PERSPECTIVE

Wastewater chemical contaminants: remediation by advanced oxidation processes

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Approximately 70% of the terrestrial area is covered with water, but only a small water fraction is compatible with terrestrial life forms. Due to the increment in human consumption, the need for water resources is increasing, and it is estimated that more than 40% of the population worldwide will face water stress/scarcity within the next few decades. Water recycling and reuse may offer the opportunity to expand water resources. For that, the wastewater treatment paradigm should be changed and adequately treated wastewater should be seen as a valuable resource instead of a waste product. It is easily understandable that the exact composition and constituent concentration of wastewater vary according to its different sources (industrial, agricultural, urban usage of water). Consequently, a variety of known and emerging pollutants like heavy metals, antibiotics, pesticides, phthalates, polyaromatic hydrocarbons, halogenated compounds and endocrine disruptors have been found in natural water reservoirs, due to the limited effectiveness of conventional wastewater treatment. The conventional approach consists of a combination of physical, chemical and biological processes, aiming at the removal of large sediments such as heavier solids, scum and grease and of organic content in order to avoid the growth of microorganisms and eutrophication of the receiving water bodies. However, this approach is not sufficient to reduce the chemical pollutants and much less the emerging chemical pollutants. In this review, after some considerations concerning chemical pollutants and the problematic efficiency of their removal by conventional methods, an update is presented on the successes and challenges of novel approaches for wastewater remediation based on advanced oxidation processes. An insight into wastewater remediation involving the photodynamic approach mediated by tetrapyrrolic derivatives will be underlined.

1. Introduction

Water is essential for life and although approximately 70% of the terrestrial area is covered with water, only a small fraction (2.5%) is freshwater compatible with terrestrial life.[1]

This low stock of available freshwater (mostly concentrated in the Antarctic and Arctic regions in the form of ice and permanent snow) is being accompanied by an increase in human consumption as a consequence of demographic growth, industry demand and living conditions. It is even estimated that in some regions of the world, water use has risen twice faster than the human population and it is expected that in 2050 the consumption will be largely higher than it is today, especially in urban areas.[1,2] This increase in water demands is putting extensive pressure not only on water, but also on land and energy resources.[3] In fact, half of the European countries are already facing water stress,[4] and it is estimated that within the next 50 years, more than 40% of the population worldwide will face water stress or scarcity.[1,4,5] All this together represents a solemn inducement to achieve sustainable management options of water resources.[1]

At the Rio + 20 Summit 2012, the United Nations Conference on Sustainable Development, *water* was recognized as a central factor for the Green Economy.[6] The United Nations Educational, Scientific and Cultural Organization (UNESCO) reinforces the awareness that good quality of water is essential for a healthy environment and sustainable development of human beings.[7]

Water recycling and reuse may offer the opportunity to expand water resources.[3] As in other kinds of wastes largely produced daily, the quality of wastewater is highly dependent on its source, the way it is collected and the received treatment.[8]

Irrigation and industrial cooling are some of the activities where wastewater reuse has been practiced from the beginning of the sixteenth century in Europe, and of the twentieth century in the USA.[1,8] Although wastewater reuse in irrigation activities can be considered a beneficial option, since it may

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Photochem. Photobiol. Sci., 2018, **17**, 1573–1598 | **1573**

represent not only an extra supply of water but also of valuable nutrients to crops, irrigation using these waters may also have some negative implications either at the microbiological or physicochemical level.[1,9] Reused water can alter the natural properties and even promote the introduction or accumulation of biological and chemical contaminants in the soil, which can not only affect soil productivity and fertility, but also increase human and environmental health risks.[1]

It is clear, however, that wastewater reuse will be in the future one of the major contributors to deal with the reduction of freshwater availability.[5] For that, the wastewater treatment paradigm should be changed.

Currently, only a small proportion of all wastewater is treated and, consequently, only a small part of the prevailing wastewater is safely reused, which entails potential health risks.[1,8] It was estimated that daily, from the 2 million tons of industrial, agricultural and urban wastewater discharged[10] (Fig. 1), more than 80% (reaching 95% in some least developed countries) is released to the environment without any kind of treatment.

The deficient or inexistent wastewater treatments can increase the risk of transmission not only of infectious diseases but also of diseases related to the presence of chemical pollutants. It is undoubtedly clear that the occurrence of these health risks is largely reduced when reused water sources result from well-operated wastewater treatment plants.[9] Within this context, adequately treated wastewater should be seen more and more as a valuable resource instead of a waste product.[9]

Generally, wastewater is composed of water and suspended dissolved and colloidal solids.[11] However, it is easily understandable that its exact composition and constituent concentrations vary over different sources.[11] As a consequence, a variety of known and emerging pollutants are found both in treated and untreated industrial effluents, municipal wastewaters and even agricultural runoffs, which can infiltrate and run into natural water reservoirs.[11] Once discharged into water bodies, even with the dilution factor, wastewater can affect the quality and availability of freshwater supplies. Pollutants have been detected in drinking water, showing that their removal by conventional wastewater treatment and even water purification processes was not effective.[11] It was estimated that, in 2012, 842 000 deaths may have occurred due to the use of contaminated drinking water and water used in handwashing facilities and/or due to inadequate sanitation services in middle/low income countries.[11]
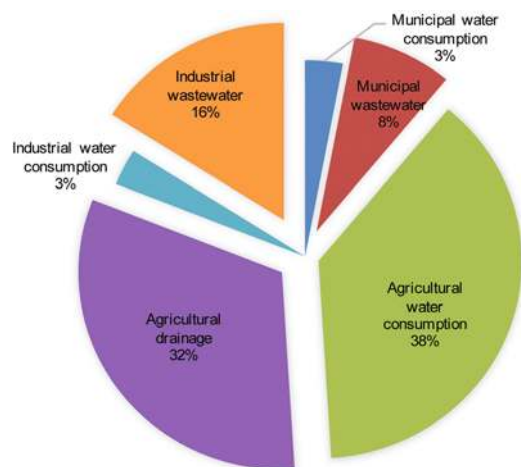

Fig. 1 Fate of freshwater withdrawals. Global consumption and wastewater production by activity sector. Based on the UN World Water Development Report 2017 (data relative to *circa* 2010).[11]

2. Pollutants and emerging pollutants in water and wastewater

Human beings play a major role in the issue of pollutants released in wastewater, whether from industrial discharges, agricultural practices or general population usage of water. All these practices generate various pollutants, which include

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1574 | *Photochem. Photobiol. Sci.*, 2018, **17**, 1573–1598

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heavy metals, antibiotics, pesticides, phthalates, polyaromatic hydrocarbons (PAHs), halogenated compounds, and endocrine disruptors.[12] However, in the last few decades, the presence of new compounds not only in wastewaters but also in aquatic environments such as surface water, groundwater and even drinking water has been reported.[12–14] These compounds have been referred to as emerging pollutants.[12] Although the potential health risks of emerging pollutants on humans and ecosystems are still very scarce, they may be understood as any synthetic or even naturally occurring chemical compound or microorganism without regulatory status that can have a potentially adverse effect on both ecological and human health.[7,10,12] It is possible that in some cases, the release of emerging pollutants to the environment has been occurring for a long time.[10] Probably, their detection was not possible due to negligence, lack of awareness of their effect on the environment or lack of adequate detection methods. Additionally, the continuous development of new chemical substances without knowledge of their environmental impact and prevalence can contribute to the spread of emerging chemical pollutants.[15] Actually, many of the emerging pollutant substances are not included in worldwide routine monitoring programs and the knowledge about their behavior and ecotoxicological effects is insufficient.[10]

More than 700 emerging pollutants in addition to their metabolites and transformation products are present in the European aquatic environment.[10,15] They can be categorized into more than 20 categories, related to their origin and function.[10,15] According to UNESCO, the main groups of contaminants are: (i) pharmaceutical drugs [e.g. antibiotics, analgesics, anti-depressives, steroids and hormones (e.g. contraceptive drugs)] mainly present in urban and stock farming effluents; (ii) personal care products (e.g. fragrances, sunscreen agents, insect repellents, microbeads and antiseptics) mostly present in urban effluents; (iii) pesticides and herbicides occurring in general from agricultural practice; and (iv) industrial additives, plasticizers and gasoline additives from industrial prac-

tice.[7,10,15] Although some of them could be released to the environment occasionally and at low concentrations, many others are released in a continuous manner. Moreover, due to their low volatility,[10,16] these pollutants may cause chronic toxicity and endocrine disruption and even promote the development of drug-resistant microorganisms.[17] Related to the release of pharmaceutical drugs, namely antibiotics, widely used not only in human care but also in veterinary and agriculture,[18] it was estimated that around the year 2050, 10 million deaths could occur per year due to drug-resistant infections, acquired by selective pressure inflicted on the bacteria in contact with the antibiotics.[17,18]

Although urban wastewater seems to be the dominant emission pathway for pharmaceuticals, emissions from industrial production, hospitals, agriculture and aquaculture are also considered as important contributors to this theme of global concern.[18] In fact, from a total of 713 pharmaceuticals and transformation products analyzed in the environment, 631 were positively detected, and the residues of 16 pharmaceutical products were noticed in groundwater, surface water and drinking water.[18]

Thus, pharmaceuticals and personal care products (PPCPs) are becoming universally present in the environment at concentrations from ng L^{-1} to μg L^{-1} not only due to their extensive applications but also due to their poor removal by conventional wastewater treatments.[19] According to Mompelat et al. (2009), only in Europe, around 4000 different pharmaceutical compounds are prone to spread and become present in every environmental compartment, in their active form. In fact, PPCPs can appear in the environment by direct discharges in surface waters (via human/animal excretion), or by indirect pathways through land runoff resulting in leaching and consequently reaching the groundwater (via agricultural practice).[18,20] The recent upgrading of analytical techniques such as gas chromatography-tandem mass spectrometry (GC-MS/MS) and liquid chromatography-tandem mass spectrometry (LC-MS/MS) allows one to monitor the dis-

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Photochem. Photobiol. Sci., 2018, **17**, 1573–1598 | **1575**

Table 1 List of frequently detected human and veterinary pharmaceuticals and personal care products (PPCPs) in water and wastewater

Pharmaceuticals			
Pharm. category	Main function	Active pharmaceutical ingredients (API) frequently detected	Average|maximum globally found[a] (μg L^{-1})
Antibiotics	Antibacterial	Amoxicillin[24]	ND
		Ampicillin[25,26]	ND
		Cefaclor[23,27]	ND
		Cefalexin[28,29]	ND
		Ciprofloxacin[14,25,28,30–32]	18.99|6500[18 a]
		Difloxacin[33]	ND
		Doxycycline[20,26,33,34]	ND
		Enoxacin[23,32]	ND
		Erythromycin[14,28,30,35]	ND
		Mecillinam[23]	ND
		Norfloxacin[36]	3.457|520.0[18 a]
		Ofloxacin[23,28,30,31,37]	0.278|17.7[18 a]
		Sulfamethoxazole[33,37–39]	0.095|29.0[18 a]
		Sulfapyridine[14,20]	ND
		Tetracycline[28,40]	ND
		Trimethoprim[14,33,37,41]	0.037|13.6[18 a]
		Tylosin[20,34]	ND
Anti-convulsants	Treatment of epileptic seizures, mood stabilizers or neuropathic pain treatment	Cabapentin[23]	ND
		Carbamazepine[24,42]	0.187|8.05[18 a]
		Dilantin[24]	ND
		Phenobarbital[23]	ND
		Primidone[14,30]	ND
Anti-depressants	Treatment of psychiatric disorders	Amitriptyline[42]	ND
		Diazepam[24]	ND
		Doxepin[20,23]	ND
		Fluoxetine[24,37,40]	ND
		Imipramine[20,23]	ND
		Meprobamate[24]	ND
		Oxazepam[30,39]	ND
		Sertraline[42]	ND
		Thioridazine[30]	ND
Anti-neoplastics	Control and/or killing of neoplastic cells	Cyclophosphamide[43]	ND
		Epirubicin[42]	ND
		Ifosfamide[42–44]	ND
		Methotrexate[30]	ND
		Tamoxifen[42]	ND
Beta-blockers	Treatment of high blood pressure and migraines	Acebutolol[30–32]	ND
		Atenolol[42]	ND
		Metoprolol[45]	ND
		Nadolol[46]	ND
		Pindolol[23]	ND
		Propranolol[42]	ND
		Sotalol[30,31]	ND
Diagnostic contrast media	Used in some diagnostic tests to enhance the visibility of internal structures	Diatrizoate acid[14,27,30]	ND
		Iomeprol[27,30]	ND
		Iopromide[24]	ND
Hormones	Regulation of metabolism and homeostasis, and control of sexual development	17-α Ethinylestradiol[47]	0.043|5.9[18 a]
		17-β Estradiol[24]	0.003|0.012[18 a]
		Androstenedione[44]	ND
		Estriol[24]	0.009|0.48[18 a]
		Estrone[24]	0.016|5.0[18 a]
		Mestranol[23]	ND
		Testosterone[30,44]	ND
Lipid regulators	Treatment of dyslipidaemias	Bendroflumethiazide[23]	ND
		Benzafibrate[42]	ND
		Clofibrate[27,32]	ND
		Clofibric acid[42]	0.022|7.91[18 a]
		Furosemide[42]	ND
		Gemfibrozil[24]	ND
		Simvastatin[42]	ND

1576 | *Photochem. Photobiol. Sci.*, 2018, **17**, 1573–1598

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Table 1 *(Contd.)*

Pharmaceuticals

Pharm. category	Main function	Active pharmaceutical ingredients (API) frequently detected	Average|maximum globally found[a] ($\mu g\ L^{-1}$)
Nonsteroidal anti-inflammatory drugs	Reduction of inflammation status and pain	Aspirin[16,44,48]	0.922|20.96[18 a]
		Diclofenac[24,42]	0.032|18.74[18 a]
		Ibuprofen[19,24,42]	0.108|303.0[18 a]
		Indomethacin[42]	ND
		Ketoprofen[42]	ND
		Naproxen[19,24,42]	0.050|32.0[18 a]
		Nimesulide[42]	ND
		Paracetamol (acetaminophen)[24,42]	0.161|230.0[18 a]
		Phenazone[42]	ND
		Salicylic acid[16,43,48]	ND
		Salicylic acid[16,43,48]	ND

Personal care products (PCP)

PCP category	Main function	Ingredients frequently detected	Average and maximum globally found ($\mu g\ L^{-1}$) #
Disinfectants	Inactivate and/or kill germs and parasites	2-Phenylphenol[23]	ND
		4-Chlorocresol[23]	ND
		4-Chloroxylenol[23]	ND
		Bromoprene[23]	ND
		Chloroprene[23]	ND
		Triclosan[24,42]	ND
		2-Phenoxyethanol[23]	ND
Preservatives	Prevention of chemical and/or microbial deterioration	Alkyl (ethyl, butyl, isobutyl, isopropyl) 4-hydroxybenzoate[23]	ND
		Methyl paraben[23]	ND
		Octocrylene[14,23,49]	ND
Sunscreen agents	Prevents skin damage due to UV radiation	Oxybenzone[24]	ND
		Ethylhexyl methoxycinnamate[23,49]	ND

ND, no data collected. [a] Average and maximum concentrations of the sixteen most found pharmaceuticals in the countries of the United Nations in all surface water compartments. Based on a study conducted by aus der Beek *et al.* in 2015.[18]

tribution of PPCPs in any type of water at the trace level (ng L^{-1}, or below).[18,20]

In the last 20 years, several studies had been conducted to assess the presence of pharmaceutical compounds in aquatic environments to evaluate the degree of contamination and the efficiency of their elimination during the treatment of drinking water and wastewater (Table 1).

Considering the relevance of the discharge of PPCPs into the environment, the European Union established as a priority in the field of water policy the disposal control of a group of substances – including pharmaceutical substances (Table 2).[21,22] In this list are included substances with a wide range of applications, such as in pharmaceuticals and PPCPs, industrial and agricultural products, household products and motor fuel constituents and/or additives, and several compound families such as alkylphenols, phthalates, PAHs, halogenated hydrocarbons, and organometallics, among others.[12,23]

Similarly to water pollutants, the transfer of emerging pollutants from diffuse sources to water bodies strongly depends on the properties of these substances, for instance, volatility, polarity, adsorption properties and persistence.[10] These pollu-

tants that are non-removable by wastewater treatment plants are often discharged into water bodies like rivers, where their possible degradation occurs, and also where their adsorption to sediments and transportation in the aqueous phase can be observed.[10] The degradation (biodegradation) occurrence varies significantly between compounds and is highly dependent on the presence of organisms able to induce transformations of these contaminants through metabolic networks.[10]

3.   Water decontamination

The composition of wastewater, as mentioned above, varies significantly accordingly to its source. However, the main wastewater pollutants can be present in all wastewater sources, even if at very different concentrations.[11] So, suspended solids, biodegradable organic matter and nutrients (*e.g.* nitrogen and phosphorus compounds), non-biodegradable organic matter (*e.g.* pesticides and detergents), metals (*e.g.* cadmium, mercury, nickel and lead), inorganic dissolved solids and pathogens tend to be present all over domestic and industrial wastewaters as urban and agricultural runoff/wastewaters.[11]

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Table 2 List of chemical substances considered as priority in the field of water policy, according to the European Parliament and the Council, adapted from Directive Decision number 2455/2001/EC of the EU Parliament and Council amending Annex X of the Directive 2000/60/EC, and guideline values for chemicals used in human activities that are of health significance, according to the 2017 Guidelines for Drinking-Water Quality from the World Health Organization (WHO)

Group category	Name of priority substance	Main applications	Guideline values for chemicals that are of health significance[b] (mg L^{-1})
Alkylphenols	Nonylphenols[a]	Industrial, household and personal care product uses[13,50–52]	NA
	Octylphenols		NA
Aromatic hydrocarbons (PAHs)	Anthracene	Agriculture and industrial uses[53]	NA
	Benzene	Industrial, motor fuel, household and pharmaceutical uses[54]	0.01
	Trifluralin	Agriculture use[55]	0.02
	Fluoranthene	Motor fuel use[56]	NA
	Naphthalene	Industrial and pharmaceutical uses[57]	NA
	Polyaromatic hydrocarbons (PAHs)[a]	Motor fuel, industrial, agriculture and pharmaceutical uses[13,50,58–60]	NA
Halogenated hydrocarbons	1,2-Dichloroethane	Motor fuel, industrial and pharmaceutical uses[61,62]	0.03
	Alachlor	Agriculture use[63–65]	0.02
	Dichloromethane	Pharmaceutical, agriculture and industrial uses[66,67]	0.02
	Endosulfan	Agriculture use[68,69]	NA
	Hexachlorobenzene[a]	Agriculture and industrial use[70]	NA
	Hexachlorobutadiene[a]	Industrial, pharmaceutical and agriculture uses[71]	0.0006
	Pentachlorobenzene[a]	Agriculture, pharmaceutical and industrial uses[72–74]	NA
	Pentachlorophenol	Agriculture use[75]	0.009
	Trichloromethane (chloroform)	Pharmaceutical and industrial uses[76]	0.3
	Hexachlorocyclohexane[a]	Agriculture use[77,78]	NA
	Trichlorobenzene	Industrial use[79]	NA
	Brominated diphenyl ethers[a]	Industrial use[80–82]	NA
	C$_{10–13}$-Chloroalkanes[a]	Industrial use[83]	NA
Metals	Cadmium and its compounds[a]	Industrial use[84,85]	NA
	Lead and its compounds	Industrial use[86]	0.01
	Mercury and its compounds[a]	Industrial use[87]	NA
	Tributyltin compounds[a]	Industrial use[82,88]	NA
	Nickel and its compounds	Industrial use[89]	0.07
Organophosphates	Chlorfenvinphos	Agriculture use[90,91]	NA
	Chlorpyrifos	Agriculture use[92]	0.03
Phthalates	Bis(2-ethylhexylphthalate)	Industrial use[12,93,94]	0.008
Urea derivatives	Diuron	Agriculture and industrial uses[14,45,95,96]	NA
	Isoproturon	Agriculture and industrial uses[97,98]	0.009
Triazine	Atrazine	Agriculture and motor fuel uses[24,45,99,100]	0.1
	Simazine	Agriculture use[101,102]	0.002

NA, no data available. [a] Identified substances as priority hazardous substances or groups that encompass compounds that are identified as hazardous substances. [b] WHO's guideline values for chemicals that are of health significance in drinking water.

Depending on the concentration of these pollutants some wastewaters could be less hazardous than others. However, it is essential to keep in mind that even if these substances are present at lower concentrations, it may cause long-term effects. Additionally, due to the fact that wastewater treatment plants do not receive, generally, disposal water from a unique source, this mixture could cause serious problems in the elimination of the pollutants, due to its complex composition.

The removal of the hazardous constituents of wastewater that occur at the treatment plants consists of a combination of physical, chemical and biological approaches.[11] Physical barriers and gravity are the first physical process approaches performed to remove large sediments and heavier solids (e.g. grit) among others – the **pre-treatment** stage – and scum and grease in the following stage by gravity action and density differences – the **primary treatment** stage.[11] Afterwards, the wastewater enters the **secondary treatment** stage, where mainly biological processes take place in order to remove the organic content, with systems created for the promotion of either aerobic or anoxic zones.[11] This step takes place in biological reactors and

is based on biochemical degradation that naturally occurs in natural water environments, such as rivers and lakes. It can be made *via* activated sludge (suspended biomass), by means of percolating beds or biological disks (fixed biomass) or by lagooning (suspended biomass in aquatic systems). In these reactors, the degradation of some pollutants occurs as per the stabilization of the sludges.

Although this phase of the treatment may seem to show easy execution and good efficiency, it is necessary to insert energy into the system to maintain the oxygen supplement in it, to allow the conversion of organic matter into degradation products such as sludge (biomass) and carbon dioxide.[103] The aerobic degradation process prevents the anaerobic process, in which the formation of methane will occur – a well-known greenhouse gas.[103] Usually, in this phase, if the wastewater parameters are below the legally imposed limits, the wastewater effluents are considered good enough to be released into the environment.[104]

The presence of microorganisms in the wastewater treatment plants is essential to promote the biodegradation of some chemicals.[105] However, many factors can compromise or potentiate the microorganism biodegradation pathway, such as their genetic potential, temperature, pH of the medium and even organic matter availability (*e.g.* nitrogen and phosphorus sources).[105] In fact, it is well known that excess nitrogen and phosphorus present in water bodies, responsible for eutrophication, are mainly due to inadequate wastewater treatment, which leads to potentially toxic algal blooms and consequent declines in biodiversity.[106]

In some circumstances, **tertiary treatment** can occur, namely, when extreme wastewater disinfection (removal of microorganisms) or decontamination (removal of suspended solids, excess nutrients and specific toxic compounds) is required. The main purpose of tertiary treatment is the inactivation of microorganisms. The addition of chlorine is most common because it is less expensive, although the removal is not completely effective. Currently, there are other more advanced processes: ozonation, UV treatment, sand filtration and use of membranes.[14,23,45,107–109]

In general, the application of these processes is expensive and, in some cases, harmful; one can induce genetic damage to the microorganisms in the tank or even to the native species of the natural receiving waters (*e.g.* chlorination by-products).[104]

The application of tertiary treatment is not very common worldwide. The urban wastewater treatment-related European Commission Directive (Directive 91/271/EEC) points to the mandatory collection and application of secondary treatment of wastewater in urban settlements. The application of more advanced treatments is, however, mandatory when the release of wastewater takes place in sensitive areas.[110]

In short, physical, chemical and biological processes are combined to accomplish the different stages of wastewater treatment.[11] The selection of the most appropriate technologies should depend on the characteristics of the components, the pollution cargo and the economic attainability. Despite the approaches from different backgrounds, one of the

by-products of wastewater treatment plants is sewage sludge which could have considerable potential as a soil fertilizer due to its nutrients and organic matter constitution. However, these sludges also simultaneously have highly hazardous potential with the presence of pathogens and heavy metals, among other harmful compounds.[11]

The need for wastewater treatment worldwide is undeniable. Disinfection and decontamination of wastewater are critical for achieving an adequate level of microbial inactivation, for removal or degradation of harmful pollutants and for preventing recontamination of the receiving waters.

3.1. Conventional water treatment methods to reduce chemical contaminants

The conventional wastewater treatment processes are designed to reduce solids in suspension, biodegradable organic products, microorganisms and nutrients, but not to reduce the chemical pollutants and much less the emerging chemical pollutants. However, some conventional methods, although not primarily designed to remove chemical pollutants, can have a positive impact on their reduction.[111–113]

Secondarily, biological treatments, such as percolation and activated sludge-based treatment, as expected, remove effectively nutrients from urban wastewaters,[114–116] but not chemical pollutants. The activated sludge-based treatment method is based on the use of aerobic granules, which consist of spherical aggregates of sludge that contain embedded bacteria in a matrix of extracellular polymeric substances (EPS).[115] In these compact aerobic structures, the oxygen content creates a diffusion gradient of aerobic, anaerobic and anoxic areas, which allows the co-occurrence of different bacterial groups that are involved in the biological processes, to treat and remove undesired nutrients such as carbon, nitrogen and phosphorus inside the granules.[117] However, due to the presence of some other environmental contaminants such as pharmaceuticals, namely antibiotics often detected in both domestic and industrial wastewaters,[46] the capacity of the system to eliminate the components for which it was designed can be highly compromised,[29,40,118] since these contaminants in the wastewater can alter the composition of the microbial communities.[34,119] Even so, several pharmaceutical substances can be removed by these biological conventional treatments. The removal of seven active pharmaceutical substances (**ibuprofen**, **ketoprofen**, **naproxen**, **diclofenac**, **clofibric acid**, **mefenamic acid**, and **gemfibrozil**) was assessed by using suspended biofilm carriers and activated sludge from several full-scale wastewater treatment plants.[120] A distinct difference between nitrifying activated sludge and suspended biofilm carrier removal of several pharmaceuticals was demonstrated. Biofilm carriers from full-scale nitrifying wastewater treatment plants demonstrated considerably higher removal rates per biomass unit of **diclofenac**, **ketoprofen**, **gemfibrozil**, **clofibric acid** and **mefenamic acid** compared to the sludges. Among the target pharmaceuticals, only **ibuprofen** and **naproxen** showed similar removal rates per unit biomass for the sludges and biofilm carriers.[120] In another study, bio-

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Photochem. Photobiol. Sci., 2018, **17**, 1573–1598 | **1579**

logical treatment showed lower reduction degrees for several pharmaceuticals in trickling filter plants compared with activated sludge plants with nitrogen removal.[121] However, the pH of the wastewater during the treatment process – typically within the range of 6.0–8.0 – may affect the sorption of the active pharmaceutical compounds into the sludge.[122] Actually, Hörsing et al. pointed to the fact that for pharmaceutical compounds whose pK_a or pK_b (acid- and base-ionization constants, respectively) values are comprehended within the pH range of 6.0–8.0, the distribution amongst water and the solid phase is affected by the pH value of the medium – as in the case of acidic compounds such as ibuprofen and diclofenac.[122] Additionally, Andersen et al., in a study where the distribution coefficients among water and activated sludge particles for the steroid estrogens **estrone**, **17-β-estradiol** and **17-α-ethinylestradiol** were measured, concluded that sorption seemed not to be so important for their removal when compared to biodegradation, due to the low concentration of suspended solids of the wastewater treatment plants.[123]

In what concerns to the tertiary treatment phase of wastewaters, one of the main used methods around the world to disinfect wastewater before it is discharged into water bodies is chlorination. In this method, chlorine is added to the water aiming only for the elimination of the pathogens present in the water[124,125] and not for the elimination or transformation of the chemical pollutants. Several types of chemical pollutants may be destroyed by chlorine but many remain unchanged.[121] Nevertheless, the formation of potentially harmful by-products[126] such as **chloroacetic acids**, **trichloroacetaldehyde** and **chlorophenols** can occur when the treated water contains phenol or related compounds.[125,127] Thus, the use of monochloramines to perform chloramination as a chlorination alternative was implemented, but the production of potentially harmful chemicals such as **cyanogen chloride**, **N-nitrosodimethylamine** and **trihalomethanes** still occurs.[125]

Another widespread tertiary treatment method is ozonation; this along with the disinfection utility is associated with the oxidation of metals such as iron or manganese, as well as of organic matter, and even with the decolorization of water.[125] Considering the fact that ozonation works through molecular oxidation, it is believed that ozone acts as a selective oxidant, which means that it will only react with certain molecules and the amount of ozone required can be in the order of mg L^{-1}. Thus, the potential of ozone to decontaminate the water of contaminants such as pharmaceutical drugs was already evaluated in a lab scale and it was shown that ozone concentrations of 0.5 mg L^{-1} were required to decrease the concentrations of the pharmaceuticals **diclofenac** and **carbamazepine** by more than 90%. Although these results seem to be promising, an extremely high level of ozone (3.0 ml L^{-1} of ozone) is required to decrease the presence of the pharmaceutical **clofibric acid** to a percentage around 30%.[128] The use of ozone is not free of harmful by-products (e.g. formaldehyde) and some of them are listed in the European Union and Australian health-related guidelines for chemical contaminants in drinking water.[125,127]

Adsorption is another conventional process of wastewater treatment, a tertiary treatment method. The process is based on the adhesion of atoms, ions, and molecules from the wastewater to an adsorbent surface, forming a film.[128,129] There are a variety of adsorption types that use different adsorbents, including activated carbon.[128] In general, when granular activated carbon is used, due to its high surface area, the elimination of pharmaceutical molecules from the wastewater is successfully achieved. However, with regard to the principle of the method, what occurs in this decontamination method of wastewater treatment is a transfer of the contaminant of the wastewater phase to the adsorbent phase, not elimination or pollutant degradation.

In the last few years, the application of filtration-based techniques as tertiary treatment – microfiltration or even ultrafiltration – has grown significantly due to the good quality, in general, of the effluent obtained after the procedure.[107] However, filtration procedures, especially with low-pressure membranes, tend to have pore sizes that are insufficient for the retention of some molecules because of their size, like pharmaceuticals.[114] However, techniques like reverse osmosis and nanofiltration have shown good results in what concerns the physical separation of a variety of pharmaceuticals from water.[114,130] Nevertheless, these systems are known for their high need for energy input to the system in parallel with high levels of maintenance and operation.[131,132] Especially when dealing with pollutant compounds, one major weakness of physical processes such as filtration, or even adsorption, is that the pollutants are just exchanged between different phases during the water treatment, retaining the noxious potential of these non-degraded pollutants.[131,132]

3.2. Water emergent treatment/decontamination methods

The efficiency of the treatment techniques used for the removal of chemical pollutant compounds from wastewater draws weighty interest. As the conventional methods used in wastewater treatment are limited and their associated operational and capital costs are high, the problem of the chemical pollutants in the environment is not completely solved.[133] Chemical oxidation processes either by using conventional oxidants, such as Fenton's reagent, permanganate or hypochlorite, or by using advanced oxidation processes (AOPs), such as photocatalysis, among others, are being selected as pollutant degradation techniques.[134]

The results achieved in recent years show that technologies based on photochemical and photocatalytic approaches seem to be very promising as viable alternatives for application in wastewater treatments of different sources, including urban and industrial effluents. These approaches allow the transformation of chemical pollutants into less toxic substances with structural features that are more readily biodegradable[134] and are based on the combination of oxidizing agents with an appropriate catalyst and/or light.[134,135] These processes may be of particular interest for the effluent's treatment containing

1580 | Photochem. Photobiol. Sci., 2018, **17**, 1573–1598

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highly toxic compounds, and for which the biological processes might not be pertinent.[134]

3.2.1. Advanced oxidation processes (AOPs). Advanced oxidation processes (AOPs) involve specific chemical reactions that generate highly reactive chemical oxidizing species which are capable of oxidizing and mineralizing almost any organic molecule, even the most recalcitrant molecules, yielding CO_2 and inorganic ions.[134–137] These processes can involve or not the use of light.

The degradation by photochemical reactions of organic pollutants present in the water media can be achieved, but the degradation degree is dependent on their chemical structure.[25] There is evidence that the presence of certain chemical structures like double bonds (–C=C–) in alkenes and polyenes; phenols (Ar–OH); carbonyl groups (–C=O); aryl chlorides (Ar–Cl); nitroaromatic moieties (–$C_6H_4NO_2$); weak C–H bond and sulfides (–S–) may increase the probability of photochemical reactions to occur, including by direct interaction (absorption) of light (even sunlight), suggesting that the compounds with these chemical functionalities are more prone to photochemical reactions.[138]

The efficiency of the oxidation processes tends to be maximized when the use of an appropriate catalyst is considered. Although there are different oxidative systems,[136] the production of powerful oxidizing agents, such as the hydroxyl radical (HO$^•$), is the main objective of most AOPs, since these oxidizing agents react rapidly. Also, their non-selective attack on organic compounds is a useful attribute for wastewater treatment and a potential solution of pollution problems. The oxidizing agents can act at various levels such as hydrogen abstraction from aliphatic carbon, electron transfer or addition to double bonds and aromatic rings.[134,137] This type of reaction generates organic radicals as intermediates, which then undergo additional reactions, resulting in the final products.[139] The hydroxyl radicals can react with a vast range of organic compounds at rates often near the diffusion-controlled limit.[134,140,141]

The versatility of AOPs is likewise enhanced by the fact that different ways to produce hydroxyl radicals exist, facilitating the compliance with specific treatment requirements according to the effluent's characteristics.[136,137]

The AOPs as a photochemical process can occur *via* homogeneous (when both the catalysts and reactants are in the same phase) and heterogeneous systems (when the reactants and catalysts are in different phases).[134] In general, both systems can be used under visible-light irradiation with or without the presence of UV radiation.[134] The region of the electromagnetic spectrum used for the photochemical process is dependent on the catalyst absorption features.[137]

The methods based on ultraviolet light (UV), and H_2O_2 or O_3 combinations use the photolysis of these molecules to produce hydroxyl radicals.[136,137] Additionally, other methods like heterogeneous photocatalysis and homogeneous photo-Fenton reaction are based on the use of a wide-band-gap semiconductor and the addition of H_2O_2 to dissolved iron salts, respectively, and irradiation with UV-Vis light. Both processes

are of singular interest since sunlight can be used, which brings a set of economic benefits.

For instance, the homogeneous processes based on the reaction between Fe^{2+} and H_2O_2 – known as the thermal-Fenton reaction (AOPs) – tend to become more effective for the mineralization of organic compounds when it is combined with UV-light (Fe^{2+}/Fe^{3+}: H_2O_2; UV-light, 250–400 nm); being this process designated as photo-Fenton reaction, one of the most efficient AOPs already described (eqn (1) and (2)).[134,140]
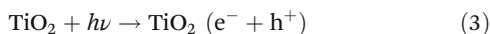
$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^• \qquad (1)$$

$$Fe^{3+} + H_2O + h\nu \rightarrow OH^• + Fe^{2+} + H^+ \qquad (2)$$
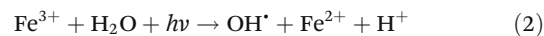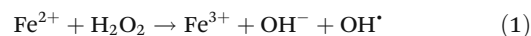
This particularly happens due to the photochemical reduction of Fe^{3+} back to the Fe^{2+} state.[134] Studies concerning the photochemical behaviour of $Fe(OH)^{2+}$, at a pH value of 3 (the optimal pH range for the occurrence of the photo-Fenton reaction), have shown that $Fe(OH)^{2+}$ undergoes an efficient photoreaction upon excitation with UV-light, leading to the production not only of Fe^{2+}, the critical catalytic species, but also of an additional chemical oxidizing species, HO$^•$, responsible for organic material degradation.[134,140] The efficiency of the photo-Fenton processes might be further enhanced if Fe^{3+} could be complexed with appropriate organic acids. The formed Fe^{3+} complexes can absorb in a larger range of wavelengths and make the photo-Fenton-based reactions more effective.[134] The H_2O_2 that might not be consumed during the reaction will decompose into water and molecular oxygen, freely converting this reagent into a "clean" reagent itself.[134,140]

In fact, the oxidation processes based on the Fenton reaction are chemically very effective for organic pollutant removal.[134] However, the Fenton reaction tends to slow down after the initial conversion of Fe^{2+} into Fe^{3+}, and the addition of quite large amounts of Fe^{2+} may be necessary to degrade the chemical pollutant of interest.[139,142] Moreover, another limiting feature of the Fenton reaction based processes is the generation of recalcitrant intermediates, which can constrain complete mineralization.[134] Additionally, the necessity of effluent acidification, due to the optimum low pH range (pH 3) for the occurrence of the photo-Fenton reaction, and the inevitable need for catalyst removal at the end of the reaction are additional limitations of these AOPs. However, even with the existence of these latent limitations, conventional Fenton reaction processes have been extensively used for effluent treatment.[134,142,143]

Meanwhile, heterogeneous AOPs that use some solid photocatalysts such as titanium dioxide (TiO_2), cadmium sulphide (CdS), zinc oxide (ZnO) and tungsten trioxide (WO_3), among others, stand out once the UV irradiation of these catalysts results in the production of HO$^•$, facilitating the oxidation and mineralization process of organic species (eqn (3)–(7)).[134,140] This occurs once an electron in the valence band of these oxides, upon light excitation, is transit into their conduction band, and once in the conduction band, the excited electron (e$^-$) will tend to react with molecular oxygen (O_2) present in

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Photochem. Photobiol. Sci., 2018, **17**, 1573–1598 | **1581**

the medium (eqn 3).[25,134] In fact, the hole (h^+) in the valence band can, then, react either with an adsorbed pollutant by electron transfer reactions or lead to the oxidation of the water molecules, producing a $HO^•$ radical bound to the surface of the solid catalyst (eqn (4) and (5)).[25,134,144]

$$TiO_2 + h\nu \rightarrow TiO_2 \ (e^- + h^+) \qquad (3)$$

$$h^+ + H_2O \rightarrow H^+ + OH^• \qquad (4)$$

$$h^+ + OH^- \rightarrow OH^• \qquad (5)$$

$$Pollutants + OH^• \rightarrow Degradation \ products \qquad (6)$$

$$e^- + O_2 \rightarrow O_2^- \qquad (7)$$

Among the insoluble semiconductors, TiO_2 has been the most used oxide for photocatalytic water treatment applications, due to some aspects such as the toxicity, the photocorrosion level of resistance, its availability and cost and its catalytic efficiency.[145] However, TiO_2 photocatalysis is shown to be a less efficient process in practical applications; the depth of penetration of the incident radiation into the TiO_2 suspensions is poor, due to the light scattering by the opaque particles of the catalyst.[134] Even with some limitations, the AOPs most extensively used in solar water decontamination processes are the TiO_2 and the photo-Fenton processes.[146]

At this point, although there is high potential of the AOP methods to be applied in wastewater decontamination, the recognized limitations of the process prompt the development of new highly effective or more advanced AOP technologies in the oxidation/mineralization of the chemical pollutants.

Table 3 lists the most representative studies of photodegradation carried out in the last 10 years which are focused on the potential application in photodegradation and eventually removal of emerging pollutants from wastewater effluents, before their release to the natural aquatic environments. In this review, we concentrate our efforts on the most frequently detected human and veterinary pharmaceuticals in water and wastewater and the pharmaceutical substances that are considered as priority in the field of water policy (according to the European Parliament and the Council) (Table 3).

Some studies of chemical decontamination have shown that oxidative processes in the presence of TiO_2 in the anatase and rutile phase mixed in different ratios could result in the effective removal of **ciprofloxacin** and **norfloxacin**, two synthetic antibiotics of the fluoroquinolone family frequently found in wastewater and even in surface and ground waters (Fig. 2).[147–149] Briefly, An *et al.* reported, with reference to pulsed radiolysis experiments under UV-light, that free radicals, such as $HO^•$, can react quickly with **ciprofloxacin**, with high reaction rate constants.[147] Additionally, these authors and Gad-Allah and co-workers confirmed that under simulated sunlight, **ciprofloxacin** can be rapidly degraded.[147,148] However, a drawback related with the usage of this photocatalyst resides in the fact that the rate constants are highly dependent on the pH of the medium and even the titanium

concentration might affect the reaction rate; at higher concentrations, limitation in light transmittance occurs.[147,148]

In a similar study, An *et al.* proposed some mechanistic considerations for heterogeneous photocatalysis of other fluoroquinolone pharmaceutical compounds, including **norfloxacin** in the presence of the commercially available TiO_2 powder Degussa P25 (now it is commercialized as Aeroxide P25), which contain the anatase and rutile phase in a ratio of about 3 : 1.[149] Once again, they concluded that AOPs involving the production of $HO^•$ radicals seem to be an efficient approach for the degradation of fluoroquinolone compounds in aqueous solutions, since the main attack pattern proposed by the radicals on these compounds leads to the high degradation/elimination of the piperazinylic ring ($-C_4H_9N_2$), along with the substitution of F atoms with hydroxyl radicals and the addition of hydroxyl radicals to the quinolone ring.[147,149,150] The authors even state that most of the intermediates produced can be mineralized into CO_2, water and mineral species.[149]

Zhang *et al.* tested bismuth oxybromide (BiOBr) as the photocatalyst, and they noticed that in the presence of BiOBr and visible light irradiation (400 W), the antibiotic **ciprofloxacin** was completely degraded after 140 min of light exposure.[151]

The photodegradation of **ciprofloxacin** and two other antibiotics **oxytetracycline** and **doxycycline** under UV radiation in the presence of H_2O_2 has been tested; this combination has been proposed as an effective method of treatment for organic contaminants in drinking water and reclaimed water (Fig. 2).[152] Although the authors achieved the detoxification of the tested antibiotics, they observed that the availability of the $HO^•$ radical is affected by diverse factors, such as the formation and scavenging rates of the radical and the occurrence of water UV absorbance (low water penetration of UV-light).[152]

More recently, Sayed *et al.* performed a study in which they immobilized TiO_2 in a faceted metallic titanium film (TiO_2/Ti).[153] In this study, it was observed that the UV-photocatalytic performance of the TiO_2/Ti film in the degradation of **norfloxacin** is, again, highly dependent on the pH of the media, being more efficient at lower pH values, and the water matrix also had its influence on the photocatalytic performance. In fact, the highest photocatalytic degradation of **norfloxacin** was achieved in Milli-Q water and the lowest in synthetic wastewater (wastewater prepared artificially).[153] Additionally, the presence of metallic cations in the medium, such as Ca^{2+}, Mg^{2+}, Cu^{2+} and Fe^{3+}, seem to inhibit the photocatalytic degradation.[153] Nevertheless, the **norfloxacin** photo-products proved to be less toxic for the Gram-negative bacteria *Escherichia coli* than **norfloxacin**, evidencing that photocatalytic approaches can be a safer and less toxic way to degrade some chemical compounds such as pharmaceuticals.[153]

Evidence that the intermediates and photo-products formed during the photocatalytic process appear to be less ecotoxic is even supported by Hapeshi *et al.* during their studies concerning **ofloxacin** degradation in the presence of Degussa P25 TiO_2 and UV(A) light (Fig. 2). The toxicity of the photo-products was assessed using the freshwater species

1582 | *Photochem. Photobiol. Sci.*, 2018, **17**, 1573–1598

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Table 3 Experimental settings of some AOPs applied to human and veterinary pharmaceuticals and personal care products detected in water and wastewater and pharmaceuticals which are considered as a priority in the field of water policy (according the European Parliament and the Council, Directive 2000/60/EC)

AOP removal technique	Suspension medium	Irradiation conditions	Chemical pollutant	Ref
Photo-Fenton	Simulated groundwater, simulated effluent wastewater, treated wastewater	Sunlight	Acetaminophen, antipyrine, atrazine, caffeine, carbamazepine, diclofenac, flumequine, hydroxybiphenyl, ibuprofen, isoproturon, ketorolac, ofloxacin, progesterone, sulfamethoxazole, triclosan	158
	Treated wastewater	UV light, simulated sunlight	17α-Ethynylestradiol	165
	Distilled water, seawater	Simulated sunlight	Sulfamethoxazole	161
TiO_2	Distilled water	UV light	Ciprofloxacin	146
	ND	Simulated sunlight	Ciprofloxacin	147
	Pure water, groundwater, treated wastewater	UV(A) light	Ofloxacin, atenolol	153
	Distilled water	Simulated sunlight	Acetaminophen, antipyrine, atrazine, caffeine, carbamazepine, diclofenac, flumequine, hydroxybiphenyl, ibuprofen, isoproturon, ketorolac, ofloxacin, progesterone, sulfamethoxazole, triclosan	154
	Treated wastewater	Sunlight	Ofloxacin, enrofloxacin, acetaminophen, diclofenac, caffeine, thiabendazole, carbamazepine, acetamiprid, trimethoprim	145
	Deionized water	Sunlight, UV light	Ofloxacin	159
	Ultrapure water, deionized water, Milli-Q water, treated wastewater	UV light, visible light	Estrone, 17β-estradiol, estriol, 17α-ethinylestradiol	164
	Demineralized water, simulated seawater	Simulated sunlight, sunlight	Trimethoprim	162
	Deionised water, groundwater, treated wastewater	UV(A) light	Diclofenac	160
	Milli-Q water	UV-Vis light, UV light	Carbamazepine	163
	Ultrapure water, treated wastewater	UV(A) light	Sulfamethoxazole	156
	Ultrapure water, groundwater, treated wastewater	UV(A) light	Sulfamethoxazole	157
	Milli-Q water, treated wastewater	Sunlight	Clofibric acid	166
	Milli-Q water	UV light	Norfloxacin, levofloxacin, lomefloxacin	148
	Milli-Q water, tap water, river water, synthetic wastewater	UV light	Norfloxacin	152
	Water	Visible light	Norfloxacin	149
	Deionized water, tap water	UV(C) light	Aspirin, paracetamol	167
	Ultrapure water	UV light, sunlight	Naproxen	168
	River water, drinking water	UV-Vis light	Naproxen, diclofenac	169
BiOBr	Deionized water	Artificial visible light	Ciprofloxacin	150
H_2O_2/UV	Ultrapure water, surface water, treated drinking water, treated wastewater	UV light	Ciprofloxacin, oxytetracycline, doxycycline	151
ZnO	Milli-Q water	UV-Vis light, UV light	Carbamazepine	163
	Milli-Q water, treated wastewater	Sunlight	Clofibric acid	166

ND, no data.

Daphnia magna and it was observed that the resulting products of AOP treatment appear to be less ecotoxic to this species.[154]

The photodegradation of the antibiotic **ofloxacin**, along with 14 other emerging contaminants, including the antibiotic **sulfamethoxazole**, the anticonvulsant **carbamazepine**, and the anti-inflammatories **diclofenac** and **ibuprofen**, was also studied using immobilized TiO_2 on glass spheres (Fig. 3). The immobilization on borosilicate glass spheres was performed using the sol–gel dip-coating technique with an acid solution of titanium isopropoxide ($Ti(OPr^i)_4$) and polyethylene glycol

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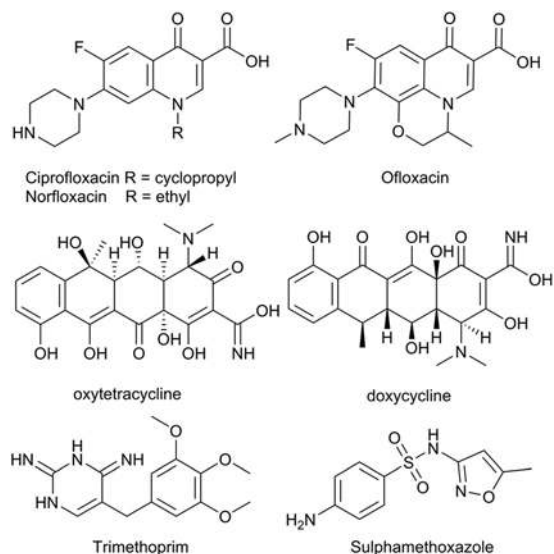*Photochem. Photobiol. Sci.*, 2018, **17**, 1573–1598 | **1583**

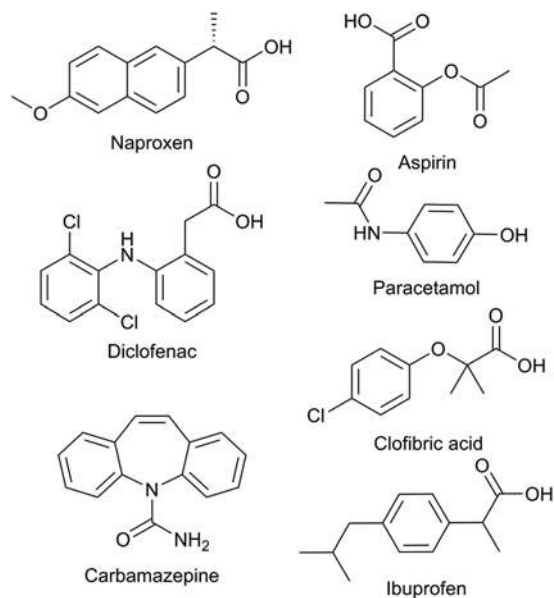Fig. 2 Antibiotics detected in water and wastewater.

Fig. 3 Active principles detected in water and wastewater.

followed by a final calcination step and the photocatalytic studies were performed in a solar pilot compound parabolic collector (CPC) reactor.[155] In this study, Miranda-García et al. achieved a removal percentage between 70% (for **sulfamethoxazole**) and 100% for most of the tested compounds.[155] In addition, the photoactivity of the immobilized photocatalyst did not decrease significantly after 5 cycles of treatment of 100 min each, contradicting one of the usual limitations of the immobilized photocatalysts that suggests that the stability of the film during prolonged use leads to photoactivity loss.[155]

A similar approach using UV-A and immobilized TiO_2 in glass was developed by Mantzavinos and co-workers to degrade **sulfamethoxazole** but this is now performed in a flat plate photo-reactor (PPL).[156,157] It was shown that the system could provide reduced effluent toxicity (evaluated in ecotoxicity tests with D. magna) resulting from the photodegradation of **sulfamethoxazole** itself and also its transformation by-products.[156]

Solar photocatalysis using Degussa P25 TiO_2 was also suggested as an efficient tertiary treatment step by Bernabeu et al. in 2011[146] and Bhatia et al. in 2016,[159] among others.[158] Bernabeu et al. evaluated the photodegradation efficiency of **trimethoprim**, **ofloxacin**, **diclofenac**, and **carbamazepine** by comparing with others, reaching, in most cases, values below their detection limit after a period of 180 min of irradiation.[145] In addition, significant effluent disinfection was observed, reaching more than 99% inactivation of faecal coliforms in 60 min of treatment and a decrease of dissolved organic carbon, during the treatment (~20 mg L^{-1}).[145] In turn, Bhatia et al., using TiO_2 nanoparticles co-doped with bismuth (Bi) and nickel (Ni), concluded that these co-doped TiO_2 nanoparticles showed higher photocatalytic activity for **ofloxacin** degradation under sunlight irradiation when compared with TiO_2 powder (Degussa P25) alone, reaching an **ofloxacin** degradation efficiency of 86% at pH 3 and after 360 min (6 h) of sunlight irradiation.[159]

The photodegradation of these emerging pollutants (**carbamazepine**, **diclofenac**, **ibuprofen**, **ofloxacin** and **sulfamethoxazole**) were also attempted in simulated and real effluents of a municipal wastewater treatment plant using photo-Fenton reaction in a CPC reactor.[160] Klamerth et al. showed that although the presence of hydroxyl radical scavengers (such as carbonate and hydrogenocarbonate ions), might highly influence the performance efficiency of the method, as well as the water matrix, it seems to be relatively independent of the pH of the medium used.[160] Thus, the emerging pollutants tested could be successfully degraded to negligible concentrations.[160] The photocatalytic degradation of **sulfamethoxazole** was also demonstrated to be highly dependent on the concentration of the added H_2O_2.[161]

On the other hand, Sirtori et al., in a study evaluating the effect of the composition of the water matrix, achieved the complete elimination of the **trimethoprim** antibiotic during Degussa P25 TiO_2 photocatalysis in two types of water matrices – demineralized water and simulated seawater, at a similar rate.[162]

Martínez et al., in a study comparing the efficiency of the photocatalytic degradation of **carbamazepine** by TiO_2 (Degussa P25) and ZnO, concluded that under the irradiation conditions used (near UV-Vis and UV), the photocatalyst Degussa P25 was more efficient than ZnO. However, certain factors such as the type and load of the photocatalyst to the system, dissolved O_2 concentration and the addition of compounds that can work as co-oxidants, such as H_2O_2, can highly affect the photodegradation process performance.[163] The authors attributed the photocatalytic efficiency difference between the two catalysts to the difference in the energy gap between their valence and conduction bands, and the different overlaps among light absorption of ZnO and TiO_2.[163]
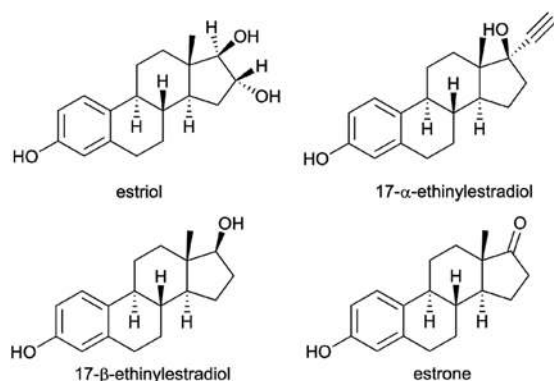
Fig. 4 Hormones detected in water and the wastewaters assessed.

The efficiency of AOPs as a possible water decontamination approach for estrogens is also meriting special attention due to their serious threat to living organisms as a result of their extensive use and consequent release to the environment.[164] In this context, Frontistis et al. developed a study which tested the efficiency of H_2O_2 under UV radiation of the photo-Fenton approach under simulated solar radiation to degrade **17-α-ethinylestradiol** (Fig. 4) in a secondary-treated wastewater matrix.[165] The UV/H_2O_2 system proved to be more efficient in the estrogen hormone degradation, although UV radiation alone could be partially responsible for its removal.[165]

Later, Sornalingam et al. extended the photodegradation studies to **17-β-estradiol**, **estriol** and **estrone** (Fig. 4) and concluded that the efficiency of the photodegradation is higher under UV radiation when compared to visible light. The authors commented that although the higher complexity of the medium matrix may decrease the removal rate of the estrogenic hormones, it can be heightened by the presence of certain constituents in the water that may behave as photosensitizers.[164] They even added that, among the most commonly tested AOPs, TiO_2 tends to remain as one of the most effective catalysts for the removal of the mentioned synthetic hormones.[164]

A study performed by Li et al. confirmed the influence of the water matrix complexity.[166] Their results showed that the degradation rates of **clofibric acid** in Milli-Q water were higher than those obtained in an effluent as the reaction medium.[166] Additionally, the presence of both the anions nitrate (NO_3^-) and hydrogenocarbonate (HCO_3^-) affected unfavorably the **clofibric acid** degradation, as previously mentioned, once they can act as hydroxyl radical scavengers.[166]

In contrast to the chlorination process that is unable to degrade **clofibric acid**, both UV photolysis alone and UV/chlorine processes could degrade **clofibric acid**, as it was shown in a recent study carried out by Tang et al..[170] The authors emphasized the advantages of the use of light, including solar light, as an enhancer of the oxidative degradation of chemicals and of their removal from aquatic environments.
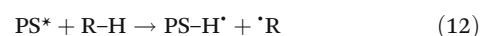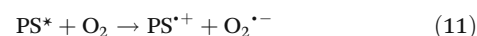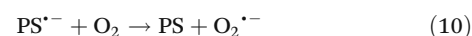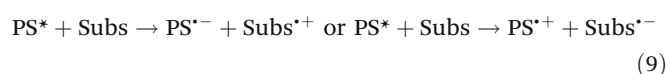
Two of the most commonly used analgesic, anti-inflammatory and fever reducer drugs **paracetamol** and **aspirin** (Fig. 3)

and their metabolites are frequently found in aquatic environments.[167] As a consequence of this troubling situation, Bianchi et al. developed a study in which they tested the degradation efficiency of both drugs, using an innovative approach: grés porcelain tiles covered with the micro-sized photoactive pure anatase TiO_2 phase by digital printing methods.[167] As a result, they obtained the full photo-conversion of both drugs into harmless inorganic species.[167]
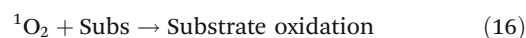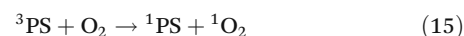
The TiO_2 photocatalytic degradation of **naproxen**, as another anti-inflammatory pharmaceutical often found in aquatic environments, was also studied.[168,169] The TiO_2 photocatalytic degradation efficiency was compared with the direct photolysis degradation rate, and it was found that the photocatalytic process is more efficient when compared with direct photolysis.[168] The tested TiO_2-UV process led to higher **naproxen** removal and to an additional reduction of chemical oxygen demand in solution – a parameter used for water/wastewater quality, as a measurement of the required oxygen to oxidize either soluble or particulate organic matter.[168] They even showed a decrease of acute toxicity, assessed by the exposure of earthworm (Eisenia andrei) as a bioindicator to the toxicity of **naproxen**-treated solutions.[168]

3.2.1.1. Photodynamic approach. The photodynamic approach consists of the use of a photosensitizer molecule (PS) that absorbs light and by transfer of the absorbed energy (type II mechanism) or electrons (type I mechanism) to molecular oxygen forms highly reactive oxygen species (ROS) that can act on different targets (Subs), namely chemical pollutant compounds (eqn (8)–(16)). This approach is being largely used in cancer treatment and in the photoinactivation of microorganisms,[171–175] but its potential to reduce chemical contaminants in wastewaters is also being considered by the scientific community.

Type I mechanism

$$PS + h\nu \rightarrow PS* \tag{8}$$

$$PS* + Subs \rightarrow PS^{\bullet-} + Subs^{\bullet+} \text{ or } PS* + Subs \rightarrow PS^{\bullet+} + Subs^{\bullet-} \tag{9}$$

$$PS^{\bullet-} + O_2 \rightarrow PS + O_2^{\bullet-} \tag{10}$$

$$PS* + O_2 \rightarrow PS^{\bullet+} + O_2^{\bullet-} \tag{11}$$

$$PS* + R-H \rightarrow PS-H^{\bullet} + {}^{\bullet}R \tag{12}$$

$${}^{\bullet}R + O_2 \rightarrow {}^{\bullet}OOR \tag{13}$$

$${}^{\bullet}OOR + R-H \rightarrow RO_2H + R^{\bullet} \tag{14}$$

Type II mechanism

$${}^3PS + O_2 \rightarrow {}^1PS + {}^1O_2 \tag{15}$$

$${}^1O_2 + Subs \rightarrow \text{Substrate oxidation} \tag{16}$$

From the wide range of dyes that can be used as sensitizers, special attention is being given to porphyrins and their analogues like phthalocyanines due to their adequate features to generate reactive oxygen species (ROS) like singlet oxygen

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Photochem. Photobiol. Sci., 2018, **17**, 1573–1598 | **1585**

($^1O_2$). These compounds have extended conjugation and have the ability to absorb light in the UV-Vis range.[176,177]

In porphyrins the most intense absorption band, known as the Soret band, is located in the blue region of the visible spectrum, and it is accompanied in general by four less intense bands (Q bands) located in the green-red region of the electromagnetic spectrum.[176] Phthalocyanines tend to have a strong absorption band in the red region (*ca.* 700 nm, Q-band) and an intense Soret band in the UV region (*ca.* 350 nm). In general, both classes of compounds tend to present long-lived triplet states with high quantum yields and consequently high efficacy to generate ROS like singlet oxygen.[176,177]

The so-far mentioned porphyrinoid features can be improved by a variety of factors like introduction of new functionalities on the macrocycle periphery, coordination with metal ions and attachment of ligands to the axial positions of the metallic center. All these can fine-tune the properties of these molecules to strong light wavelength absorption, longer triplet lifetimes and high ability to generate ROS.[176]

In Table 4 is summarized the main studies conducted to photodegrade water chemical pollutants based on the photodynamic action of tetrapyrrolic derivatives and analogues.

The efficacy of aluminium(III)phthalocyanine tetrasulfonic acid and of 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin to oxidize parabens at different concentrations was also analyzed and compared.[177] It was noticed by the authors that the increase in the photosensitizer concentrations leads to a higher initial rate of paraben concentration reduction.[177] However, they also noticed that after exceeding the photosensitizer concentration responsible for the highest oxidation rate, the paraben concentration decay diminished probably due to some photosensitizer aggregation responsible for the decrease of singlet oxygen formation.[177] The almost complete inhibition of paraben photodegradation in the presence of sodium azide allowed one to conclude that the dominating role of singlet oxygen in this oxidative process and the photooxidation efficiency was dependent on the photosensitizer photostability.[177]

In a recent study, based on the promising results of the photodynamic inactivation of microorganisms obtained by using cationic 5,10,15,20-tetrakis(1-methylpyridinium-4-yl)porphyrin tetra-iodide (**Tetra-Py$^+$-Me**), Bartolomeu *et al.* investigated the applicability of the method to photodegrade chemical pollutants, namely phenol, used generally at higher concentrations than other chemicals found in urban wastewater treatment plants.[104] The cationic porphyrin **Tetra-Py$^+$-Me** was shown to be also effective against phenol pollutants.[104] In this study, the authors tested the efficiency of the method under different light irradiation conditions – visible light (wavelength range between 380 and 700 nm, with an irradiance of 40 W m^{-2}) and natural sunlight (with an irradiance light average of ~790 W m^{-2}) and showed that **phenol** photodegradation was faster and more efficient under natural sunlight.[104]

Parallelly, the authors investigated the photosensitizer photostability – *autobleaching* – under sunlight irradiation. They observed a slight decrease in the photosensitizer absorbance band at ~425 nm, the wavelength corresponding to the Soret band.[104] However, the authors tend to be positive towards these results. Since the pollutant photodegradation happened faster than the photosensitizer bleaching, *autobleaching* could have a positive impact once, due to its degradation, the photosensitizer does not remain active in the aqueous suspension.[104] Actually, the bleaching of the photosensitizer from the carrier in order to produce an inactive material is highly preferential as opposed to a permanent activity in the environment, as a consequence of the photo-treated wastewater release. In the context of reducing wastewater contaminants, the immobilization of photosensitizers on various supports has shown to be a looked-for tactic, once it allows the easy recovery of the photosensitizer from the reaction mixture and its reuse.[178] In general, the immobilization of photocatalysts like tetrapyrrolic photosensitizers has been associated with some $^1O_2$ quantum yield decrease, which may occur due to the limitations of oxygen diffusion into and from the support material, but the referred advantages surmount this drawback.[178]

Gmurek *et al.* studied the heterogeneous photodegradation of butyl- and benzyl-paraben – a class of preservative compounds frequently detected in wastewater, rivers, *etc.* and listed among the compounds suspected of endocrine disrupting activity by the US National Institute of Environmental Health Science (NIEHS) and World Wildlife Fund (WWF)[177] – using 5,10,15,20-tetraphenylporphyrin (**TPP**) immobilized in polyurethane.[178] The porphyrin was immobilized in a polyurethane nanofiber material at a concentration of 1 wt% and the photodegradation experiments were performed using a xenon lamp as a simulator of sunlight irradiation.[178] Concerned with the hypothesis that once immobilized the absorption features of the immobilized TPP could suffer a sharp decrease, they tested it and showed that the immobilized **TPP** efficiently absorbed the light emitted by a xenon lamp, achieving a 50% decrease of the contaminants in the testing solution, after 2 h of irradiation.[178] To investigate the possibility whether the immobilized **TPP** could be reused, the authors performed a series of successive experiments using the same **TPP**-nanofiber material and concluded that although each subsequent use of the **TPP**-nanofiber material resulted in a decrease of photodegradation (about twice lower after the four-fold **TPP**-nanofiber material reuse), the supported **TPP**-nanofiber material can be used several times.[177] Additionally, they showed that applying a mixture of two different photosensitizers (TPP 1 wt% and zinc(II) phthalocyanine 0.3 wt%) higher degrees of contaminant reduction were achieved (70% reduction) after the first exposure.[178] The decrease in the efficiency of the immobilized photosensitizers in the following reuses was justified as a result of their *autobleaching* since after 8 h of irradiation, a luminescence decrease was observed, leading to a reduction of their efficiency to generate $^1O_2$.[178]

Although the reused **TPP**-nanofiber material showed structural changes and its mechanical resistance to damage decreased,[178] the toxicity test results remain similar to those previously mentioned with the use of TiO_2 among others. In

1586 | *Photochem. Photobiol. Sci.*, 2018, **17**, 1573–1598

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Table 4 Main studies conducted to photodegrade chemical pollutants of water based on the photodynamic action of tetrapyrrolic derivatives and analogues
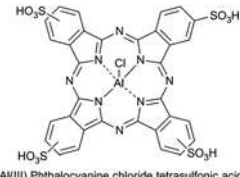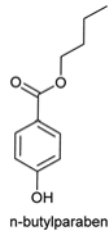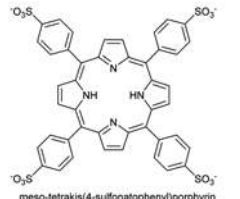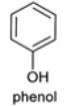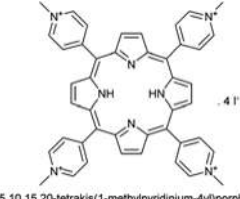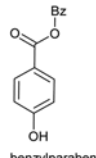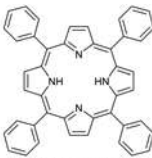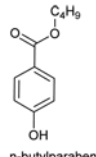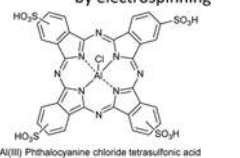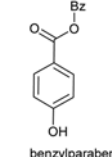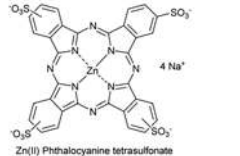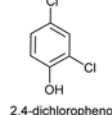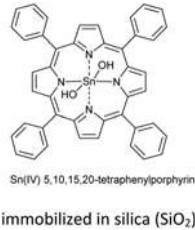
Photodynamic removal approach		Chemical pollutant	Suspension medium	Irradiation conditions	Ref
Tetrapyrrolic photosensitizers	Al(III) Phthalocyanine chloride tetrasulfonic acid	n-butylparaben	Distilled water	Simulated sunlight	177
	meso-tetrakis(4-sulfonatophenyl)porphyrin				
	5,10,15,20-tetrakis(1-methylpyridinium-4yl)porphyrin	phenol	Distilled water	Simulated and natural sunlight	104
Tetrapyrrolic photosensitizers immobilized in supports	5,10,15,20-tetraphenylporphyrin Zn(II) Phthalocyanine immobilized in polyurethane nanofiber by electrospinning	benzylparaben n-butylparaben	Distilled water	Simulated sunlight	178 179
	Al(III) Phthalocyanine chloride tetrasulfonic acid Zn(II) Phthalocyanine tetrasulfonate immobilized in chitosan	benzylparaben 2,4-dichlorophenol	Distilled water and buffered water solutions	Simulated and natural sunlight	180
	Zinc(II) tetracarboxyl- tetra(1,4-dithiin) porphyrazine immobilized activated Amberlite CG-400 anion exchange resin	Rhodamine B	Distilled water	Simulated sunlight	181

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Photochem. Photobiol. Sci., 2018, **17**, 1573–1598 | **1587**

Table 4 *(Contd.)*

Photodynamic removal approach	Chemical pollutant	Suspension medium	Irradiation conditions	Ref
Sn(IV) 5,10,15,20-tetraphenylporphyrin immobilized in silica (SiO₂)	Caffeine Acetaminophen Amoxicillin Trimethoprim Atorvastatin Tolmetin Losartan Propranolol Cimetidine Ranitidine	Wastewater treated effluent	Artificial visible light	182

fact, the toxicity level of the pollutant compounds decreased significantly after the photosensitized process, with the detection of 4-hydroxybenzoic acid and monohydroxy parabens as the main photoproducts formed as the result of photodegradation of parabens *via* singlet oxygen. The results indicate that the reduction of paraben concentration is an actual detoxification of the treated solution.[178]

In another study, Gmurek *et al.*, using singlet oxygen and quenchers of hydroxyl radicals, proved that singlet oxygen plays the main role in paraben decay in the presence of the PS–polyurethane nanofiber material.[179] However, the authors also point to the possibility that the quenching of the excited photosensitizer (at the triplet state) and singlet oxygen may have a negative impact in substrate oxidation. This de-activation can occur, owing to physical quenching by the adsorbed substrate, solvent or the molecular oxygen located on the nanofiber material surface or even by the support itself.[179]

A more recent study evaluated the potential of two highly stable photosensitizers (Zn(II) phthalocyanine tetrasulfonate tetrasodium and Al(III) phthalocyanine chloride tetrasulfonic acid) immobilized in chitosan for the photodegradation of benzylparaben and 2,4-dichlorophenol selected as pollutant models.[180] The authors evaluated the influence of pH, oxygen and immobilized photosensitizer concentration, multiple reuses of the photoactive chitosan beans and also the irradiation intensity as a new issue for this investigation.[180] In this study, the authors assessed the real potential of natural sunlight as a light source for the photosensitizer stimulus. They proved once more that from the photosensitizing mechanism point of view, the presence of molecular oxygen in the solution is vital for the ROS production, mainly singlet oxygen.[180] The study showed that in solutions aerated with air the reduction of 50% for paraben and phenol occurred respectively after 5 h and 2 h of irradiation; in solutions aerated with pure oxygen the reduction of 70% for paraben (5 h of irradiation) and 90% for phenol (3 h of irradiation) was attained.[180] However, it was also shown that above a certain oxygen concentration, some kind of oxygen saturation occurs, leading to a point in which further increase in the oxygen content seemed to have no influence on the reaction rate/efficiency.[180]

Once irradiance is a critical parameter to achieve ROS generation and consequently the photodegradation of the chemical pollutants, it was observed that the decay of the pollutant concentrations in solution is directly correlated with the light power (150 and 780 W) used and it is faster when the photoreaction occurs under natural sunlight.[180]

To investigate the reusability of phthalocyanines immobilized in chitosan, several successive cycles of photodegradation were performed once more. The photoactive chitosan materials proved to be stable after several cycles of irradiation during the photodegradation of parabens and phenol derivatives, highlighting the potential that some support matrixes may not negatively interfere with the photosensitizer photodynamic action and stability.[180] Moreover, the ecotoxicity of reaction mixtures determined by the toxicity test based on the use of *Vibrio fischeri*, a marine luminescent bacterium, which as result of its normal metabolic process emits light, demonstrated a larger ecotoxicity decay in the cases when natural sunlight was used, when compared to simulated sunlight.[180] Thus, the reuse of chitosan with immobilized phthalocyanines is possible and sunlight can be applied not only to lower the treatment costs, but also to decrease the ecotoxicity of the chemical pollutants in a faster way.

In fact, the need for inert and robust supports able to face the photodegradation conditions used in environmental applications mobilized other research groups to investigate the reuse of immobilized photosensitizers in different matrixes (*e.g.* chitosan and inserted into the interlamellar space of CTMA-modified bentonite).[183,184] The obtained results are highly dependent on the support, the photosensitizer, the pollutant under degradation[183,184] and even the reaction medium characteristics. In one of the studies, the researchers stated that the combination of sorption and photosensitization was an efficient way of phenol removal from aqueous solutions.[184] However, after four successive irradiation cycles, both sorption and photodegradation rate were diminished – a phenomenon that was attributed to the intermediates formed that could be adsorbed on the photoactivated material surface.[184] Such a phenomenon was also observed when porphyrins and phthalocyanines were immobilized into silica and polyurethane nanofibers (as presented throughout the text).

Zhang *et al.*, in 2013, demonstrated that zinc(II) tetracarboxyl-tetra(1,4-dithiin)porphyrazine immobilized on the Amberlite CG-400 resin could be reused five times without noticing the loss of photoactivity during 12 h.[181]

1588 | *Photochem. Photobiol. Sci.*, 2018, **17**, 1573–1598

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Kim *et al.* evaluated the potential application of a tin porphyrin, *trans*-dihydroxo-(5,10,15,20-tetraphenylporphyrinate)tin(IV), immobilized in silica (SnP/silica) as $^1O_2$ generating systems for the photochemical degradation of a variety of pharmaceutical drugs (**naproxen**, **trimethoprim**, and **propranolol**, among others), using as the reaction medium real secondary wastewater effluents, which implied the presence of other dissolved organic matter.[182] They demonstrated that the activation of the immobilized photosensitizer by visible light is possible since SnP/silica is shown to have an intense absorption band at 420 nm (Soret band), and a few moderate to weak absorption bands at 519, 550 and 590 nm (Q bands).[182] Their work showed that no significant adsorption of the pharmaceutical compounds occurred on SnP/silica, in contrast to other previous studies. However, they proposed the occurrence of *self-sensitized* degradation (*e.g.* for propranolol) as a result of photochemical reactivity leading to ROS production.[182] The authors also suggested that $^1O_2$ was the primary oxidant in the photochemical oxidation with SnP/silica.[182]

The presence of specific chemical moieties that are susceptible to $^1O_2$ electrophilic attack in the structures of some pharmaceutical compounds seemed to result in faster photochemical decay.[182] In particular, in the case of the aromatic rings, the photosensitized degradation kinetics of pharmaceuticals such as **propranolol** and **naproxen** were significantly different, regardless of both drugs containing a naphthalene moiety.[182] However, the authors also pointed to the fact that some preferable singlet oxygenation compounds were not markedly degraded in irradiated aqueous suspensions possibly due to the presence of electron-withdrawing substituents.[182]

When comparing the OH$^•$ radical to the $^1O_2$ oxidation of the pollutants of interest, in the presence of background organic matter such as wastewater treatment effluents, the results are interesting. Once in the presence of complex water matrices, background organic substances are prone to be present, and so they can act as electron-withdrawing substances to the formed ROS. As a consequence, the oxidation of priority chemical pollutants can be kinetically retarded.[182]

It has been suggested that OH$^•$ radical-mediated oxidation, as a non-selective oxidant, leads to slower degradation of chemical contaminants in complex secondary wastewater effluent matrices, when compared to selective oxidants such as $^1O_2$. This fact is justified by considering that the efficacy of the oxidant is dependent on the competition between the target substrates and the dissolved background organic matter. So, selective oxidants are potentially more effective in real water matrices than photoactive compounds that mediate OH$^•$ radical production as TiO_2 and Fe^{3+} in photo-Fenton processes.[182]

4. Final remarks

The operation and management of wastewater treatment plant systems are very intricate activities. It is necessary to evaluate and deal with the chain of components that together structure the global system. Such evaluation can help ensure their proper functioning under expected levels of efficiency and highlight weaker links in the chain that could cause health and safety issues.[11] The greatest risk in relation to wastewater treatment plants is undoubtedly the difficulty in choosing the treatment type or the combination of different types of treatment to apply, since effluents do not always have the same origin.

In order to diminish the disease cargo, the subtraction of pathogens is regularly the primary objective of wastewater treatment systems. However, the disease spread problem cannot only be associated with the pathogen cargo on the effluents because of the wide content range of chemical pollutants that they may contain.

Since the end of the twentieth century, with the recognition of water as a key issue, even as a central factor for the Green Economy, water treatment has become a global concern. The cumulative sums of wastewater as a result of population growth, increasing economic activity and expanding agriculture, as well as the release of manure with no or inadequate treatment have a direct impact on ecosystems and the community services provided.[7,11,185,186]

Globally, and not only in the developing countries, the data and control on wastewater collection and treatment are, after all, scarce.[7,11,185,186] Consequently, emerging pollutants, which encompass a wide range of chemical compound categories, are rarely controlled and analyzed and so the impact of these compounds on human and environmental health is not completely understood. So, more research is needed to assess their real impact. Furthermore, these research conclusions might help in the strengthening of the legislation regarding the use and release of not only emerging pollutants, but also chemical pollutants in general.[11]

According to a research conducted in 2013 by Sato *et al.*, only a total of 181 countries worldwide have available information data on what concerns the volumes of wastewater generation, treatment, and use at the country level.[187] From these analyzed data, only 55 out of the 181 countries had reliable information.[187] This lack of information should bring emphasis to the following key challenge with data collection: the urgent need for generating data at the national level that are sufficiently detailed, consistent and comparable with other countries.[11] It is necessary to increase the knowledge on the pollutants that are present in the effluents and the percentage of them that are released into the environment even after passing through wastewater treatment plants. This information and the notion that the number and concentration of pollutants in the environment will tend to increase are expected to encourage further development of renewed and more effective technologies for water treatment, like solar-driven oxidative processes, photodynamic treatment, or solar-driven oxidative processes possibly combined with other complementary techniques.

Among the AOPs, heterogeneous photocatalysis has proven its efficiency to degrade recalcitrant organic compounds. After

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Photochem. Photobiol. Sci., 2018, **17**, 1573–1598 | **1589**

its development in the 1970s, significant attention has been given to it with a view to decompose and mineralize recalcitrant organic compounds.[188]

The great hope in this technology lies in its ability for water decontamination and, in addition, the killing of pathogenic microorganisms. However, despite the already existing vast current study on the efficacy of the photodynamic approach applied to the inactivation of microorganisms even with several tested catalysts, the study of its effectiveness in the degradation of chemical pollutants is still very scarce. In addition to this potential, there is the possibility of immobilization of the photocatalyst on solid matrices and thus to be easily removed, recovered, and reused,[174,189] making it an effective, less expensive and even environmentally friendly technology.[104]

Moreover, compared with the most used method to disinfect wastewater, chlorine, no residual effect is associated with the photodynamic approach, which, in contrast to that considered for the case of drinking water treatment, is a positive aspect since the receiving waters are not affected and neither are the organisms that grow in these waters.

Additionally, solar-driven processes can be considered as a green technology once they can employ sunlight as the irradiation source, thus circumventing the use of very high energy consuming UV-lamps.

5. Conclusions

It was highlighted in this review that municipal wastewater may significantly vary due to the variety of effluents released by domestic, agricultural/livestock, hospital and industrial sources that could carry a complex combination of all types of contaminants in a variety of concentrations.

This leads to the need to develop and implement pollution control monitoring, and to know what exists and what needs to be degraded/transformed to less toxic or unharmful by-products. This will help in the more thoughtful implementation of treatment strategies and techniques of wide action to be carried out before water disposal.

Finally, for a possible industrial application it will be critical that photocatalytic processes can be advanced and established to a stage where the processes can be implemented as (1) cost-efficient when compared to other processes; (2) sustainable; (3) robust in a way that inescapable fluctuations to the wastewater stream should not bring distress to the operability and efficiency of the wastewater plant; (4) easy to implement in a way that the process can start without massive initial investment costs; (5) easy to operate and maintain; (6) not carrying risks for staff safety and health; (7) environmentally safe; and (8) beneficial to the industry since it shows its concern to the environmental health and sustainability policy.

After our analysis and with the data at hand, we think that photodynamic wastewater treatment may be worth drawing the attention from the scientific community and of political decision-makers. This approach has the potential to become,

soon, a very robust solution to overcome the increasing need for water and wastewater treatment. This type of treatment would be very useful to be used as tertiary treatment for hospital and industrial wastewaters, which although dangerous are mostly only secondarily treated, and only after their discharge in the municipal sewage system.

In conclusion, the most important attitude to possess regarding the problem of water scarcity will have to be the execution of measures to reduce water consumption. Even then, once water is used and contaminated with both microorganisms and chemical pollutants, the solution will be to use an approach to achieve efficient disinfection and chemical decontamination together and, preferably, at a lower cost.

We expect that the information compiled in this review can motivate the research community to put in more efforts in photodynamic wastewater treatment in order to gain progressive recognition.

Conflicts of interest

The authors declare no conflict of interest. The funding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of the data; in the writing of the manuscript; or in the decision to publish the results.

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