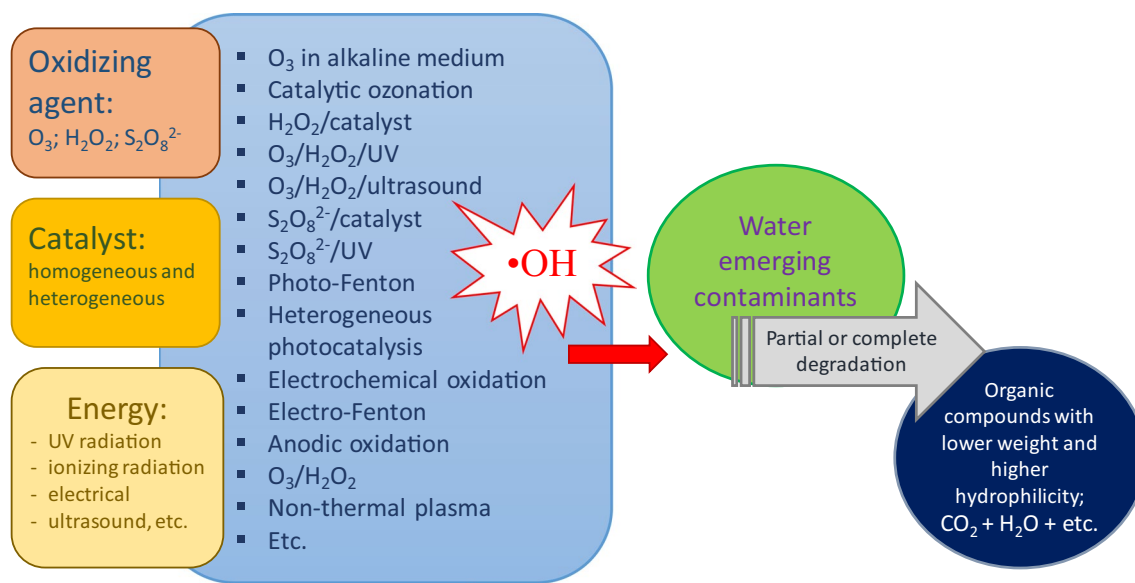


Fig. 5 Advanced oxidation processes for wastewater treatment. Source Corina Bradu, Bucharest, Romania

photo-Fenton: $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{UV}$) or heterogeneous systems (heterogeneous photo-catalysis: $\text{TiO}_2/\text{H}_2\text{O}_2/\text{UV}$; anodic oxidation or photo-electrocatalysis). Different energy sources and/or 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 , $\text{H}_2\text{O}_2/\text{UV}$, $\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$, or photo-Fenton $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{UV}$); (ii) ultrasound energy ($\text{O}_3/\text{ultrasound}$, $\text{H}_2\text{O}_2/\text{ultrasound}$) 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 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). As alternatives, the photo-assisted Fenton process can be more efficient than Fenton alone, mainly due to the faster regeneration of Fe^{2+} and electro-Fenton is another option, 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 involving 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. Fenton, photo-Fenton, photocatalysis, and ozonation-based processes have been commonly studied, while 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. They 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 include easiness 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 for example 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). 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. 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). 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 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, e.g., water matrix characteristics, and contaminant concentration. The authors also

demonstrated that electrochemical advanced oxidation was a pertinent approach for *Staphylococcus aureus* disinfection in wastewater treatment plants (Valero et al. 2017).

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. 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 and two of losartan were identified by high-resolution mass spectrometry using hybrid quadrupole-time-of-flight mass spectrometry. The several organic compounds remaining after 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 are powerful to degrade emerging pollutants such as antibiotics, although some processes are not capable to completely mineralize the organic pollutants. The two main advantages of

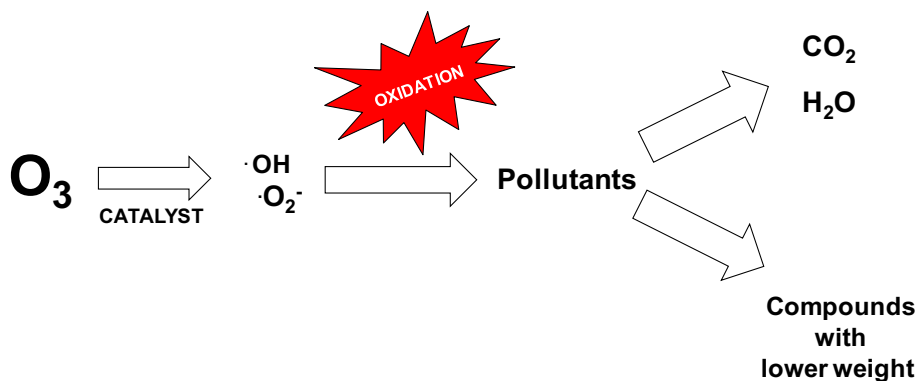
these advanced oxidation processes are: (i) the oxidizing species are generated in situ (no need of chemicals storage and handling) and (ii) most of processes (except the Fenton type) do not require a rigorous control of solution pH. Other advantages include operation control simplicity, reactor design 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 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.

Carbon nanomaterials for the catalytic ozonation of emerging contaminants

An effective technology to degrade 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. 6).

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, 2016c). 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, research efforts have been done for the development of metal-free catalyst. Among metal-free catalysts, carbon materials such as

Fig. 6 Radical pathway of catalytic ozonation process *source* Mohammad Mahmudul Huq, Saskatoon, Canada



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 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. (2009a, b). 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 and -OH on catalyst surface leading to inferior performance of multi-walled carbon nanotubes. The catalytic activity decrease could 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 (Gonçalves et al. 2013). In terms degradation of this antibiotic, 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 its oxidation by-products by Microtox® bioassays. It was found that the lowest toxicity was achieved when the ozonation was carried on in the presence of multi-walled carbon nanotubes.

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 including heteroatom-doping, oxidation, and grinding. Qu et al. (2015) studied carboxylated carbon nanotubes in catalytic ozonation of indigo. The modified nanotubes showed higher indigo removal both 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 was 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 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 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 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 sulfamethoxazole. Wang et al. (2019a, 2019b) used a novel microwave method to dope N into reduced-graphene oxide. This method generates higher amounts of N-doped 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 for catalytic ozonation degradation of *p*-chlorobenzoic acid and benzotriazoles and for elimination of bromate (BrO_3^-). Bromates are carcinogenic by-products of ozone-based 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 was found to be unstable given the increase on 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 counterproductive. 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).

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 led to a removal of ciprofloxacin of 87.5% in 15 min as opposed to 40.2% elimination 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 nano-material-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.

Non-thermal plasma 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. 2008). The efforts are directed toward elaborating technically and economically feasible solution, toward bringing new insight the 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 collision of the high energy 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, and plasma jet, on the discharge characteristics, solution properties and gas composition (Brissetet al. 2008; Park et al. 2013). A number of reactive oxygen species and reactive nitrogen species have been detected in the gas and/or liquid phase of the cold plasma discharge systems, such as: $\cdot\text{OH}$, $\text{HO}_2\cdot$, H_2O_2 , $\text{O}\cdot$, $\cdot\text{O}_2^-$, O_3 , $\cdot\text{NO}$, $\cdot\text{NO}_2$, NO_2^- , NO_3^- , and ONO_2^- . (Lukes et al. 2012; Locke et al. 2012; Bruggeman et al. 2009).

Ozone, hydrogen peroxide and hydroxyl radical are the most investigated reactive oxygen species in such plasmas. 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. Its formation in electrical discharges actually includes plasma processes among the advanced oxidation process. Due to its short lifetime, $\cdot\text{OH}$ interacts with organic pollutants very near the gas-water interface (Kanazawa et al. 2013; Marotta et al. 2011; Ajo et al. 2015). In the bulk liquid, 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 radical recombination reaction leading to stable molecular species may limit the process effectiveness (Locke et al. 2012). However, H_2O_2 is a potential source of hydroxyl radicals, which may be used judiciously. For instance, H_2O_2 decomposition with the regeneration of $\cdot\text{OH}$ radicals could be promoted by an adequate catalyst (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 either soluble transitional metal salts such as Fe^{2+} , Fe^{3+} , Mn^{2+} , and Co^{2+} (Dojčinović et al. 2011; Jović et al. 2014) or heterogeneous catalysts such as TiO_2 , activated carbon, and based-graphene materials (He et al. 2015; Hama Aziz et al. 2018; Vanraes et al. 2015, 2017; Guo et al. 2019a, 2019b, 2019c).

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. 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 a plasma reactor and an ozonation reactor in which the effluent gas from the plasma reactor was bubbled through the aqueous solution (Fig. 7). With this combined plasma-ozonation system, faster removal of the target compound and higher degree of mineralization was obtained compared to the single plasma or ozonation processes. The improvement was

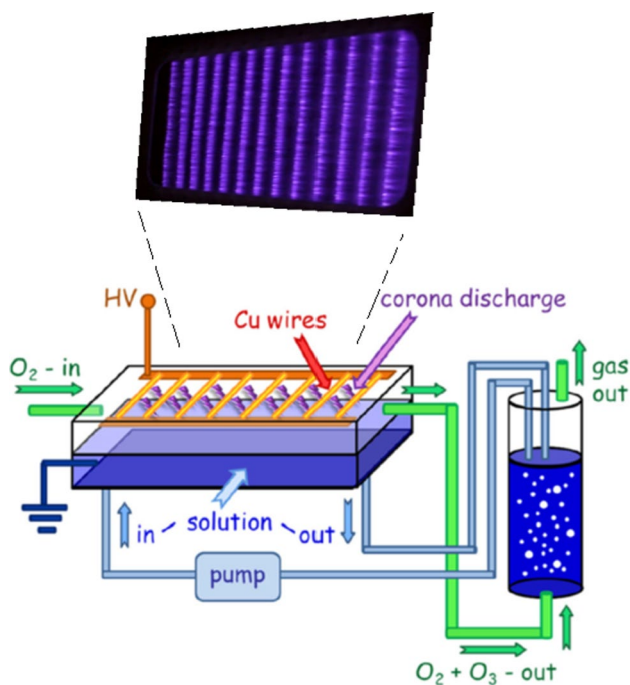


Fig. 7 Experimental set-up for plasma-ozonation system. *Source:* Monica Magureanu, Magurele, Romania

attributed to the 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 ($N\cdot$, $O\cdot$, $\bullet OH$) in gas phase. In further reactions, $\bullet NO$ can effectively fix oxygen atoms through the interaction with $O\cdot$ or with O -donor species produced in the discharge (e.g., O_3 and $HO_2\cdot$) 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 peroxyntrous 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 favored in acidic pH), or via the reaction between dissolved nitric and nitrous oxides and different radical reactive oxygen species ($\bullet OH$, $HO_2\cdot$ and $\bullet O_2^-$) (Goldstein et al. 2005; Mousa et al. 2007; Lukes et al. 2012; Tian and Kushner 2014). The generation of peroxyntic acid (O_2NOOH) through the reaction between peroxyntrous 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. 2009; Bradu et al. 2020).

Even if the reactive nitrogen species involvement in the organic compounds' degradation was less studied, there is solid evidence 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 Cadorin et al. (2015). It was assumed that the organic molecules interact with peroxyntrous acid either directly or indirectly via dissociation into NO_2 and $\bullet OH$ (Moussa et al. 2007; Cadorin et al. 2015).

A large variety of discharge configurations has been used to produce plasma either directly in liquid (i.e., with both electrodes submerged in liquid) or 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; Stara et al. 2009). An analysis of reported results revealed that the energy efficiency of the process is significantly higher for the plasma in gas phase as compared to liquid-phase discharges, 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 et al. 2010).

Therefore, 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 (Hijosa-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. When 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 abovementioned 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. Several authors provided information on the energy efficiency of the removal process. For instance, Xu et al. (2020) 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 H_2O_2 and Fe^{2+} 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 H_2O_2 (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, 2019b, 2019c). 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, 2015; Lee et al. 2018; Tang et al. 2018a, 2018b, 2019; Wang et al. 2019c; Li et al. 2020a). 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 upward 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 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, 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, already mentioned previously, is to bubble the effluent gas from the plasma through the solution (Gerrity et al. 2010; Magureanu et al. 2011; Bradu et al. 2017). Very high energy efficiency has been reported in such dual plasma-ozonation 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 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 health care 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 optimization of the electrical discharge, 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 characterization of the plasma treated water from both chemical and (eco)toxicological points of view. There are only few studies dealing with this complex characterization 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.

Conclusion

We have described advanced treatment methods for treating emerging contaminants. 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 ecofriendly, 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 full scale treatment plants. Among the various disinfection methods, chlorination and ozonation appear to give better results in terms of removing both pathogens and emerging contaminants. However, additional investigations are needed to determine the possible toxic characteristics of disinfection by-products compared to their parent compounds, as well as the possible synergic adverse effects of cocktails of by-products even at trace concentrations. The approach consisting in the use of ozonation and adsorption on activated carbon has been used for about ten years in countries such as Switzerland and Germany, due to its efficiency, simplicity and technical feasibility at industrial scale, and for economic

reasons. Another feature of these technologies is their facile integration into existing treatment facilities. Biological approaches such as constructed wetlands, biomembrane reactors, strategies based on the use of algae, fungi and bacteria, and enzymatic degradation are also a field of research in full development and significant advances are expected in the future. Finally, advanced oxidation processes represent one of the most promising strategies because of their efficiency and simplicity; they can also be integrated into existing treatment facilities as primary, secondary and/or tertiary methods. Significant advances are expected in the next few years, although here again, investment, operation and maintenance costs must be considered. Industrialists will now have to be persuaded to use these technologies in their municipal wastewater treatment plants.

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Declarations

Conflict of interest The authors declares no conflict of interest.

References

- Abarques 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. *Biomacromol* 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 P. *Plasma Chem Plasma* 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>
- 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
- Ahmed I, Iqbal DK (2017) Enzyme-based biodegradation of hazardous pollutants - an overview. *J Exp Biol Agric 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, Mänttäri 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.
- Aksu Z (2005) Application of biosorption for the removal of organic pollutants: a review. *Process Biochem* 40:997–1026.
- 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 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>
- Alsaiee 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 Manage* 203:831–837
- Alvaro M, Carbonell E, Ferrer B, Llabrés IX, Garcia H (2007) Semiconductor behavior of a metal-organic framework (MOF). *Chem Eur J* 13:5106–5112
- Ameta R, Chohadia AK, Jain A, Punjabi PB (2018) Fenton and photo-Fenton processes. In: advanced oxidation processes for waste water treatment. 3: 49–87. DOI: <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 review. *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 Macrocylic 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 NOx 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
- 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* 581:734–740. <https://doi.org/10.1016/j.scitotenv.2016.12.192>
- 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 Co₃O₄ compositing. *J Environ Sci* 50:38–48. <https://doi.org/10.1016/j.jes.2016.03.029>
- Bedia J, Muelas-Ramos V, Peñas-Garzón M, Gómez-Avilés A, Rodríguez JJ, Belder 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>
- 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>
- Bennett JL, Mackie AL, Park Y, Gagnon GA (2018) Advanced oxidation processes for treatment of 17[β]-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
- 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, ENVR-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>
- 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>
- Borea L, Ensano BMB, Hasan SW, Balakrishnan M, Belgiorno V, de Lun DG, Ballesteros FC Jr, Naddeo 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, McArdell 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/ab795aBraga>
- Brião GV, Andrade JR, Silva MGC, Vieira MGA (2020) Removal of toxic metals from waters using chitosan-based magnetic adsorbents: a review. *Environ Chem Lett* 18:1145–1168. <https://doi.org/10.1007/s10311-020-01003-y>
- Brisset JL, Moussa D, Doubla A, Hnatiuc E, Hnatiuc B, Kamgang Youbi G, Herry JM, Naïtali M, Bellon-Fontaine MN (2008) Chemical reactivity of discharges and temporal post-discharges in plasma treatment of aqueous media: examples of gliding

- discharge treated solutions. *Ind Eng Chem Res* 47:5761–5781. <https://doi.org/10.1021/ie701759y>
- 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>
- Bruiggeman 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>
- Burlica R, Kirkpatrick MJ, Finney WC, Clark RJ, Locke BR (2004) Organic dye removal from aqueous solution by glidarc discharges. *J Electrostatics* 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>
- 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>
- Collivignarelli MC, Abbà A, Benigna I, Sorlini S, Torretta V (2018) Overview of the main disinfection processes for wastewater and drinking water treatment plants. *Sustainability* 10:86. <https://doi.org/10.3390/su10010086>
- 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>
- Cova TF, Murtinho D, Aguado R, Pais AACC, Valente AJM (2021) Cyclodextrin polymers and cyclodextrin-containing polysaccharides for water remediation. *Polysaccharides* 2:16–38. <https://doi.org/10.3390/polysaccharides2010002>
- Crini G (2010) Wastewater treatment by sorption. In: sorption processes and pollution. Besançon: PUFC, chapter 2, pp. 39–78
- Crini G (2014) Review: a history of cyclodextrins. *Chem Rev* 114:10940–10975. <https://doi.org/10.1021/cr500081p>
- Crini G, Badot PM (2007) *Traitement et épuration des eaux industrielles polluées* (in French). Presses Universitaires de Franche-Comté, France, Besançon
- Crini G, Badot PM (2010) Sorption processes and pollution. Presses Universitaires de Franche-Comté, France, Besançon
- 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%3c789::aid-jssc789%3e3.0.co;2-j](https://doi.org/10.1002/1615-9314(20020901)25:13%3c789::aid-jssc789%3e3.0.co;2-j)
- Crini G, Lichtfouse E (2018) Wastewater treatment: an overview. In: Crini G, Lichtfouse E (eds) *Green adsorbents for pollutant removal*. Springer Nature, Cham
- Crini G, Lichtfouse E (2019) Advantages and disadvantages of techniques used for wastewater treatment. *Environ Chem Lett* 17:145–155. <https://doi.org/10.1007/s10311-018-0785-9>
- 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%3c1419::aid-app17%3e3.0.co;2-o](https://doi.org/10.1002/(sici)1097-4628(19980815)69:7%3c1419::aid-app17%3e3.0.co;2-o)
- 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* 17:195–213. <https://doi.org/10.1007/s10311-018-0786-8>
- 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, Sarrà 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, Rodríguez-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
- Cyclopure (2020) www.cyclopure.com

- 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 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*. <https://doi.org/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* 229:446–449. <https://doi.org/10.1016/j.jhazmat.2012.05.106>
- 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
- Delgado N, Bermeo L, Hoyos DA, Peñuela GA, Capparelli A, Marino D, Navarro A, Casas-Zapata JC (2020) Occurrence and removal of pharmaceutical and personal care products using subsurface horizontal flow constructed wetlands. *Water Res* 187:116448. <https://doi.org/10.1016/j.watres.2020.116448>
- 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* 234:389–396. <https://doi.org/10.1016/j.cej.2013.08.114>
- 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, Roglić 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, Plaza-Ozóg P (2007) Efficiency of municipal wastewater treatment with membrane bioreactor. *J Water Land Development*. <https://doi.org/10.2478/jwld-2019-0026>
- 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* 40:971–983. <https://doi.org/10.1007/s11090-020-10076-0>
- 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 *Tetrademus obliquus* for the removal of pharmaceuticals from water. *J Appl Phycol* 29:1179–1193. <https://doi.org/10.1007/s10811-016-1010-5>
- Fenyvesi É, Zsardon B, Szejtli J, Tüdös 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, Sente 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, Záray G, Sente L (2020) Removal of hazardous micropollutants from treated wastewater using cyclodextrin bead polymer – A pilot demonstration case. *J Hazard Mater* 383:121181.
- 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
- 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. Int Sci Index Chem Mol Eng* 9:717–722
- 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* 24:16682–16689. <https://doi.org/10.1007/s11356-017-9295-8>
- Frömming 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>
- 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.
- Ghughe SP, Saroha AK (2018) Catalytic ozonation for the treatment of synthetic and industrial effluents - Application of mesoporous materials: a review. *J Environ Manage* 211:83–102. <https://doi.org/10.1016/j.jenvman.2018.01.052>
- Gilbert-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-P (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>
- 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. *Groundwater Sustain Develop* 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>
- 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. *Catalysis Comm* 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 Hydrology* 356:46–55. <https://doi.org/10.1016/j.jhydrol.2008.03.023>
- 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>
- 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, Rashid MAM (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*. <https://doi.org/10.1155/2012/270320>
- Haque E, Lee JE, Jang IT, Hwang YK, Chang JS, Jegal J, Jhung 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* 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 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>
- Hube S, Wu B (2021) Mitigation of emerging pollutants and pathogens in decentralized wastewater treatment processes: a review. *Sci Total Environ* 779:146545. <https://doi.org/10.1016/j.scitotenv.2021.146545>
- 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, McArdell 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
- Ibrahim H, Szali N, Wan Salleh WN, Abidin MNZ (2021) A short review on recent utilization of nanocellulose for wastewater remediation and gas separation. *Mater Today Proc* 42:45–49. <https://doi.org/10.1016/j.matpr.2020.09.245>
- 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/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/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>
- Jalilnejad E, Sadeghpour P, Ghasemzadeh K (2020) Advances in membrane bioreactor technology. In Basile A, Ghasemzadeh and Jalilnejad E (eds) current trends and future developments on biomembranes Ceramic membranes bioreactors. Elsevier, Amsterdam
- Janus L, Crini G, El-Rezzi V, Morcellet M, Cambiaghi 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)
- 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>
- 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, Zárny 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>
- 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*. <https://doi.org/10.1088/1742-6596/418/1/012102>
- Karigar CS, Rao SS (2011) Role of microbial enzymes in the bioremediation of pollutants: a review. *Enzyme Res*. <https://doi.org/10.4061/2011/805187>
- Karpińska J, Kotowska U (2021) New aspects of occurrence and removal of emerin pollutants. *Water* 13:2418. <https://doi.org/10.3390/w13172418>
- Kaur R, Talan A, Tiwari B, Pilli S, Sellamuthu B, Tyagi RD (2020) Constructed wetlands for the removal of organic micro-pollutants. In: current developments in biotechnology and bioengineering. Emerging organic micro-pollutants. Varjani S, Pandey A, Tyagi RD, Ngo HH and Larroche C (Eds.). Amsterdam: Elsevier. Chapter 5, pp. 87–140
- 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>
- 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 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>
- 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
- 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
- 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>
- Lado Ribeiro AR, Moreira NFF, Puma GL, Silva MT (2019) Impact of water matrix on the removal of micropollutants by advanced oxidation technologies. *Chem Eng J* 363:155–173. <https://doi.org/10.1016/j.cej.2019.01.080>
- 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
- 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 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>
- 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 (2019) 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 (2020a) 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>
- Li J, Wang H, Yuan XZ, Zhang JJ, Chew JW (2020b) Metal-organic framework membranes for wastewater treatment and water regeneration. *Coordination Chem Rev* 404:213116. <https://doi.org/10.1016/j.ccr.2019.213116>
- 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, 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>
- 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 ZH, Kanjo Y, Mizutami S (2009a) 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 ZQ, Ma J, Cui YH, Zhang BP (2009b) Effect of ozonation pretreatment on the surface properties and catalytic activity of multi-walled carbon nanotube. *Appl Catalysis b: Environ* 92:301–306. <https://doi.org/10.1016/j.apcatb.2009.08.007>
- 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
- Liu B, Zhang SG, Chang CC (2019) Emerging pollutants - Part II: treatment. *Water Environ Res* 91:1390–1401. <https://doi.org/10.1002/wer.1233>
- 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) Elementary chemical and physical phenomena in electrical discharge plasma in gas-liquid environments and in liquids. In: plasma chemistry and catalysis in gases and liquids. Parvulescu VI, Magureanu M and Lukes P (Eds.). Weinheim: Wiley VCH. Chapter 6, pp.185–241
- Lofrano G (2012) Emerging compounds removal from wastewater: natural and solar based treatments. Netherlands: Springer. DOI: <https://doi.org/10.1007/978-94-007-3916-1>
- Loftsson T, Jarho P, Måsson M, Järvinen T (2005) Cyclodextrins in drug delivery (review). *Expert Opinion 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* 38:409–416. <https://doi.org/10.1088/0022-3727/38/3/010>
- Lukes P, Locke BR, Brissett JL (2012) 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
- 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>
- 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* 165:507–514. <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
- 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*. <https://doi.org/10.1155/2013/796373>
- Malik MA, 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>
- 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* 8:867–875. <https://doi.org/10.1002/ppap.201100036>
- Martínez-Pachón D, Espinosa-Barrera P, Rincón-Ortiz 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/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. *Polymer Int*. <https://doi.org/10.1002/pi.5993>
- 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, Diaz-Chavez R, Velásquez-Arredondo H, Cárdenas-Chávez DL, Parra R, Ruiz-Colorado AA (2016) Sustainable energy from agro-industrial wastewaters in Latin America. *Renew Sust Energy Rev* 56:1249–1262. <https://doi.org/10.1016/j.rser.2015.12.036>
- 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
- 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* 12:84. <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
- Mohsenpour SF, Hennige S, Willoughby N, Adeloje A, Gutierrez T (2021) Integrating micro-algae into wastewater treatment: a review. *Sci Total Environ* 752:142168. <https://doi.org/10.1016/j.scitotenv.2020.142168>
- 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>
- 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*. [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 FC, Boaventura RAR, Brillas E, Vilar VJP (2017) Electrochemical advanced oxidation processes: a review on their application to synthetic and real wastewaters. *Appl Catalysis 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). Besançon, PUFC, p 513
- 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>
- Morin-Crini N, Lichtfouse E, Fourmentin M, Ribeiro ARL, Noutsopoulos C, Mapelli F, Fenyvesi É, Vieira MGA, Picos-Corrales LA, Moreno-Piraján JC, Giraldo L, Sohajda T, Huq MM, Soltan J, Torri G, Magureanu M, C. Bradu, Crini G (2021) Remediation of emerging contaminants. In: *Emerging Contaminants: Remediation*. G. Crini and E. Lichtfouse, eds. Springer Nature, *Environmental Chemistry for a Sustainable World*, volume 2, chapter 2, pp. 1–106
- 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* 485:711–719. <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 peroxyntic acid. *J Chromatogr A* 1431:89–93. <https://doi.org/10.1016/j.chroma.2015.12.054>
- 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>
- 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 T (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>
- 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>
- Pakdel PM, Peighambarioust SJ (2018) Review on recent progress in chitosan-based hydrogels for wastewater treatment application. *Carbohydr Polym* 201:264–279. <https://doi.org/10.1016/j.carbpol.2018.08.070>
- 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>
- Parde D, Patwa A, Shukla A, Vijay R, Killedar DJ, Kumar RK (2021) A review of constructed wetland on type, treatment and technology of wastewater. *Environ Technol Innovation* 21:101261. <https://doi.org/10.1016/j.eti.2020.101261>
- 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* 39:3805–3813. <https://doi.org/10.1088/0022-3727/39/17/015>

- Park DP, Davis K, Gilani S, Alonzo C, Dobrynin D, Friedman 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:S19-29. <https://doi.org/10.1016/j.cap.2012.12.019>
- Parlade E, Hom-Diaz A, Blanquez 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>
- 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>
- Patel N, Khan MZA, Shahane S, Rai D, Chauhan D, Kant C, Chaudhary VK (2020) Emerging pollutants in aquatic environment: source, effect, and challenges in biomonitoring and bioremediation - a review. *Pollution* 6:99–113. <https://doi.org/10.22059/poll.2019.285116.646>
- Pathak N, Tran VH, Phuntsho S, Shon HY (2020) Membrane reactors for the removal of organic micro-pollutants. In: current developments in biotechnology and bioengineering. Emerging organic micro-pollutants. Varjani S, Pandey A, Tyagi RD, Ngo HH and Larroche C (Eds.). Amsterdam: Elsevier. Chapter 10, pp. 231–252
- 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>
- Petroselli A, Giannotti M, Marras T, Allegrini E (2017) Integrated system of phytodepuration and water reclamation: A comparative evaluation of four municipal wastewater treatment plants. *Int J Phytodepuration* 19:563–571. <https://doi.org/10.1080/15226514.2016.1267702>
- 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, Hermosillo-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>
- Plöhn M, Spain O, Sirin S, Silva M, Escudero-Onate C, Ferrando-Climent L, Allahveriyeva Y, Funk C (2021) Wastewater treatment by microalgae. *Physiol Plant* 173:568–578. <https://doi.org/10.1111/ppl.13427>
- 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. *Arabian J Chem* 10:S3749–S3773. <https://doi.org/10.1016/j.arabjc.2014.05.011>
- Putro JN, Kurniawan A, Ismadji S, Ju YH (2017) Nanocellulose based biosorbents for wastewater treatment: Study of isotherm, kinetic, thermodynamic and reusability. *Environ Nanotechnol Monitor 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-Rodríguez 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) Electrochemical oxidation processes. In: advanced oxidation processes for waste water treatment. Chapter 11, pp. 359–373. DOI: <https://doi.org/10.1016/B978-0-12-810499-6.00011-5>
- 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>
- 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>
- 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
- 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* 239:249–256
- 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>
- 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>
- 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. *Biomolecules* 9:571. <https://doi.org/10.3390/biom9100571>
- 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) Removal of emerging pollutants by fungi. In: fungal bioremediation: fundamentals and applications. Publisher: CRC Press Taylor & Francis Group. Chapter 7, pp. pp.186–237. DOI: <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>
- Rolli E, Vergani L, Ghitti E, Patania G, Mapelli F, Borin S (2021) Cryo-for-help in contaminated soil: a dialogue among plants and soil microbiome to survive in hostile conditions. *Environ Microbiol* 23:5690–5703. <https://doi.org/10.1111/1462-2920.15647>
- 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.ccllet.2013.11.003>
- 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>
- Russo V, Hmoudah M, Broccoli F, Iesce MR, Jung OS, Di Serio M (2020) Applications of metal organic frameworks in wastewater treatment: a review on adsorption and photodegradation. *Front Chem Eng*. <https://doi.org/10.3389/fceng.2020.581487>
- 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, Bacsa 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, Chaini 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
- 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>
- Sayyed AJ, Pinjari DV, Sonawane SH, Bhanvase BA, Sheikh J, Silanpää M (2021) Cellulose-based nanomaterials for water and wastewater treatments: a review. *J Environ Chem Eng* 9:106626. <https://doi.org/10.1016/j.jece.2021.106626>
- Serna-Galvis EA, Silva-Agreto 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
- 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 Biodeterioration Biodegradation* 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 Scie Technol* 58:1129–1135
- Singh RN, Sharma S (2012) Development of suitable photobioreactor for algae production -a review. *Renew Sustain Energy 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/10.1080/01919510601039726>
- 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
- 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* 53:5337–5338
- Song Z, Zhanf YT, 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. *Chem 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>
- 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>
- 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>
- 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 Electrostatics* 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 GuJ (2018b) Evaluation of antibiotic oxytetracycline removal in water using a gas phase dielectric barrier discharge plasma. *J Environ Manage* 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>
- Thakur V, Guleria A, Kumar S, Sharma S, Singh K (2021) Recent advances in nanocellulose processing functionalization and applications: a review. *Mater Adv* 2:1872–1895. <https://doi.org/10.1039/D1MA00049G>

- 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>
- Thurman M (2006) Accurate-mass identification of chlorinated and brominated products of 4-nonylphenol, nonylphenol dimers, and other endocrine disruptors. *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-A, de la Cruz QR, Barceló D, Iqbal HMN, Parra-Saldívar 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
- Torres-Palma RA, Serna-Galvis EA (2018) Sonolysis. In: advanced oxidation processes for waste water treatment. Chapter 7, pp. 117–213. DOI: <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, Mosteo R, Ormad MP, Torres-Palma RA (2017) Electrochemical advanced oxidation processes for *Staphylococcus aureus* disinfection in municipal WWTP effluents. *J Environ Manage* 198:256–265. <https://doi.org/10.1016/j.jenvman.2017.04.070>
- 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 Manage* 180:228–237. <https://doi.org/10.1016/j.jenvman.2016.05.035>
- Vidal RRL, Moraes JS (2019) Removal of organic pollutants from wastewater using chitosan: a literature review. *Int J Environ Sci Technol* 16:1741–1754. <https://doi.org/10.1007/s13762-018-2061-8>
- Vieira WT, de Farias MB, Spaoloni MP, da Silva MGC (2020) Vieira MGA (2020) Removal of endocrine disruptors in waters by adsorption, membrane filtration and biodegradation. *A Review Environ Chem Lett*. <https://doi.org/10.1007/s10311-020-01000-1>
- 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 Manage* 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 *Nanomaterials* 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>
- Vymazal J, Zhao Y, Mander Ü (2021) Recent challenges in constructed wetlands for wastewater treatment: a review. *Ecological Eng* 169:106318. <https://doi.org/10.1016/j.ecoleng.2021.106318>
- 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 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 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 peroxymonosulfate 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 Catalysis 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>
- 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 JNJ, Eck VPV (1969) Properties of cyclodextrins. III cyclodextrin-epichlorhydrin resins. *Prep Anal 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: Minutes Int. Symp. Cyclodextrins, 6th (1992), 106–9. Hedges AR (Ed.). Publisher: 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 H, Yang Y, Liu J, Kang Y, Zhang J, Hu Z, Liang S (2018) Enhanced triclosan and nutrient removal performance in vertical up-flow constructed wetlands with manganese oxides. *Water Res* 143:457–466. <https://doi.org/10.1016/j.watres.2018.05.061>
- 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/10.1088/0022-3727/48/42/424008>
- 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 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 H₂O₂ or Fe²⁺. *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 Nature Switzerland. <https://doi.org/10.1007/978-3-030-10480-1>
- Yadav M, Thakore S, Jadeja R (2021) A review on remediation technologies using functionalized cyclodextrin. *Environ Sci Pollut Int.* <https://doi.org/10.1007/s11356-021-15887-y>
- 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 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/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 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/H₂O₂. *Water Res* 43:1766–1774. <https://doi.org/10.1016/j.watres.2009.01.008>
- Zango ZU, Jumbri K, Sambudi NS, Ramli A, Bakar NHHA, Saad B, Rozaini MNH, Isiyaka HA, Jagaba AH, Aldaghri O, Sulieman A (2020) A critical review on metal-organic frameworks and their composites as advanced materials for adsorption and photocatalytic degradation of emerging organic pollutants from wastewaters. *Polymers* 12:2648. <https://doi.org/10.3390/polym12112648>
- Zhang S, Grimm D (2005) Naproxen removal from water by chlorination and biofilm processes. *Water Res* 39:668–676
- Zhang Y, Geiben 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/H₂O₂ 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 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 Macrocyclic 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>

Zraunig A, Estelrich M, Gattringer H, Kisser 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>

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