

## **Impact of water matrix on the removal of micropollutants by advanced oxidation technologies**

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### **Abstract**

Micropollutants (MPs) in the aquatic compartments originate from many sources and particularly from the effluents of urban wastewater treatment plants (UWWTPs). Advanced oxidation technologies (AOTs) usually applied after biological processes, have recently emerged as effective tertiary treatments for the removal of MPs, but the oxidation rates of the single compounds may be largely affected by the constituent species of the water matrix. These species include dissolved organic matter and inorganic species (e.g., carbonate, bicarbonate, nitrite, sulphate, chloride). This review analyses the impact of such substances on common AOTs including photolysis, UV/H<sub>2</sub>O<sub>2</sub>, Fenton, photocatalysis, and ozone-based processes. The degradation efficiency of single MPs by AOTs results from the combined impact of the water matrix constituents, which can have neutral, inhibiting or promoting effect, depending on the process and the mechanism by which these water components react. Organic species can be either inhibitors (by light attenuation; scavenging effects; or adsorption to catalyst) or promoters (by originating reactive oxygen species (ROS) which enhance indirect photolysis; or by regenerating the catalyst). Inorganic species can also be either inhibitors (by scavenging effects; formation of radicals less active than hydroxyl radicals; iron complexation; adsorption to catalyst or decrease

of its effective surface area) or promoters (e.g., nitrate ions by formation of ROS; iron ions as additional source of catalyst). The available data reviewed here is limited and the role and mechanisms of individual water components are still not completely understood. Further studies are needed to elucidate the wide spectrum of reactions occurring in complex wastewaters and to increase the adoption of AOTs in UWWTPs.

**Keywords:** Advanced oxidation processes; Chemical oxidation technologies; Contaminants of emerging concern; Matrix effect; Micropollutants; Wastewater constituent.

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## 1 **1. Introduction**

2 Micropollutants (MPs) are natural or anthropogenic substances occurring in the aquatic  
3 environment at low concentrations, usually between  $\text{ng L}^{-1}$  and  $\mu\text{g L}^{-1}$  levels. MPs comprise a  
4 vast array of substances, namely pesticides, industrial compounds, pharmaceuticals, personal care  
5 products, steroid hormones, drugs of abuse and others [1]. Many of them are considered  
6 contaminants of emerging concern (CECs), a term currently used in the framework of  
7 environmental sciences for: (i) compounds recently known (e.g., new synthetic substances); (ii)  
8 hazardous compounds recently identified as such despite the previous knowledge about their  
9 occurrence in the environment (e.g., estrogens); and (iii) previously unknown compounds present  
10 in the environment, which have only been detected due to advances in analytical methods and  
11 instrumentation [2].

12 The anthropogenic sources of MPs are numerous and include domestic, hospital and industrial  
13 wastewater, agriculture runoff, livestock and aquaculture [2]. The treated effluents released by  
14 urban wastewater treatment plants (UWWTPs) are consensually recognised as a significant origin  
15 of MPs, since UWWTPs using conventional physicochemical and biological treatments are not  
16 designed to fully eliminate organic compounds occurring at trace concentrations [1-3]. MPs in  
17 domestic and hospital wastewater reach UWWTPs after metabolism and excretion as parent  
18 compounds and/or metabolites, although the release by direct discharge of unused or expired  
19 drugs may also be a significant contributing factor [3]. MPs in industrial effluents discharged into  
20 UWWTPs are generally poorly removed, even when these have been previously treated at  
21 industrial level [3]. Therefore, the uninterrupted discharge of MPs and their metabolites into  
22 UWWTPs can be considered a continuous source of toxicity which harms the receiving aqueous  
23 compartments, such as surface, ground and drinking waters.

24 Innovative advanced oxidation technologies (AOTs), including chemical oxidation technologies  
25 (COTs) and advanced oxidation processes (AOPs), have recently gaining interest as polishing  
26 post-treatment methods usually applied after biological processes in water and wastewater  
27 treatment. Such processes are designed to enhance the degradation and mineralization of MPs or

28 to transform them into less toxic compounds [1]. In highly toxic water effluents, AOTs can be  
29 applied as a pre-treatment, to enhance the biodegradability of the water and reduce its toxicity.  
30 The installation of supplementary AOTs after secondary biological treatment has been triggering  
31 a huge interest among the water industry, due to the recognized efficiency of such processes for  
32 the removal of a wide range of MPs from UWWTPs effluents [1]. The reduction of the release of  
33 MPs into the aquatic compartments, therefore, improves the effluent quality and can promote the  
34 reuse of reclaimed water.

35 AOTs are widely studied technologies for the oxidation of organic MPs via reactions with the  
36 highly reactive radicals. Hydroxyl radical-mediated AOTs utilize hydroxyl radicals ( $\text{HO}^\bullet$ ), the  
37 most powerful oxidizing species after fluorine, with an  $E^0 = 2.80 \text{ V}$  [4]. These unselective radicals  
38 might mineralize the parent compounds with no generation of secondary waste, yielding  $\text{CO}_2$ ,  
39  $\text{H}_2\text{O}$  and inorganic ions as final products [1]. AOTs can be classified as chemical, photochemical,  
40 electrochemical, sonochemical and hydrochemical processes, depending on the way the  $\text{HO}^\bullet$  are  
41 generated, or as homogeneous and heterogeneous processes, depending on the number of phases  
42 involved during the transport and reaction of the species. Homogeneous processes include  
43 processes that utilize UV,  $\text{H}_2\text{O}_2$ , the Fenton reagent, dissolved  $\text{O}_3$ , wet oxidation (WO) and wet  
44 peroxide oxidation (WPO); whereas heterogeneous AOTs comprise heterogeneous  
45 photocatalysis, heterogeneous Fenton-like processes, catalytic and photocatalytic ozonation,  
46 catalytic wet oxidation (CWO) and catalytic wet peroxide oxidation (CWPO). UV, UV/ $\text{H}_2\text{O}_2$  and  
47 ozonation processes have been successfully implemented in full-scale UWWTPs to degrade MPs.  
48 AOTs not yet applied at full-scale include UV/ $\text{O}_3$ , UV/ $\text{O}_3/\text{H}_2\text{O}_2$ , UV/ $\text{H}_2\text{O}_2/\text{Fe}$  (mild photo-  
49 Fenton) and other advanced processes such as heterogeneous photocatalysis, heterogeneous  
50 photo-Fenton, photocatalytic ozonation, photocatalytic membrane processes, electrochemical  
51 oxidation and sonolysis [1]. This review focuses on the treatment of MPs by hydroxyl radical-  
52 mediated AOTs and related processes and on the impact of the water matrix components, which  
53 is particularly deficient on sulphate and chlorine radical-mediated AOTs. Sulphate radical-  
54 mediated AOTs have recently gained a great attention due to the high redox potential of  $\text{SO}_4^{\bullet-}$ ,

55 which is comparable with that of HO<sup>•</sup> [5]. While HO<sup>•</sup> is reported to react with MPs through three  
56 competing pathways (addition, hydrogen abstraction, and electron abstraction), SO<sub>4</sub><sup>•-</sup> reacts  
57 preferentially through an electron transfer mechanism. Both radicals can react with inorganic ions  
58 (e.g., Cl<sup>-</sup> and CO<sub>3</sub><sup>2-</sup>), generating secondary reactive species (Cl<sup>•</sup>/CO<sub>3</sub><sup>•-</sup>) with relatively high  
59 reactivity with MPs [5]. Conversely, chlorine radical-mediated AOTs (e.g., UV/chlorine) are  
60 based on selective oxidants produced by photolysis of chlorine: Cl<sup>•</sup> (selective and with higher  
61 reactivity than HO<sup>•</sup> for certain organic compounds, such as benzoic acid, chlorobenzene, and  
62 phenol), Cl<sub>2</sub><sup>•-</sup> (selective for olefinic compounds and aromatics ring-substituted with hydroxy,  
63 methoxy and amino groups) and ClO<sup>•</sup> (selective for aromatics possessing methoxy groups), with  
64 redox potentials of 2.4, 2.0, and 1.5 – 1.8 V, respectively [6]. The use of AOTs in hybrid processes  
65 has been also envisaged through integration with membrane technologies and through the  
66 coupling of two or more AOTs. This last strategy can result: (i) typically in a synergistic effect  
67 due to the positive interactions among the single processes; (ii) in a cumulative effect caused by  
68 the increased generation of reactive oxygen species (ROS); and less commonly (iii) in an  
69 antagonistic effect, due to excessive formation of ROS, which may act as self-scavengers [7].

70

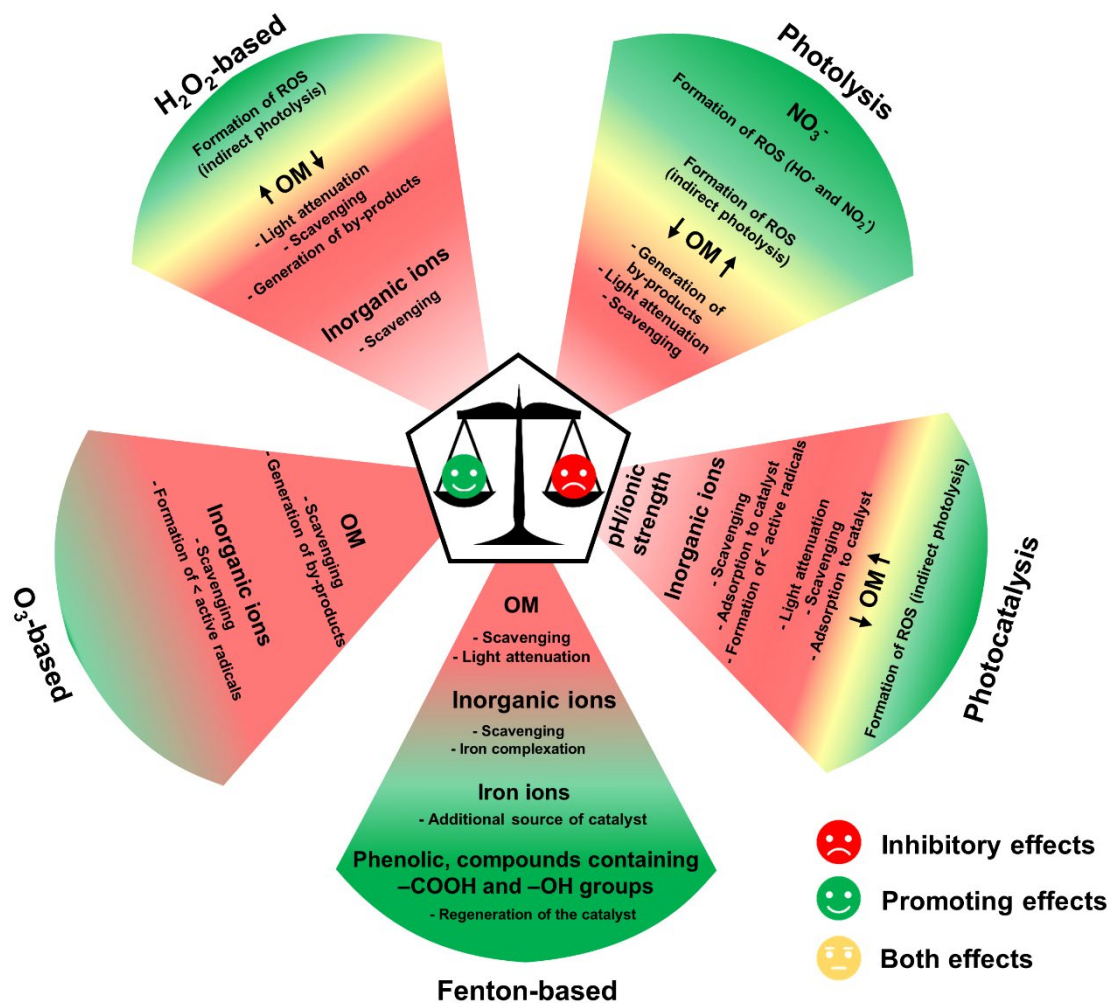
## 71 **2. AOTs and matrix effects**

72 Overall, the elimination of MPs by AOTs is largely influenced by the quality of the water matrix  
73 that needs to be treated, and the effectiveness results from the impact of the dissolved components,  
74 which can have neutral, inhibitory or promoting effects. The composition of the water matrix can  
75 also have a significant impact on the inactivation of bacteria in water disinfection processes, as  
76 shown in the literature [8, 9].

77 The occurrence of scavengers in the matrix may also hinder the removal of dissolved organic  
78 matter (DOM), representing the main fraction of the effluent organic matter (a heterogeneous  
79 mixture of recalcitrant organic compounds comprising natural organic matter (NOM), soluble  
80 microbial products and trace MPs) present in biologically treated urban wastewater [10]. The  
81 composition of DOM depends on the wastewater sources (domestic, industrial, agricultural, etc.),

82 location, the season of the year and the operating conditions (temperature, pH, flow, etc.) [11].  
83 The structural and functional complexity of DOM turns difficult its full characterization,  
84 therefore, the DOC is commonly used as a surrogate parameter for its quantification, providing a  
85 general assessment and lacking on structural elucidation [10]. Its transformation and the  
86 generation of by-products during WWTP processes may change the biological properties and  
87 environmental impact of the DOM, but the knowledge about its transformation in the WWTPs is  
88 still limited. A recent review on this subject described the characterization of DOM based on its  
89 MW distribution, hydrophobicity and optical properties [11]. Several analytical techniques have  
90 been used to characterize the chemistry and reactivity of the DOM components, including  
91 physicochemical analysis, spectroscopic, chromatographic, and thermal degradation methods,  
92 and other fractionation techniques [10]. Wastewater components include a broad range of organic  
93 (e.g., NOM composed by humic and fulvic acids, carbohydrates, proteins) and inorganic species  
94 (e.g., carbonate, bicarbonate, nitrite, sulphate, chloride), which react with HO<sup>•</sup>, either competing  
95 with organic MPs for oxidation [1, 10] or forming the respective radicals with lower oxidation  
96 potential [12]. Moreover, some wastewater components are able to favour the efficiency of certain  
97 AOTs. Figure 1 summarizes the key factors that contribute to the removal efficiency of MPs by  
98 the AOTs discussed in this review, acting as either promoters or as inhibitors.

99



100

101 **Figure 1.** Schematic representation of the reported inhibitory and promoting effects of wastewater  
 102 components, affecting the efficiency of photolysis, H<sub>2</sub>O<sub>2</sub>-based, Fenton-based, photocatalysis, and ozone-  
 103 based processes.

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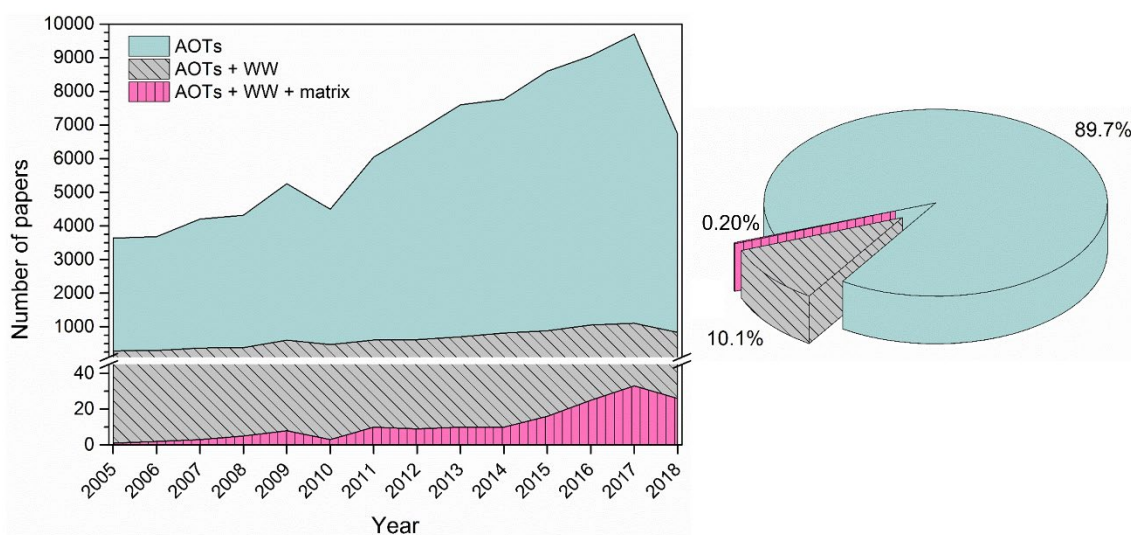
105 The main scavengers of HO• in natural waters include NOM, bromide (which forms BrOH<sup>-</sup> by  
 106 reacting with HO•) [5], and carbonate/bicarbonate species [13]. Hence, different water matrices  
 107 containing NOM exhibit different scavenging rates, reducing the fraction of ROS available to  
 108 degrade MPs, which triggers the need of considering such scavengers in the optimization of  
 109 AOTs. In most cases, the MPs removal kinetics decrease with an increase in the complexity of  
 110 the water matrix, since this may contain numerous non-target organic and inorganic species that  
 111 compete with the target contaminants for oxidants [14]. The inhibitory effects of co-existing



112 substances in the matrix include also light absorption and attenuation in processes utilizing UV  
113 radiation. It may also result in the formation of less active complexes with iron species in Fenton-  
114 based processes and in the competition for catalytic active sites, catalyst deactivation by poisoning  
115 of the active sites or fouling of the surface area of the catalysts in heterogeneous catalytic  
116 processes, as well as the modification of the electrical surface charge due to the pH or ionic  
117 strength. However, it has been reported that non-target species may also act as promoters in  
118 selected AOTs [4, 14]. Photosensitizers organic and inorganic species in the water matrix can  
119 promote the production of ROS by UV irradiation, leading to indirect photolysis [15]. For  
120 instance,  $\text{NO}_3^-$  is able to produce  $\text{HO}^\bullet$  and  $\text{NO}_2^\bullet$  radical species, promoting the photodegradation  
121 of MPs, especially those in which indirect photolysis is the main reactive pathway (e.g., caffeine,  
122 carbamazepine, diuron, simazine, 2,4-dichlorophenoxyacetic acid) [15]. Fenton-based processes  
123 are generally promoted by natural occurring iron in the wastewater which acts as an additional  
124 catalytic source, by the presence of phenolic compounds that may reduce the ferric ions to ferrous  
125 ions regenerating the catalyst, and by dissolved compounds containing -COOH and -OH groups  
126 which complexes ferric ions in solution, where the complexes may have higher quantum yields  
127 [16].

128 Despite the great attention given to AOTs (**Figure 2, left**), only ca. 10% of the published papers  
129 refer to the treatment of actual wastewater and a few of them (ca. 0.2%) have addressed the impact  
130 of the water matrix (**Figure 2, right**).

131



132

133 **Figure 2.** Number of papers published by year in the period 2005-2018 (left) and their relative frequency  
 134 in the whole period (right), displayed by searching publications dealing with the different types of AOTs  
 135 discussed in this review, using as keywords (abstract, title, keywords): “photolysis” or “UV/H<sub>2</sub>O<sub>2</sub>“ or  
 136 “Fenton” or “photocatalysis” or “ozonation” or “ozonolysis” or “UV/O<sub>3</sub>“ or “peroxone” (■); and  
 137 “wastewater” (▨); and “matrix effect” or “matrix component” or “matrix constituent” or “water  
 138 matrix” or “water matrices” or “water component” or “water constituent” (■). Source: Scopus; July  
 139 2018.

140

141 Interestingly, although the amount of publications in this field has been markedly increasing, the  
 142 number of papers dealing with wastewater treatment and the impact of the water matrix follows  
 143 the same trend, with almost no variations on their relative frequency. In fact, most studies on  
 144 AOTs for water/wastewater treatment have been performed using aqueous solutions spiked with  
 145 model contaminants. Often, ultrapure or distilled water is spiked with the contaminant at  
 146 concentration levels higher than those actually reported in environmental compartments [14]. This  
 147 methodology allows: (i) to exclude the interactions between the contaminant, the oxidizing  
 148 species and the matrix components; (ii) to study degradation pathways of specific compounds;  
 149 (iii) to evaluate the performance of the studied treatment for target contaminants; and (iv) to use  
 150 simple and widely used analytical techniques. However, the quality of the aqueous matrix for  
 151 which the treatment is proposed is crucial to draw accurate conclusions about the effectiveness of

152 the AOT, its suitability and practicability for the treatment of real contaminated waters. Therefore,  
153 this review focuses on the available data of matrix effects on the removal of MPs from effluents  
154 of UWWTPs by using photolysis, UV/H<sub>2</sub>O<sub>2</sub>, Fenton, photocatalysis, or ozone-based processes,  
155 and give insights about the options that improve the effectiveness of AOTs already implemented  
156 or under investigation. The search comprised publications since 2005 in Scopus database, using  
157 the following keywords (abstract, title, keywords): “photolysis” or “UV/H<sub>2</sub>O<sub>2</sub>” or “Fenton” or  
158 “photocatalysis” or “ozonation” or “ozonolysis” or “UV/O<sub>3</sub>” or “peroxone” and “wastewater” and  
159 “matrix effect” or “matrix component” or “matrix constituent” or “water matrix” or “water  
160 matrices” or “water component” or “water constituent” (**Figure 2**). From this survey, only studies  
161 dealing with real wastewater were considered, namely by comparing it with ultrapure water or  
162 other matrices, testing wastewater from different origins, or by assessing the effect of adding  
163 supplementary water components.

164 In the last decade, many studies using actual matrices have been reported in the literature, most  
165 showing an application for a real matrix, after screening studies on synthetic aqueous solutions,  
166 and/or dealing with spiked MPs at concentration levels higher than those found in the  
167 environment. More recently, some reports have shown the influence of the quality and/or quantity  
168 of water components, on the process efficiency. Most of these works are focused on the  
169 comparison of removal efficiencies of MPs and/or dissolved organic carbon (DOC) in  
170 distilled/ultrapure water versus synthetic wastewaters [17, 18] and/or actual wastewaters [4].  
171 Some studies comparing wastewaters from different origins [19] or at different treatment stages  
172 in the UWWTP [20], have been recently reported. Several authors have also shown the effects of  
173 wastewater components (e.g., humic acids (HA), fluvic acids, surfactants, inorganic species) on  
174 the removal of selected MPs frequently found in urban wastewater; however, these studies often  
175 address the impact on ultrapure or distilled water, rather than in real wastewater. A current  
176 approach has been performed by adding different components (organic and/or inorganic) to  
177 natural water, giving more accurate insights on the effects of wastewater components on the  
178 removal efficiencies of either MPs or DOC. Studies using environmental matrices at real

179 concentrations and providing a deep understanding on the effects of the organics and inorganics  
180 occurring in the matrices, are still limited.

181

## 182 **2.1. Photolysis**

183 UV water treatment can involve two mechanisms, direct or indirect photolysis. The direct  
184 photolysis of organic substances by UV radiation (typically at  $\lambda = 254$  nm) promotes the electronic  
185 excitation of the molecules, leading to: (i) electron transfer from an excited state of the organic  
186 compounds to molecular oxygen; or (ii) homolysis of the organic substance, producing organic  
187 radicals that further react with oxygen [20-22].

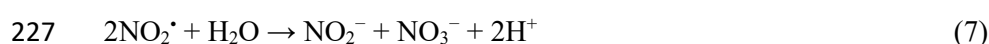
188 The water matrix can play an essential role on the yield of photodegradation reactions, depending  
189 on the presence of promoting and inhibitory substances. Table 1 summarizes the reports published  
190 since 2005 referring to the evaluation of matrix effects on photolysis (more details can be found  
191 in Table S1). Generally, lower contaminants removal rates are expected in wastewater effluents  
192 in comparison to a ultrapure water matrix, which can be enlightened by the presence of NOM  
193 absorbing a fraction of the incident radiation [23]. The main factors regulating the inhibitory effect  
194 of NOM are: (i) light attenuation caused by suspended particles; (ii) scavenging effects of NOM;  
195 and (iii) generation of NOM by-products [24]. Nevertheless, the wastewater components might  
196 enhance the removal rate of certain MPs by mean of indirect photolysis, resulting from the action  
197 of ROS originated by the irradiation of photosensitizers dissolved in the water matrix [4].  
198 Photosensitizers comprise a wide variety of organic compounds found in DOM that can undergo  
199 diverse photochemical reactions, producing ROS that initiate MPs degradation. Such ROS may  
200 in certain cases offset the reduction of transmittance of NOM containing matrices, which in turn  
201 diminishes the degradation by direct photolysis (e.g., studies in wastewater and in drinking water)  
202 [25]. DOM photosensitizers act by absorption of light (Reaction 1) followed by excitation to a  
203 single state ( $^1\text{DOM}^*$ ), which has typical short lifespans (ps to ns) and consequent little interaction  
204 with organic MPs. This is partially transformed to their excited triplet state ( $^3\text{DOM}^*$ ), which has  
205 a longer lifespan (order of  $\mu\text{s}$ ) [21, 26]. The  $^3\text{DOM}^*$  species are believed to be the main reactive

206 species in the reactive pathways and the deactivation of the excited triplet state can occur by  
207 reaction with other organic molecules (e.g., target MPs), which are consequently oxidized [24].  
208 These species can play an important role in indirect photolysis for phenols and aromatic amines  
209 [27]. Another deactivation mechanisms of  $^3\text{DOM}^*$  include the transition to their ground state or  
210 the transfer of energy to  $\text{O}_2$  (Reaction 2), producing singlet molecular oxygen ( $^1\text{O}_2$ ), which also  
211 act as a photo-oxidant [21].



214 For instance, the photodegradation of cocaine in a synthetic municipal wastewater effluent by  
215 direct sun-light exposure was higher (90% after 20 h of irradiation) than that observed in distilled  
216 water (22% after 60h of irradiation), without mineralization taking place in both investigated  
217 matrices [17]. This phenomenon has also been reported for the degradation of diclofenac under  
218 UVA radiation, with a higher removal rate registered in wastewater than in ultrapure water, due  
219 to some naturally occurring substances in the effluent, acting as photosensitizers [28].

220 The anion  $\text{NO}_3^-$  may also play an important role in the UV treatment. This inorganic species can  
221 generate  $\text{HO}^*$  and  $\text{NO}_2^*$  (Reactions 3-7) under direct UV photolysis (mainly at wavelength below  
222 240 nm), consequently increasing the degradation of some compounds [24].



228 This promoting effect has been observed during the degradation of several phenolic compounds  
229 [29], cytostatic drugs [24], pharmaceuticals [30] and pesticides [15]. A study on the  
230 photodegradation of antibiotics suggested that the promoting effect of  $\text{NO}_3^-$  on the photolysis of

231 salinomycin resulted from the reaction with produced reactive nitrogen species, besides the  
232 indirect photolysis [30]. Another study reported an appreciable promoting effect of  $\text{NO}_3^-$  on those  
233 compounds which followed an indirect degradation photolytic pathway, while the impact was  
234 minor on those compounds more susceptible to direct photolysis [15]. This fact can be explained  
235 by the reduction of the photonic energy in the aqueous solution, when the target compounds  
236 strongly absorb in the same UV range as  $\text{NO}_3^-$  [31].

237

## 238 **2.2. $\text{H}_2\text{O}_2$ -assisted processes**

239 UV/ $\text{H}_2\text{O}_2$  is an AOT that combines the instantaneous UV photolytic effect (either direct or  
240 indirect) and the reaction with  $\text{HO}^\bullet$  originated from the homolytic disruption of  $\text{H}_2\text{O}_2$  (initiation,  
241 propagation and termination, Reactions 8-12, Table S2 summarizes the reaction rate constants)  
242 [20]. UV/ $\text{H}_2\text{O}_2$  is an alternative solution for the elimination of organic MPs with low reactivity  
243 towards  $\text{O}_3$  and  $\text{HO}^\bullet$  and high photoactivity (e.g., N-nitrosodimethylamine) [13], as well as for  
244 the treatment of wastewaters with high concentration of bromide since this process avoids  
245 bromate formation [13].



251 Although  $\text{H}_2\text{O}_2$  produces  $\text{HO}^\bullet$  under UV irradiation, at elevated concentrations it also scavenges  
252  $\text{HO}^\bullet$  (Reactions 9-12), hindering the oxidation of the target organic MPs, therefore the dose of  
253  $\text{H}_2\text{O}_2$  needs to be controlled very carefully in order to maximize the removal rate of MPs [25].  
254 Furthermore,  $\text{H}_2\text{O}_2$  is a major contributor to the operating cost of the UV/ $\text{H}_2\text{O}_2$  process [25].

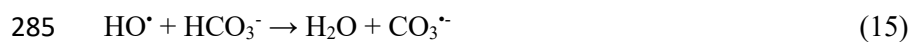
255 In the H<sub>2</sub>O<sub>2</sub>-assisted photocatalysis, it is likely that H<sub>2</sub>O<sub>2</sub> promotes the degradation of target water  
256 contaminants by reacting with conduction band electrons (Reaction 13) and the superoxide radical  
257 (O<sub>2</sub><sup>•-</sup>) (Reaction 14) to produce HO<sup>•</sup> and anions [32]. The formation of additional oxidizing  
258 species and the suppression of the recombination of e<sup>-</sup>/h<sup>+</sup> pairs, in the case of photocatalysis,  
259 enhance the effectiveness of this AOT [32].



262 Similarly to the UV/H<sub>2</sub>O<sub>2</sub> process, an optimum H<sub>2</sub>O<sub>2</sub> concentration can also be determined in the  
263 H<sub>2</sub>O<sub>2</sub>-assisted photocatalysis process, depending on the reaction and system conditions, above  
264 which H<sub>2</sub>O<sub>2</sub> acts as electron and radical scavenger, ultimately reducing the degradation rate of  
265 MPs [32].

266 Water quality parameters, such as the specific UV absorbance and the presence of HO<sup>•</sup> scavengers  
267 (e.g., NOM and high alkalinity), can adversely affect the degradation of MPs [33]. Diverse water  
268 matrices may have different scavenging rates since the rate constant for the reaction of DOM with  
269 HO<sup>•</sup> depends on the nature of the DOM [13]. Table 1 summarizes the studies published since  
270 2005 reporting the evaluation of water matrix effects on the effectiveness of H<sub>2</sub>O<sub>2</sub>-assisted  
271 processes (more details can be found in Table S1). In the UV/H<sub>2</sub>O<sub>2</sub> process, the matrix  
272 components may: (i) absorb UV light which is required to generate HO<sup>•</sup> from H<sub>2</sub>O<sub>2</sub>; and (ii)  
273 compete with the MPs for the reaction with HO<sup>•</sup>, therefore, lowering the steady-state  
274 concentration of radicals in solution [34]. The NOM competes with MPs by consuming a fraction  
275 of the oxidant, and consequently higher oxidant doses are usually required to achieve a specific  
276 removal of MPs in the presence of NOM [35]. In addition, the water components may affect the  
277 chemical nature of the oxidation by-products formed, which in turn may affect the water quality  
278 characteristics [33]. Moreover, the breakdown of DOM into smaller molecules can promote the  
279 faster decay rates of MPs due to the formation of HO<sup>•</sup>, peroxy radicals, and excited singlet,  
280 doublet or triplet states of oxygen, which may increase the removal of organics MPs in DOC-  
281 enriched waters [36].

282 Another important factor that may affect the performance of H<sub>2</sub>O<sub>2</sub>-assisted processes is the  
283 concentration of inorganic carbon (IC) in the water sample [37]. A high carbonate/bicarbonate  
284 content may scavenge HO<sup>•</sup>, according to the following reactions (Reactions 15-16):



287 The carbonate radical (CO<sub>3</sub><sup>•-</sup>) can be also formed via the reaction of carbonate/bicarbonate with  
288 <sup>3</sup>DOM\* [27]. Regardless of the origin, this radical is a potent oxidant with a one electron reduction  
289 potential of 1.78 V (pH 7). It is more selective than HO<sup>•</sup> as oxidant, mainly reacting with electron  
290 rich compounds such as phenols, S- and N-containing compounds [27].

291 Therefore, both effects can occur in wastewater samples with high DOC and IC: (i)  
292 carbonate/bicarbonate scavenge or compete for HO<sup>•</sup>, besides other inorganic scavengers that may  
293 interfere with the degradation of MPs [37], such as nitrate, chloride, and sulphate [25, 38]; and  
294 (ii) the CO<sub>3</sub><sup>•-</sup> formed may react with those selected compounds with high second-order rate  
295 constant values [27].



**Table 1.** Matrix effects occurring in studies dealing with the AOTs discussed in this review, published since 2005 (\* refers to different sources of wastewater and/or wastewater collected at different stages of treatment). Details of each study can be found in Supplementary Material (Tables S1/S3-S5).

AOT	Target pollutant	Concentration	Matrices tested						Addition of components						Observed effect	Reference
			UPW DI	DW	GW	SW	SWW	WW	OM HA	NO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>	Other		
UV	Bisphenol A	520 µM	X						X						Promoting effect	[4]
UV/H <sub>2</sub> O <sub>2</sub>	Bisphenol A	520 µM	X						X						Inhibiting effect	[4]
UV/H <sub>2</sub> O <sub>2</sub>	Benzoylcegonine	2.8×10 <sup>-5</sup> ± 4.0×10 <sup>-6</sup> mol L <sup>-1</sup>	X			X	X	X							Promoting effect (NO <sub>3</sub> <sup>-</sup> ) Inhibiting effect (OM)	[39]
UV/H <sub>2</sub> O <sub>2</sub>	Benzoylcegonine	0.6–18.5 mg L <sup>-1</sup>	X			X	X	X							Inhibiting effect (organics, inorganics)	[40]
UV/H <sub>2</sub> O <sub>2</sub>	Atrazine, sulfamethoxazole, N- nitrosodimethylamine	0.5 – 11 µM				X		X							Inhibiting effect (OM)	[13]
UV UV/H <sub>2</sub> O <sub>2</sub>	Pharmaceuticals, benzotriazole, mecoprop	ng L <sup>-1</sup> to µg L <sup>-1</sup> levels						X*							Dependent on the origin	[20]
UV	Hydrochlorothiazide	1 µM	X			X		X							Inhibiting effect (OM)	[23]
UV	Pharmaceuticals	100 µg L <sup>-1</sup>	X					X	X	X	X	X	X		Promoting effect (NO <sub>3</sub> <sup>-</sup> ) Inhibiting effect (HA, OM)	[24]
UV	E1, E2, EE2	1.3-1.5 mg L <sup>-1</sup>		X				X							No noteworthy differences	[25]
UV/H <sub>2</sub> O <sub>2</sub>	E1, E2, EE2	1.3-1.5 mg L <sup>-1</sup>		X				X							Inhibiting effect (OM, anions)	[25]

UV	O-phenylphenol, methyl paraben, propyl paraben, triclosan, bisphenol A	0.5 mg L <sup>-1</sup>	X		X		X		X			Promoting effect (NO <sub>3</sub> <sup>-</sup> )	[29]
UV	Monensin, salinomycin, narasin	0.5 mg L <sup>-1</sup>	X				X	X				Promoting effect (OM, NO <sub>3</sub> <sup>-</sup> )	[30]
UV	Pharmaceuticals, pesticides, caffeine, triclosan, 2,4-dichlorophenoxyacetic acid	150 µg L <sup>-1</sup>	X				X	X	X			Promoting effect (OM for some compounds, NO <sub>3</sub> <sup>-</sup> )	[15]
UV	Monensin, salinomycin, narasin, nigericin	0.8 – 3.0 µM	X		X		X					Promoting effect (OM, NO <sub>3</sub> <sup>-</sup> , Cl <sup>-</sup> )	[34]
UV/H <sub>2</sub> O <sub>2</sub>	Monensin, salinomycin, narasin, nigericin	0.8 – 3.0 µM	X		X		X					Inhibiting effect	[34]
UV/H <sub>2</sub> O <sub>2</sub>	Pharmaceuticals, bisphenol A	4 µM	X		X		X					Inhibiting effect (OM and ions)	[38]
UV	Sulfamethoxazole	1.0, 2.0, 5.0 and 10 mg L <sup>-1</sup>	X				X	X	X	X	X	Promoting effect (Cl <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup> , NO <sub>3</sub> <sup>-</sup> , 5 mg L <sup>-1</sup> of HA)	[41]
UV UV/H <sub>2</sub> O <sub>2</sub>	Pharmaceuticals	0.68-1.72 µM	X				X*					Inhibiting effect (HCO <sub>3</sub> <sup>-</sup> , HA at higher concentrations)	[19]
UV UV/H <sub>2</sub> O <sub>2</sub>	Oxytetracycline, doxycycline, ciprofloxacin	5 µM	X	X	X		X					Inhibiting effect	[35]
UV UV/H <sub>2</sub> O <sub>2</sub>	1-H-Benzotriazole, N,N-diethyl-m-toluamide (DEET), chlorophene, 3-methylindole, nortriptyline HCl	1 µM	X		X		X					Inhibiting effect (OM)	[42]

UV UV/H <sub>2</sub> O <sub>2</sub>	Fungicides	10 µg L <sup>-1</sup>		X		X				No noteworthy differences	[43]
Fenton-like	Bisphenol A	285-14200 µg L <sup>-1</sup>	X	X	X	X				Promoting effect (Cl <sup>-</sup> ) Inhibiting effect (OM, HCO <sub>3</sub> <sup>-</sup> )	[14]
Bio-electro-Fenton	Ketoprofen, diclofenac, ibuprofen and naproxen	40 µg L <sup>-1</sup>	X							Inhibiting effect (OM, anions)	[44]
Fenton	Trimethoprim	0.05 mM	X				X	X		Inhibiting effect (OM)	[45]
Fenton Photo-Fenton UV UV/H <sub>2</sub> O <sub>2</sub>	Prednisolone	100 mg L <sup>-1</sup>	X						X	Inhibiting effect (organics, inorganics)	[46]
Fenton Photo-Fenton	Pharmaceuticals, benzotriazole, mecoprop	ng L <sup>-1</sup> to µg L <sup>-1</sup> levels							X	Dependent on the origin	[20]
Photo-Fenton	Tetracycline	24 mg L <sup>-1</sup>	X						X	Inhibiting effect (organics, inorganics)	[37]
Photo-Fenton	62 MPs	3-66,379 ng L <sup>-1</sup>							X*	EDDS; H <sub>2</sub> SO <sub>4</sub> Promoting effect (EDDS) Inhibiting effect (HA)	[47]
Photo-Fenton	Pharmaceuticals, pesticides, estrogens, triclosan, hydroxybiphenyl, caffeine	100 µg L <sup>-1</sup>							X*	EDDS; H <sub>2</sub> SO <sub>4</sub> No noteworthy differences	[48]
Photo-Fenton	Pharmaceuticals, pesticides, estrogens, triclosan, hydroxybiphenyl, caffeine	5 and 100 µg L <sup>-1</sup>							X* X	Oxalate; H <sub>2</sub> SO <sub>4</sub> Promoting effect (HA, oxalate)	[49]
Photo-Fenton	Ofloxacin	10 mg L <sup>-1</sup>	X			X	X	X		Inhibiting effect (OM, Cl <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup> )	[50]

Photo-Fenton	Trimethoprim	10 mg L <sup>-1</sup>	X		X	X	X											Inhibiting effect (OM, inorganics)	[12]
Fenton	Nonionic surfactants	1.4 mg L <sup>-1</sup>	X				X											Inhibiting effect	[51]
Photo-Fenton	Sulfamethoxazole, clarithromycin	100 µg L <sup>-1</sup>	X				X	X										Inhibiting effect (OM, Cl <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup> )	[52]
Photo-Fenton	Pharmaceuticals, pesticides, estrogens, triclosan, hydroxybiphenyl, caffeine	100 µg L <sup>-1</sup>					X	X					H <sub>2</sub> SO <sub>4</sub>					Promoting effect (HA) Inhibiting effect (CO <sub>3</sub> <sup>2-</sup> , HCO <sub>3</sub> <sup>-</sup> )	[53]
Fenton	Hydroquinone	100 mg L <sup>-1</sup>	X					X										No noteworthy differences	[54]
Fenton	51 MPs	ng L <sup>-1</sup> - µg L <sup>-1</sup> levels						X*										Inhibiting effect	[55]
Fenton	Pharmaceuticals, estrogens, triclosan	ng L <sup>-1</sup> to µg L <sup>-1</sup> levels						X*										Inhibiting effect	[56]
UV/H <sub>2</sub> O <sub>2</sub> Photo-Fenton	Pharmaceuticals, methylbenzotriazole, benzotriazole	2 µM	X		X			X										Promoting effect (HA, CO <sub>3</sub> <sup>2-</sup> , Cl <sup>-</sup> )	[57]
Photocatalysis	Diclofenac	5–20 mg L <sup>-1</sup>	X	X				X										Inhibiting effect (OM, other species)	[32]
Photocatalysis	Clofibric acid	1 mg L <sup>-1</sup>	X					X	X	X	X	X	X					Inhibiting effect (inorganics)	[58]
Photocatalysis	Pharmaceuticals, pesticides, disinfectants	100 µg L <sup>-1</sup>					X	X										Inhibiting effect	[59]
Photocatalysis UV/H <sub>2</sub> O <sub>2</sub>	Pharmaceuticals	100 µg L <sup>-1</sup>	X					X										Inhibiting effect (OM, CO <sub>3</sub> <sup>2-</sup> , other anions)	[60]
Photocatalysis	Propyl paraben	420 µg L <sup>-1</sup>	X	X	X			X										Inhibiting effect (HA, HCO <sub>3</sub> <sup>-</sup> , Cl <sup>-</sup> )	[61]
Photocatalysis	Pharmaceuticals, pesticides, industrial compounds	2 mg L <sup>-1</sup>	X					X										Inhibiting effect (OM, ions)	[62]
Photocatalysis	E1	1000 µg L <sup>-1</sup>	X				X	X										Inhibiting effect (OM, anions)	[63]

Photocatalysis	Bisphenol A, EE2	100-300 $\mu\text{g L}^{-1}$	X			X	Inhibiting effect (OM, anions)	[64]
Photocatalysis	Bisphenol A	100 $\mu\text{g L}^{-1}$	X		X	X	Inhibiting effect ( $\text{CO}_3^{2-}$ , $\text{Cl}^-$ )	[65]
Photocatalysis	Amoxicillin, carbamazepine, diclofenac	2.5-10 $\text{mg L}^{-1}$			X	X	Inhibiting effect (OM, other species)	[66]
Photocatalysis	EE2	100 $\mu\text{g L}^{-1}$	X	X		X	Inhibiting effect (OM, $\text{HCO}_3^-$ , $\text{Cl}^-$ , $\text{SO}_4^{2-}$ )	[67]
Photocatalysis	EE2	100 $\mu\text{g L}^{-1}$	X	X		X	Inhibiting effect (HA, organics, inorganics)	[68]
Photocatalysis	EE2	100–500 $\mu\text{g L}^{-1}$	X			X	Inhibiting effect (OM, $\text{HCO}_3^-$ , $\text{Cl}^-$ , $\text{SO}_4^{2-}$ )	[69]
Photocatalysis	Ibuprofen	6 $\mu\text{g L}^{-1}$ 6, 60, 213 $\text{mg L}^{-1}$	X			X	Inhibiting effect (OM, $\text{NO}_2^-$ , $\text{NO}_3^-$ , $\text{PO}_4^{3-}$ )	[70]
Photocatalysis	Tetracycline	55 $\text{mg L}^{-1}$	X	X		X	Promoting effect (OM) Inhibiting effect (OM, $\text{HCO}_3^-$ , $\text{Cl}^-$ )	[71]
Photocatalysis	Azo dye congo red, carbamazepine	10 $\text{mg L}^{-1}$	X		X	X	Inhibiting effect (anions, $\text{Ca}^{2+}$ )	[72]
Photocatalysis	Acetaminophen, thiabendazole, imazalil, acetamiprid	100 $\mu\text{g L}^{-1}$	X		X	X	Inhibiting effect (OM, inorganics)	[73]
Photocatalysis	Metoprolol	50 $\text{mg L}^{-1}$	X			X	Inhibiting effect (OM, inorganics)	[74]
Photocatalysis	Carbamazepine	5 $\text{mg L}^{-1}$				X	$\text{PO}_4^{3-}$ Inhibiting effect (OM, inorganics)	[75]
Photocatalysis	Ofloxacin, atenolol	10 $\text{mg L}^{-1}$	X	X		X	Inhibiting effect (OM, inorganics)	[76]
Photocatalysis	Diclofenac, fluoxetine	$\text{mg L}^{-1}$ levels	X			X	Inhibiting effect (suspended solids)	[77]

Photocatalysis	Sulfamethoxazole	10 mg L <sup>-1</sup>	X	X	X			Inhibiting effect (ionic strength)	[78]
Photocatalysis	Sulfathiazole, sulfamethoxazole, sulfadiazine	5 mg L <sup>-1</sup>	X			X		Inhibiting effect	[79]
Photocatalysis	Carbamazepine	133 ng L <sup>-1</sup>	X			X		Inhibiting effect	[80]
Photolysis	Diclofenac, carbamazepine, ibuprofen, propranolol	5 mg L <sup>-1</sup>	X			X		Promoting effect (OM, NO <sub>3</sub> <sup>-</sup> )	[81]
Photocatalysis	Diclofenac, carbamazepine, ibuprofen, propranolol	5 mg L <sup>-1</sup>	X			X		Inhibiting effect	[81]
Photocatalysis	Pharmaceuticals	0.35-11.30 µg L <sup>-1</sup>	X			X		No noteworthy differences	[82]
Photocatalysis–DCMD	Diclofenac, naproxen, ibuprofen	100 µg L <sup>-1</sup>	X	X		X		Promoting effect (suspended solids) Inhibiting effect	[83]
Photocatalysis	Carbamazepine	50 µM	X			X		Inhibiting effect (OM, Cl <sup>-</sup> )	[84]
Photocatalysis	Diatrizoate, acetaminophen, carbamazepine, atenolol	736-757 µg L <sup>-1</sup>				X*		Inhibiting effect	[85]
Photocatalysis	Trimethoprim	1 mg L <sup>-1</sup>		X	X	X	X	Inhibiting effect	[86]
O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub>	Atrazine, sulfamethoxazole, N-nitrosodimethylamine	0.5 – 11 µM				X	X	Inhibiting effect (OM, CO <sub>3</sub> <sup>2-</sup> , HCO <sub>3</sub> <sup>-</sup> )	[13]
Ozonation	Hydrochlorothiazide	1 µM	X			X	X	Inhibiting effect (OM)	[23]
UV Photocatalysis O <sub>3</sub> O <sub>3</sub> /UV O <sub>3</sub> /TiO <sub>2</sub> O <sub>3</sub> /UV/TiO <sub>2</sub>	Diclofenac, sulfamethoxazole, caffeine	10 mg L <sup>-1</sup>	X			X		Inhibiting effect (OM)	[28]
Ozonation	Metoprolol, naproxen, amoxicillin, phenacetin	1 µM		X	X	X*		Inhibiting effect (OM)	[87]

UV Photocatalysis (TiO <sub>2</sub> )	Acetamiprid	100 µg L <sup>-1</sup>	X		X	X						HA, LS, lignin	Inhibiting effect (HA)	[88]
Photo-Fenton Photocatalysis (PS) UV/PS/Fe	Acetamiprid	100 µg L <sup>-1</sup>	X		X	X						HA, LS, lignin	Inhibiting effect (lignin)	[88]
Photocatalysis O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub>	Carbamazepine, diclofenac	10-1000 µg L <sup>-1</sup>	X			X							Inhibiting effect	[16]
Photo-Fenton	Carbamazepine, diclofenac	10-1000 µg L <sup>-1</sup>	X			X							Promoting effect	[16]
O <sub>3</sub>	Tetrabromobisphenol	100 mg L <sup>-1</sup>	X	X		X*	X	X	X	X	X		No noteworthy differences	[89]
O <sub>3</sub>	Flumequine	20 µg L <sup>-1</sup> -20 mg L <sup>-1</sup>	X	X		X*	X		X	X	X	K <sup>+</sup> , Ca <sup>2+</sup> , Mg <sup>2+</sup>	Promoting effect (OM) Inhibiting effect (OM)	[90]
O <sub>3</sub> O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub>	Metoprolol, naproxen, amoxicillin, phenacetin	1 µM	X			X*							Inhibiting effect (OM)	[91]
Photocatalytic ozonation	Diclofenac	10 <sup>-4</sup> and 10 <sup>-6</sup> M	X			X							Inhibiting effect (organics, inorganics)	[92]
O <sub>3</sub>	APIs	1 µg L <sup>-1</sup>				X*							Inhibiting effect (COD and alkalinity)	[93]
O <sub>3</sub>	Ofloxacin	22 mg L <sup>-1</sup>			X	X							Inhibiting effect (OM)	[94]
O <sub>3</sub>	Benzalkonium chloride	10 mg L <sup>-1</sup>			X	X							Inhibiting effect (OM)	[95]
O <sub>3</sub>	Pesticides	5-20 mg L <sup>-1</sup>			X	X							Inhibiting effect (COD, HCO <sub>3</sub> <sup>-</sup> , PO <sub>4</sub> <sup>3-</sup> , Cl <sup>-</sup> )	[96]
O <sub>3</sub> Catalytic ozonation	Mesoxalic and oxalic acids	50 mg L <sup>-1</sup>				X			X	X	X	PO <sub>4</sub> <sup>3-</sup>	Inhibiting effect (anions, suspended solids)	[97]
O <sub>3</sub> O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub>	Sulfamethoxazole, diclofenac	30 mg L <sup>-1</sup>			X	X							Inhibiting effect (CO <sub>3</sub> <sup>2-</sup> , HCO <sub>3</sub> <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup> , PO <sub>4</sub> <sup>3-</sup> )	[98]

O <sub>3</sub> O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub>	Pharmaceuticals	ng L <sup>-1</sup> levels			X*				Inhibiting effect	[99]
Catalytic ozonation	Diclofenac, sulfamethoxazole, EE2	10 mg L <sup>-1</sup>			X*			H <sub>2</sub> SO <sub>4</sub>	No noteworthy differences	[100]
Photocatalytic ozonation	Diclofenac, amoxicillin	0.1 mM	X		X				Inhibiting effect	[101]
O <sub>3</sub> Catalytic ozonation	Formic, acetic, oxalic and maleic acids	7 mg L <sup>-1</sup>			X*				Inhibiting effect (OM)	[102]
O <sub>3</sub> Photocatalysis Photocatalytic ozonation	Pharmaceuticals and hydroxyl-biphenyl	50 µg L <sup>-1</sup>	X		X				Inhibiting effect (organics, inorganics)	[103]
O <sub>3</sub> UV UV/H <sub>2</sub> O <sub>2</sub> O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub>	Pharmaceuticals	1 µM		X	X	X			Inhibiting effect (OM)	[104]
O <sub>3</sub> UV/H <sub>2</sub> O <sub>2</sub>	Organophosphate esters	50 µg L <sup>-1</sup>	X		X	X			Inhibiting effect (OM, Cl <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup> , NO <sub>3</sub> <sup>2-</sup> , HCO <sub>3</sub> <sup>-</sup> )	[105]
O <sub>3</sub> UV UV/H <sub>2</sub> O <sub>2</sub> UV/O <sub>3</sub> , O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub> O <sub>3</sub> /UV/ H <sub>2</sub> O <sub>2</sub>	E1	3 µg L <sup>-1</sup> – 5 mg L <sup>-1</sup>	X		X				Inhibiting effect (OM)	[106]
Catalytic ozonation	Benzotriazole	10 mg L <sup>-1</sup>	X		X				No noteworthy differences	[107]

**Abbreviations:** API, active pharmaceutical ingredient; COD, chemical oxygen demand; DCMD, direct contact membrane distillation; DI, distilled water; DW, drinking water; E1, estrone; E2, 17-beta-estradiol; EE2, 17-alpha-ethinylestradiol; EDDS, ethylenediamine-N,N'-disuccinic acid; GW, groundwater; HA, humic acids, LS, lauryl sulphate; OM, organic matter; PS, persulphate; SW, surface water; SWW, synthetic wastewater; UPW, ultrapure water; WW, wastewater.



### 2.3. Fenton-based processes

The conventional Fenton process employs the “Fenton's reagent” [108], a mixture of  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  that yields  $\text{HO}^\bullet$  and  $\text{Fe}^{3+}$  as reaction products (Reactions 17-18). This reagent combines the use of the fourth most abundant element in the earth's crust, which has environmental compatibility and low-toxicity [109], with the oxidant  $\text{H}_2\text{O}_2$ , which self-decomposition leads to non-toxic products ( $\text{H}_2\text{O}$  and  $\text{O}_2$ ) [110]. The low cost of the Fenton's reagent and the negligible activation energy, coupled to the simplicity of the process, are attractive advantages. However, the regeneration of  $\text{Fe}^{2+}$  under darkness in the conventional Fenton process is very slow and governed by the following reactions (Reactions 19-21) [20].



The main shortcomings of the Fenton process include: (i) the fast depletion of  $\text{Fe}^{2+}$  and the slow regeneration rate; (ii) the amount of sludge produced needing additional treatment; (iii) the complexation of some iron species; (iv) the potential loss of oxidants by scavenging effect or auto-degradation; and (v) the requirement of a pH between 2.5 and 3.0 to achieve optimal performance and below 4.0 to avoid the iron precipitation [111]. The latter originate the need to neutralize the wastewater with bases after treatment, but the consequent raised salt concentration would be deleterious for specific reuses of the treated water, such as for irrigation [47].

Modifications of the Fenton reaction in “Fenton-like” processes using  $\text{Fe}^{3+}$  (Reactions 22-23) [112] or zero-valent iron ( $\text{Fe}^0$ ) (Reaction 24) [113] have also been investigated, the former producing peroxy radicals ( $\text{HO}_2^\bullet$ ) and the latter as a source of  $\text{Fe}^{2+}$  in the Fenton reaction.





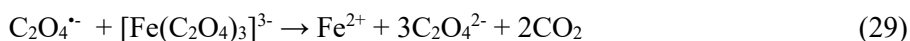
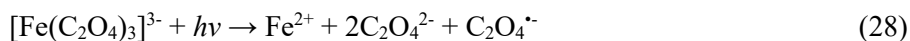
Photo-Fenton based processes are assisted by UV-Vis irradiation, accelerating the regeneration rate of  $\text{Fe}^{2+}$  from  $\text{Fe}^{3+}$  complexes (Reactions 26-26). The most photoactive complex  $[\text{Fe}(\text{OH})]^{2+}$  is predominant at acidic pH, limiting the use of photo-Fenton. Temperature is also an important parameter that has an impact on both Fenton and photo-Fenton reaction rates, since raising the temperature accelerates the oxidation of  $\text{Fe}^{2+}$  by  $\text{H}_2\text{O}_2$  (thermal Fenton) and enhances the light absorption coefficient of  $\text{Fe}^{3+}$  [44]. However, the increase of temperature may lead to higher leaching of iron and consequent deactivation of catalyst in successive cycles, as well as to the thermal decomposition of  $\text{H}_2\text{O}_2$  to water and oxygen above 40 °C [108].



The higher costs of the photo-Fenton process in comparison to the conventional Fenton reaction, due to the use of an irradiation source, are compensated by the lower amount of catalyst required to efficiently generate  $\text{HO}\cdot$  and by the smaller amount of sludge produced [1], which was reported to be 25 times less in a study dealing with the treatment of landfill leachate by conventional Fenton and photo-Fenton processes [114]. It has been suggested that no supplementary iron is required in wastewater effluents containing at least 1.5 mg L<sup>-1</sup> of total iron, to employ the photo-Fenton process [21, 115].

Photo-Fenton at neutral pH has been applied using chelating agents, namely ferrioxalate ( $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ ), ethylenediamine-N,N'-disuccinic acid (EDDS), humic acids (HA) and mixing the wastewater effluents with small amounts of influent sample [47-49]. The former is a photosensitive complex with an extended absorption range, enabling the efficient use of solar light. Besides, in comparison to  $\text{Fe}^{2+}$  hydroxyl-complexes (Reaction 27), ferrioxalate gives a higher quantum yield of  $\text{Fe}^{2+}$  (Reactions 28-29) [116] and generates a higher amount of  $\text{HO}\cdot$

(Reactions 30-33), by providing additional sources of oxidant H<sub>2</sub>O<sub>2</sub> and catalyst Fe<sup>2+</sup> for the Fenton reaction [49].



Solar photo-Fenton using EDDS as an iron-complexing agent can be a feasible process to degrade contaminants (phenol, bisphenol A, sulfamethoxazole, carbamazepine and pyrimethanil) from wastewater effluents, even at neutral and slightly alkaline pH and in the presence of high DOC values [117]. HA can be also used to promote the photo-Fenton reaction due to their characteristics: (i) HA are organic substances resulting from chemical and microbiological transformation of organic matter and are ubiquitous in the environment; (ii) they have a complex chemical structure, which include carboxylic acids, phenolic, alcoholic quinone, amino and amido groups, as well as high amounts of stable free radicals; (iii) HA are able to photoinduce the transformation of non-absorbing organic chemicals due to the absorption of sunlight and consequent generation of HO<sup>•</sup>, ROS, excited triplet states (<sup>3</sup>HA<sup>\*</sup>), singlet oxygen (<sup>1</sup>O<sub>2</sub>) and H<sub>2</sub>O<sub>2</sub> [49]; they are able to improve the process at natural pH due to the enhanced reduction of Fe(III) humate-complexes in comparison with the Fe(III) aquo-complexes [88]. However, HA at high concentrations can also scavenge radicals [88], therefore the overall effect on the MPs removal may be either promoting, neutral or inhibitory. Table 1 summarizes the reports published since 2005 referring the evaluation of matrix effects on Fenton-based processes (more details can be found in Table S3).

Another approach commonly used in photo-Fenton like processes involves the use of radiation to assist the photo-decarboxylation of ferric carboxylates (Reaction 34) [118].



The photoactive ferric complexes are formed between  $\text{Fe}^{3+}$  and carboxylate or polycarboxylate groups, which are functional moieties frequently present in DOM [119]. These are soluble in wastewater under a wide pH range, avoiding the precipitation of  $\text{Fe}^{3+}$  at neutral pH and the consequent need of acidification and pH control of Fenton processes. Another main advantage is the higher molar absorption coefficients in the near UV-Vis spectral regions in comparison to the Fe(III) aquo-complexes [117, 119]. However, such compounds typically able to form photoactive  $\text{Fe}^{3+}\text{L}$  (e.g., oxalic acid, lactic acid, quinolinic acid, fusaric acid, pinolenic acid) are usually highly biodegradable and often absent in wastewater effluents [119]. For this reason, the mixing of effluent with small amounts of influent (3:1 ratio) as a source of these substances has been investigated, as a mean to avoid the addition of supplementary chemical reactants during the treatment process [49]. The effectiveness of this approach for the degradation of the MPs is, however, dependent on the concentration ratio of carboxylate or polycarboxylate compounds and the organic load in the water influents [49].

The electro-Fenton process, is an eco-friendly, electrically assisted Fenton process, consisting in the use of a reactor with inert electrodes which are able to electro-regenerate  $\text{Fe}^{2+}$  from  $\text{Fe}^{3+}$ . In such process, the  $\text{Fe}^{2+}$  is provided from sacrificial cast iron anodes and the  $\text{H}_2\text{O}_2$  is either added to the reactor or generated *in-situ* by the two-electron oxygen reduction reaction in an acidic medium (Reaction 35) [111].



The electricity costs of the electro-Fenton (or photo-electro-Fenton) process, similarly to the photo-Fenton process, are overcome by the smaller amount of catalyst required to efficiently generate  $\text{HO}^\cdot$  and by the smaller quantity of sludge produced, in comparison to the conventional Fenton process.

The water matrix components may raise a negative and/or a positive impact on the effectiveness of Fenton-based processes and the overall result depends on their balance [12, 16, 50]. In complex water matrices containing many species, the degradation of MPs is generally lower than in pure water when Fenton-based processes are employed, implying the use of higher doses of reactants (iron species and H<sub>2</sub>O<sub>2</sub>) [51]. The following factors have a negative impact: (i) light scattering inhibiting the photo-reduction of Fe<sup>3+</sup>; (ii) the scavenging of HO• by water matrix constituents, such as organic acids, NOM (e.g., humic and fulvic acids), inorganic ions (e.g., bicarbonate, carbonate) [120]; and (iii) the formation of complexes (e.g., FeCl<sub>2</sub><sup>+</sup>, FeCl<sub>2</sub><sup>2+</sup>, and Fe(SO<sub>4</sub>)<sub>2</sub><sup>-</sup>) by reaction between iron ions and inorganic anions, reducing the catalytic activity of the free iron species [16]. Specifically, chloride and sulphate can decrease the photo-Fenton reaction rate with MPs by scavenging HO• and producing chlorine and sulphate radicals (Cl<sub>2</sub><sup>-•</sup> and SO<sub>4</sub><sup>-•</sup>), which overall are less reactive than HO•. They can also complex the iron species (Fe<sup>2+</sup> and Fe<sup>3+</sup>), interfering with the reduction of Fe<sup>3+</sup> to Fe<sup>2+</sup> that is required to sustain an efficient Fenton mechanism [12, 52]. Very recently, these species were shown to decrease the conversion of dichlorophenoxyacetic acid from 74.25% in demineralised water to 70.98% in the presence of sulphate and 66.65% in the presence of chloride [121]. In consequence, high organic and inorganic species in water matrices may decrease the removal rates of contaminants [52] and DOC in general, interfering with the degradation pathways and consequently affecting the composition and toxicity of the by-products formed [12, 50]. For instance, the presence of chloride in the water matrix has been linked to the production of chlorinated transformation by-products [14]. Other inhibiting effect can arise from the formation of iron complexes with the by-products generated during the degradation of a certain compound, as observed in the case of prednisolone [46].

In contrast, the following factors have a positive impact on Fenton-based processes: (i) the iron ions naturally occurring in the water matrix may act as an additional source of catalyst for the Fenton reaction; (ii) inherent reductants present in the water matrix (e.g., phenolic compounds) might reduce Fe<sup>3+</sup> to Fe<sup>2+</sup>, increasing the regeneration rate of the catalyst; and (iii) Fe<sup>3+</sup> can react

with compounds containing -COOH and -OH groups, originating complexes with higher quantum yield, which might undergo photo-reduction through a ligand-to-metal charge transfer to  $\text{Fe}^{2+}$  [16, 122]. Although high content of organic species (e.g.,  $16.5 \text{ mg L}^{-1}$  of DOC) may reduce the removal rates of MPs [52], some studies have demonstrated higher removal rates of MPs in actual wastewaters in comparison to simulated wastewater matrices. In a study where this phenomenon was observed for 15 compounds (pharmaceuticals, estrogens, personal care products, and pesticides), a similar DOC reduction in both matrices suggested that the HA present in the wastewater effluents probably produced solvated electrons and  $\text{HO}^\bullet$  upon irradiation [53]. In another report, a DOM content approximately 2000 times higher than the concentration of MPs in the wastewater did not denote a shortcoming on their removal rates, since certain species in the DOM could either act as photosensitizers or complex iron to keep it dissolved, promoting the degradation of MPs by the photo-Fenton reaction mechanism [115].

#### 2.4. Photocatalysis

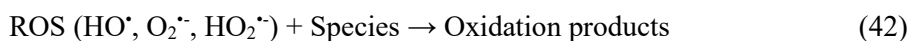
Heterogeneous photocatalysis has been extensively reported in the last decades, not only for water/wastewater and air treatment, but also for production of fuels [1]. Heterogeneous photocatalysis is based on the use of wide band-gap semiconductors, which generate conduction band electrons and valence band holes, under irradiation with light energy ( $h\nu$ ) equal to or higher than the semiconductor band-gap energy (Reaction 36) [123, 124].



The photogenerated conduction band electrons and valence band holes can either recombine to dissipate heat, or migrate to the semiconductor surface, where they can react with species adsorbed on the catalyst surface [123]. The photogenerated valence band holes produce reactive  $\text{HO}^\bullet$  which are strong oxidizing agents, by reaction with water (Reaction 37) and with hydroxide ion under alkaline conditions (Reaction 38), or can also react directly with adsorbed species (Reaction 39) [1].



The photogenerated conduction band electrons usually reduce the adsorbed molecular oxygen (and/or adsorbed reducible species) and generate superoxide radicals (Reaction 40), which can further react with protons to produce peroxide radicals (Reaction 41) [123]. The substrate species then can react with the ROS generated (Reaction 42).



An ideal photocatalyst should be chemically and photochemically stable, should have a high surface area for the adsorption of the reacting species, a high photon absorption coefficient, a small scattering albedo, be easily available and of low cost whenever possible. Generally, the photodegradation rate of MPs increases with catalyst loading up to an optimum concentration corresponding to the maximum amount of catalyst at which all particles are efficiently irradiated, beyond which the efficiency drops off due to the lower penetration of activating photons through the turbid water [58]. Such process is dependent on reactor geometry, the design of which has been rationalised in terms of optimum dimensionless optical thickness of photoreactors [125]. In the last decades, the most common, commercially available photocatalyst has been  $\text{TiO}_2$ , either in bulk or supported on a substrate, due to its relatively high photoactivity, high mineralization efficiency, low cost and toxicity, high photochemical stability and suitable band-gap energy [1, 124].  $\text{ZnO}$  has also been largely used mainly due to its higher electronic conductivity and near band-gap energy [126]. However, its susceptibility to photo-corrosion limits its use and thus  $\text{TiO}_2$  is still the most used photocatalyst. Although it has higher performance in an aqueous slurry suspension, the separation of  $\text{TiO}_2$  from the treated water may in some cases present a minor challenge in industrial scale applications [127]. In consequence, a range of support materials have

been used for the immobilization of TiO<sub>2</sub>, including polymers, metals, silica, carbon materials or ceramics [59]. Ideally, an active support must also promote the interaction between the photocatalyst and the contaminants, without hindering the absorption of active photons, and should be resistant to the oxidizing conditions [59].

The two major shortcomings of heterogeneous photocatalysis over TiO<sub>2</sub> are: (i) the limited absorption of natural sunlight since near-UV radiation is needed for photo-activation and this part represents only ca. 3-5% of the solar radiation reaching the earth surface; and (ii) the relatively high rate of electron-hole pairs recombination which reduces the available charges for the redox reactions. Several studies have been published using different approaches to develop photocatalysts that can address the above shortcoming [7], by creating defect structures on the catalyst [128], by metal deposition on the catalyst surface [129], by semiconductor coupling of the energy bands [130] and by doping with metals/non-metal ions [131]. TiO<sub>2</sub> combinations with noble metals (e.g., silver, gold and platinum) [63] or with carbon-based materials such as graphene-based materials [132, 133], have also been examined. Other carbon materials have been widely studied, including activated carbons [134, 135], carbon xerogels [136], carbon nanotubes [137, 138], graphite [139], and more recently graphitic carbon nitride [140]. The suppression of the recombination of photo-generated charge carriers has been attempted, by adding oxidizing agents/electron acceptors (e.g., inorganic peroxides (S<sub>2</sub>O<sub>8</sub><sup>2-</sup>), Fe<sup>3+</sup>, H<sub>2</sub>O<sub>2</sub>), doping the material with metal ions or anions, by noble metal loading, dye sensitization or using composite semiconductors [126, 141, 142].

The detrimental effect of components co-existing in the water matrix is attributed to the organic and inorganic species intrinsically present in the wastewater [64], including: (i) light attenuation by suspended particles and dissolved species [77]; (ii) the NOM partially consuming HO<sup>•</sup> and other oxidizing species, thus competing with the degradation of MPs [32, 64-67, 69, 70]; (iii) the anions present in wastewater (e.g., bicarbonate, sulphate and chloride) which scavenge HO<sup>•</sup> to form the respective radicals with lower oxidation potential [58, 64-67, 69-72]; and (iv) both organics and inorganics adsorbing onto the catalyst surface, fouling and/or competing for the



active reaction sites [63, 73-76]. Table 1 summarizes the reports published since 2005 referring to the evaluation of matrix effects on photocatalytic processes (more details can be found in Table S4).

The impact of NOM on the photocatalytic degradation of organic compounds has been recently reviewed [143]. NOM plays an important role in sunlight-induced photochemical processes, generally retarding the photocatalytic degradation of pollutants by the combination of radiation attenuation, competition for adsorption on active sites of the catalyst and surface deactivation, and by scavenging both valence band holes and conduction band electrons [144]. The water matrix may not show an effect on the degradation of the MPs, but may strongly affect the rate of mineralization, as shown in a study on solar TiO<sub>2</sub> photocatalytic oxidation of a mixture of four pharmaceuticals (atenolol, hydrochlorothiazide, ofloxacin and trimethoprim) in a synthetic effluent [145]. The impact of the water matrix on the photocatalytic degradation of clofibric acid resulted in a strong decrease of the photocatalytic activity resulting from the competition of NOM, for active sites on the catalyst surface and for reactive species [58]. UV light attenuation plays an additional significant role on the reduction of the rate of degradation of MPs in wastewater.

Inorganic salts in the water matrix (NaCl, FeCl<sub>3</sub>, FeCl<sub>2</sub>, AlCl<sub>3</sub>, CaCl<sub>2</sub>) can have negative impact on the photocatalyst activity, with a generally more pronounced deactivation effects observed at higher salt concentrations [58]. The deactivation of the TiO<sub>2</sub> catalyst by inorganic species has been linked to the competition for free radicals and to the blockage of the active sites on the catalyst surface [58]. Sulphate and carbonate anions might cause strong catalyst deactivation, since both species are strong ROS scavengers, whereas sodium chloride can produce ambiguous effects on the photocatalytic activity of TiO<sub>2</sub>, depending on the salt concentration [58]. The pH and the ionic strength of the wastewater play important roles on the degree of catalyst agglomeration in a suspension, which impact on the effective surface area of the photocatalyst [78] and on the rate of photon absorption [146]. High pH and/or ionic strength of the aqueous solution might result in a higher agglomeration of TiO<sub>2</sub>, decreasing the effective surface area of the photocatalyst [147, 148]. This phenomenon has been observed for the photocatalytic

degradation of sulphonamides, whose removal was favoured at acidic pH [78-80]. The photocatalytic degradation of clofibric acid was shown to be inhibited by chloride ions at low concentrations, which adsorbed on the TiO<sub>2</sub> surface reducing the available active sites. This is justified by the acidic nature of the contaminant and the positively charged surface of the catalyst, resulting from the sample pH lower than the point of zero charge (pH<sub>PZC</sub>) of TiO<sub>2</sub> [58]. At high concentration of NaCl, the ionic strength was the dominant factor of the photocatalytic efficiency, since the electric double layer become more compressed and the clofibric acid could easily reach the catalyst surface [58].

Phosphate can affect positively the degradation of pollutants by generating the reactive radical H<sub>2</sub>PO<sub>4</sub><sup>•</sup> in the presence of holes (Reaction 43) which favours the photocatalytic degradation of carbamazepine over TiO<sub>2</sub> [72]:



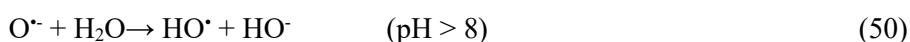
The impact of coexisting substances on the photocatalytic degradation of bisphenol A was studied under simulated solar light irradiation and using bismuth tungstate (Bi<sub>2</sub>WO<sub>6</sub>) as catalyst, suggesting that photogenerated holes are predominant in the reaction system [149]. The degradation of bisphenol A was accelerated in the presence of a low concentration of HA (1 mg L<sup>-1</sup>), while a hindrance was found at concentrations higher than 5 mg L<sup>-1</sup>. The presence of anions (nitrate, chloride, sulphate and bicarbonate) and cations (sodium, potassium, calcium and magnesium) led to inhibitory effects, the latter being ascribed to the chloride resulting from the addition of the chloride salts of each cation [149]. At solution pH lower than 8.7 (pH<sub>PZC</sub> of Bi<sub>2</sub>WO<sub>6</sub>), the positively charged surface of the catalyst attracted anions, decreasing the free active sites and diminishing the reaction rate of bisphenol A. Sulphate had a much stronger inhibition effect than chloride, nitrate and bicarbonate, due to its double charge and larger molecular size which increases the steric hindrance [149]. A minor impact was observed for bicarbonate and nitrate ions, the latter favouring the reaction rate at low concentrations, which can be explained by its photolysis and consequent production of HO<sup>•</sup> [149]. At high salt concentrations, nitrate could be adsorbed on the catalyst surface, competing for the active sites with the target pollutant,

while bicarbonate scavenged HO<sup>•</sup>, producing weakly oxidizing carbonate radicals. The impact of bicarbonate is more significant when the photocatalytic degradation of the target contaminant follows HO<sup>•</sup> attack, rather than hole oxidation. On the contrary, the presence of inorganic Fe<sup>3+</sup> ion in the water and the use of H<sub>2</sub>O<sub>2</sub> oxidative reagent played different effects depending on their concentrations. At concentrations lower than 0.01 mmol L<sup>-1</sup> Fe<sup>3+</sup> or 1 mmol L<sup>-1</sup> H<sub>2</sub>O<sub>2</sub>, there was no effect; at concentrations in the range of 0.01–0.1 mmol L<sup>-1</sup> of Fe<sup>3+</sup> or in the range of 0.1–3 mmol L<sup>-1</sup> of H<sub>2</sub>O<sub>2</sub>, a suppression of the photogenerated holes (the main oxidizing species by Bi<sub>2</sub>WO<sub>6</sub>) was observed; however, higher concentrations of these interfering species enhanced the degradation rate of bisphenol A due to the generation of HO<sup>•</sup> produced by Fe(OH)<sup>2+</sup> under UV irradiation or by photolysis of H<sub>2</sub>O<sub>2</sub> [149].

## 2.5. Ozone-based processes

Ozonation is an AOT widely applied for the purification of drinking water due to the power of O<sub>3</sub> as disinfectant and oxidant. Ozonation has also been used for the treatment of either raw wastewaters, as pre-treatment, or secondary wastewater effluents, as post-treatment, to minimize the release of MPs into the receiving waters [89]. In Switzerland, full-scale UWWTPs have already implemented ozonation as a post-treatment process, aiming 80% average removal of target organic MPs [150].

The transformation of organic substances by ozonation occurs by either reaction with molecular O<sub>3</sub> or reaction with less selective HO<sup>•</sup>, resulting from the decomposition of O<sub>3</sub> at neutral and alkaline pH [13]. In comparison to molecular O<sub>3</sub>, which is a selective oxidant attacking predominantly electron-rich organic moieties (phenols, anilines, olefins, sulphur, and amine moieties), HO<sup>•</sup> are non-selective radicals, more reactive than ozone. The contribution of each pathway depends on the O<sub>3</sub> and HO<sup>•</sup> exposures (i.e., ∫ [O<sub>3</sub>] dt and ∫ [HO<sup>•</sup>] dt) and second order reaction rate constants (Reaction 44-51) [151, 152]. In many cases, high pH values favour the degradation efficiency due to the decomposition of O<sub>3</sub> into HO<sup>•</sup> [153].



Ozonation is an oxidation process that can take place at both the gas-liquid interface and in the bulk liquid, depending on the concentration of the reactants and on the Hatta number [154]. Therefore, the polarity can play an important role in the reaction rate, since non-polar organic compounds tend to accumulate at the interface and be more reactive, while more polar or dissociated substances remain in the bulk liquid [155].

$\text{O}_3$  decomposition is fast during the initial phase ( $t < 20$  s) of natural water ozonation, known as “instantaneous ozone demand”, while during the second phase ( $t > 20$  s) it follows an apparent first-order rate law attributed to radical-type chain reactions, during which  $\text{HO}^\bullet$  are generated [156]. NOM and carbonate/bicarbonate ions interfere with the rate of  $\text{O}_3$  decomposition depending on their concentrations and pH, affecting the yield of  $\text{HO}^\bullet$  [157]. Besides the scavenging effect of  $\text{HO}^\bullet$  by NOM [13, 23, 87, 90-95] and carbonate/bicarbonate [13, 92, 93, 97, 98], other anions (e.g., chloride, phosphate, sulphate) can also act as ozonation inhibitors [97, 98].

The main mechanism of  $\text{O}_3$  decomposition and generation of  $\text{HO}^\bullet$  in wastewater is the direct reaction with specific reactive moieties of the NOM (e.g., phenolic, amino and olefinic groups), considering that the initiation step of the radical chain reaction between  $\text{O}_3$  and hydroxide anions has a small rate constant [156]. The reactions of  $\text{O}_3$  with DOM (Reactions 52-55) are summarized as the follows [158, 159].



Both the concentration and the composition of DOC determine the rate of decomposition of aqueous  $\text{O}_3$ , therefore DOC is a crucial water quality parameter that is monitored to normalize the dosing of  $\text{O}_3$  [156]. Table 1 summarizes the reports published since 2005 referring the evaluation of matrix effects on ozone-based processes (more details can be found in Table S5). The  $\text{O}_3$  dose required to degrade the antibiotic ofloxacin was strongly affected by the matrix (synthetic water vs wastewater effluent), showing the competition between the NOM and the target pharmaceutical for  $\text{O}_3$  and suggesting that certain moieties of NOM present in wastewater were preferably attacked [94]. Even when the degradation rate of the organic MPs is not affected, total organic carbon (TOC) removal can be significantly affected due to the refractory nature of the organic matter, as observed in synthetic effluents treated by ozonation [145].

The impact of the inorganic ions (chloride, sulphate and bicarbonate, potassium, calcium and magnesium) or extracts of NOM, and the type of water matrices (ultrapure, river water, influent and effluent wastewaters) on the removal of flumequine by ozonation, has been shown to be insignificant [90]. However, rice straw and pig manure NOM extracts, promoted the oxidation of the target pollutant [90]. The scavenging of NOM and carbonate/bicarbonate on  $\text{HO}^\bullet$  in different water matrices containing similar DOC and bicarbonate contents demonstrated different DOM reactivity [13]. Moreover, the higher carbonate-alkalinity led to slower kinetics of pCBA removal, ascribed to the slower kinetics of  $\text{O}_3$  decomposition due to the inhibition by the carbonate/bicarbonate ions in the water [13].

Another study reported that nitrate enhanced the degradation rate of phenazone by ozone, whereas other anions (chlorine, sulphate and bicarbonate) reduced the rate, following the order: sulphate > chloride > bicarbonate [160]. While the scavenging of  $\text{HO}^\bullet$  by bicarbonate is well-known, the

lower degradation rate of phenazone in the presence of sulphate and chloride was attributed to the formation of weaker  $\text{Cl}_2^{\cdot-}$  and  $\text{SO}_4^{\cdot-}$  radicals [160].

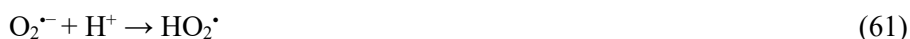
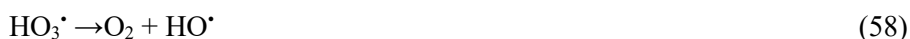
The main drawback of the ozonation process is the generally limited rate of DOC mineralization and consequent accumulation of unknown reaction by-products, resulting from the incomplete oxidation of the target compounds and from the reaction with the water matrix constituents [161]. Undesirable toxic oxidation by-products include nitrosamines (e.g., N-Nitrosodimethylamine, NDMA), bromate and formaldehyde [161]. Although these by-products may increase the toxicity of the treated wastewater, they are typically biodegradable and therefore a biological post-filtration is usually applied [161]. The limited extent of DOC mineralization can be overcome by adding catalysts or  $\text{H}_2\text{O}_2$ .

The peroxone process combining  $\text{O}_3/\text{H}_2\text{O}_2$  accelerates the conversion of  $\text{O}_3$  to  $\text{HO}^{\cdot}$ , which can decrease the reaction time needed to degrade the MPs [13]. The degradation efficiency of the MPs reaches a maximum at certain concentration of  $\text{H}_2\text{O}_2$  beyond which inhibition occurs [160]. Two  $\text{HO}^{\cdot}$  are produced from the reaction between two  $\text{O}_3$  and one  $\text{H}_2\text{O}_2$  molecule, therefore the ratio between the  $\text{H}_2\text{O}_2$  supply rate and the  $\text{O}_3$  absorption rate should be 0.5 or slightly higher [162]. A low  $\text{H}_2\text{O}_2$  dose can catalytically decompose  $\text{O}_3$  to generate a substantial amount of  $\text{HO}^{\cdot}$ , which favours the oxidation of MPs, whereas an excessive  $\text{H}_2\text{O}_2$  dose can favour the reaction with  $\text{HO}^{\cdot}$  to form a weaker hydroperoxyl radical ( $\text{HO}_2^{\cdot}$ ) [160].

The use of heterogeneous catalysts or photocatalysts is an attractive solution in ozonation, since the combination of two or more AOTs can lead to higher removal rates in comparison to the single processes. Usually, the application of ozonation alone rarely lead to complete mineralization of MPs, since some reaction intermediates, including specific carboxylic acids, may not be easily destroyed by  $\text{O}_3$  or by its produced oxidizing radicals. When the organic compounds are not completely degraded, the partial oxidation may produce by-products that are more toxic than the parent pollutants [163, 164]. Thus, the addition of catalysts in catalytic ozonation can improve the oxidation efficiency of ozone and also its potential to convert oxidation by-products into  $\text{CO}_2$  [100]. The most widely used catalysts include transition metal oxides ( $\text{TiO}_2$ ,  $\text{MnO}_2$ ,  $\text{Al}_2\text{O}_3$ ,

FeOOH, and CeO<sub>2</sub>), metals (Cu, Ru, Pt and Co) on supports (SiO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub> and activated carbon), zeolites modified with metals, activated carbon and natural minerals [165].

Recently, photocatalytic ozonation has been studied as an alternative to photocatalysis and ozonation due to the increased production of HO<sup>•</sup> through the formation of an ozonide radical (O<sub>3</sub><sup>•-</sup>) in the adsorption layer of a semiconductor (e.g., TiO<sub>2</sub>) and lower electron-hole recombination, in comparison to ozonation and photocatalysis, respectively [1]. Specifically, the O<sub>3</sub><sup>•-</sup> species (Reaction 56) generated from the reaction of ozone with the semiconductor electrons react with H<sup>+</sup> in the solution, forming HO<sub>3</sub><sup>•</sup> radicals (Reaction 57) which then evolve to produce oxygen and HO<sup>•</sup> (Reaction 58). In this scenario, it must be also considered that HO<sup>•</sup> can react with ozone (Reaction 59). When ozone is completely consumed, dissolved O<sub>2</sub> can accept the semiconductor conduction band electrons, generating O<sub>2</sub><sup>•-</sup> (Reaction 60), which in turn can be protonated (Reaction 61). HO<sub>2</sub><sup>•</sup> radicals can also originate HO<sup>•</sup>, according to the pathway shown by Reactions 62-63 [166].

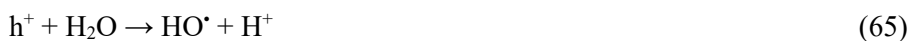


Another possible reaction pathway has been proposed by Kopf et al. [167]. These authors suggested that the photocatalytic ozonation reactions are initiated by an electron transfer from TiO<sub>2</sub> to O<sub>2</sub> (Reactions 64-67), followed by reaction of O<sub>2</sub><sup>•-</sup> with O<sub>3</sub> (Reaction 68), giving place to Reactions 57-58, as well as to Reactions 69-72.

Charge separation:



Charge transfer of positive charge:



Electron transfer and further reactions:



Oxidation of the organic compound R:



or



There are some factors that can affect the photocatalytic ozonation process, some of them similar to those affecting the single processes, such as the ozone dosage, pH and nature of the photocatalyst. The TOC removal can increase with the ozone dosage, but low ozone dosages are economically more attractive [168]. The pH of the wastewater has a stronger influence on the ozonation reactions, and may impact the degradation pathways and the kinetics in the reaction process, which can also occur in the photocatalytic ozonation process [169, 170]. The synergistic effect between both processes can reduce the treatment costs and reaction time under optimum operating conditions (e.g., ozone concentration, the catalyst properties, the loading in the reactor and the usage of more cost-efficient and long-lasting UV sources, such as UV LEDs) [165]. Catalytic and photocatalytic ozonation has been studied for the removal of pharmaceuticals in



effluents from UWWTPs, however the available data about the impact of water matrix are still unclear. Catalytic ozonation was more efficient than ozonation to degrade mesoxalic and oxalic acids, being almost unaffected by the presence of the inorganic anions or suspended solids. Catalytic ozonation of oxalic acid using copper oxide supported on mesoporous silica as catalyst in the presence of inorganic anions ( $\text{HCO}_3^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ ), was inhibited only in the presence of  $\text{PO}_4^{3-}$ , while ozonation alone was almost inhibited by the suspended solids and strongly depended on presence of these inorganic anions [97]. In turn, in other work dealing with the degradation of carboxyl acids (formic, acetic, oxalic and maleic acid), the copper-catalysed continuous ozonation was strongly influenced by the water matrix, ascribing the negative effect to the complexation with organic matter reducing the availability of metal as catalyst [102]. Although the reaction time needed to reach 99% conversion of 3 compounds (diclofenac, sulfamethoxazole and caffeine) was similar, the removal rates were slightly slower in wastewater effluents than in ultrapure water, by catalytic and photocatalytic ozonation in the presence of  $\text{TiO}_2$  [28]. The degradation of diclofenac and amoxicillin by photocatalytic ozonation, using  $\text{TiO}_2$  as photocatalyst, was similar in both ultrapure and wastewater, however, the oxamic acid formed as by-product was refractory to photocatalytic ozonation in the case of spiked wastewater effluents [101]. Another study on the degradation of diclofenac by  $\text{TiO}_2$ -photocatalytic ozonation showed that it was only slightly affected by the organic–inorganic matter of the urban wastewater [92].

### **3. Future challenges and conclusions**

Wastewater quality is critical for the performance of AOTs, namely for those here reviewed: photolysis, UV/ $\text{H}_2\text{O}_2$ , Fenton-based processes, photocatalysis, and ozone-based processes. The efficiency of each process results from the complex interplay of inhibitory and promoting effects originated by the water matrix constituents. Wastewater components leading to inhibitory effects on the removal of MPs include NOM (light attenuation; scavenging effects; generation of by-products; adsorption to catalyst in photocatalytic processes); and inorganic anions (scavenging effects; formation of less active radicals; iron complexation in the case of Fenton; adsorption to

the catalyst surface or decrease of its effective surface area, in the case of photocatalytic processes). Promoting effects can result from NOM originating ROS, which enhance indirect photolysis; from nitrate ions producing ROS in the case of photolysis; iron ions as additional source of catalyst in Fenton-based processes; and phenolic or other compounds containing -COOH and -OH groups, which can regenerate the catalyst. However, it is difficult to understand and discriminate the role of each single component. Table 2 summarizes the inhibitory and promoting mechanisms of different wastewater components, aiming to provide a guide on the most suitable treatment as function of the wastewater composition. The available information on the water matrix effects on the removal efficiency of MPs in UWWTPs effluents is still limited and more studies are needed to enlighten the mechanisms and the impact of the main components of the water.

**Table 2.** Summary of inhibitory (-) and promoting (+) effects of wastewater components, affecting the efficiency of the processes discussed in this review, namely photolysis, UV/H<sub>2</sub>O<sub>2</sub>, Fenton-based, photocatalysis, and O<sub>3</sub>-based processes.

	Photolysis	UV/H <sub>2</sub> O <sub>2</sub>	Fenton-based	Heterogeneous photocatalysis	O <sub>3</sub> -based
Organic matter Humic acids	+/-	+/-	-	+/-	-
Inorganic ions	+/-	+/-	+/-	-	-
NO <sub>3</sub> <sup>-</sup>	+	+		-	
NO <sub>2</sub> <sup>-</sup>				-	
PO <sub>4</sub> <sup>3-</sup>				-	-
Cl <sup>-</sup>	+		+/-	-	-
SO <sub>4</sub> <sup>2-</sup>	+		-	-	-
HCO <sub>3</sub> <sup>-</sup>	-		-	-	-
CO <sub>3</sub> <sup>-</sup>			-	-	-
Ca <sup>2+</sup>				-	
Iron ions			+		

Phenolic compounds (containing -COOH and -OH groups)			+		
pH/ionic strength				-	
Number of papers (2005-2018)	19	18	20	32	24

On the other hand, it is well known that removal efficiencies of MPs depend on their chemical nature and on the AOT under study, but limited information is available on the effect of wastewater coexisting substances on the elimination of different types of substances by different AOTs. For instance, under UV, UV/H<sub>2</sub>O<sub>2</sub>, and photo-Fenton, gabapentin and metformin were found as the most recalcitrant compounds from a set of 8 MPs, which followed the same order of degradation [57]. Another report on the degradation of pharmaceuticals showed the same trend for UV-C radiation, heterogeneous photocatalysis, Fenton and photo-Fenton systems (amoxicillin > naproxen > metoprolol > phenacetin), but metoprolol was the most recalcitrant in the ozone-based processes [91], showing that the removal depends also on the MP nature. A recent study on UV/chlorine treatment showed that the degradation of MPs having electron-withdrawing groups (e.g., -NO<sub>2</sub>, -Cl, -F) was largely attributed to HO<sup>•</sup>, while the degradation of those containing electron-donating groups (e.g., phenol, aniline, alkyl-/alkoxy aromatics, or olefins) was highly ascribed to other reactive species such as Cl<sup>•</sup>, Cl<sub>2</sub><sup>-•</sup> and ClO<sup>•</sup> [6]. In the same study, it was shown that the scavenging of NOM on ClO<sup>•</sup> was much higher than that observed on HO<sup>•</sup> and Cl<sup>•</sup>, suggesting that the removal of MPs that are readily degradable by ClO<sup>•</sup> can be largely inhibited by the presence of NOM. On the contrary, alkaline components were ascribed to scavenge HO<sup>•</sup> and Cl<sup>•</sup> at higher extent and thus the MPs degraded primarily by these radicals are those which removal is most inhibited by alkalinity [6].

Moreover, the scarce data available on the effects of wastewater components on the removal of MPs with different chemical nature by hydroxyl radical-mediated AOTs show ambiguous results. For example, a better performance was reported for UV/H<sub>2</sub>O<sub>2</sub> to degrade several organophosphate esters and some of them (chlorinated and one aliphatic) were recalcitrant to ozonation, but the

presence of HA improved only the ozonation process, with an opposite trend observed in UV/H<sub>2</sub>O<sub>2</sub> treatment [105]. On the contrary, the same order of degradation rates (UV < UV/H<sub>2</sub>O<sub>2</sub> < Fenton < solar irradiation < photo-Fenton) was observed regardless of the type of WW analysed, in a study comparing the effluents from activated sludge, moving bed bioreactor and coagulation-flocculation treatments [20].

Besides interfering with the process performance, the water matrix might also have an impact on the production and on the nature of the transformation by-products. The degradation of MPs is usually accompanied by the formation of numerous transformation by-products through unaccountable pathways and the matrix components may impact these pathways. For example, reactions in the presence of chlorides are prone to originate toxic chlorinated by-products. However, more studies addressing the effect of diverse water matrix components on the transformation products, are still needed to better understand their possible impacts. Other important parameters that are important to consider for the evaluation of the impact of the water matrix are the biodegradability and the toxicity of the effluents that are generated. A thorough investigation on the nature of the wastewater components is required not only to improve the performance of advanced water treatment systems, but also to minimize the formation of toxic reaction by-products, to enhance the biodegradability of the treated effluents and to reduce the ecotoxicity of the treated effluents. Complete mineralization of the organic matter is difficult and in general not needed if the by-products formed are biodegradable and non-toxic. Standard biodegradability and toxicity tests may be used to establish the levels of treatment needed to achieve a safe effluent.

Future research on treatment technologies should consider the complex interactions between matrix constituents and the oxidative species formed, aiming to maximize the performance of AOTs, since lower efficiencies and higher costs could be expected in real case scenario. With this review, we attempted to provide a comprehensive data analysis of the available studies using real water matrices, showing the lack of systematic understanding of the role of each wastewater component for all AOTs herein reviewed and encouraging the need of more studies applying real

matrices. Although complex, the role of matrix constituents is fundamental for future employment of AOTs in industrial-scale water treatment processes to remove MPs and to protect the environment.

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## Supplementary Information

### **Impact of water matrix on the removal of micropollutants by advanced oxidation technologies**

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**Table S1.** Matrix effects occurring in studies dealing with photolysis and UV/H<sub>2</sub>O<sub>2</sub>, published since 2005. Unless otherwise stated, the experimental conditions refer to the tested conditions for the evaluation of matrix effects.

AOT	Target pollutant Concentration	Matrices	Experimental conditions	Main conclusions	Reference
UV UV/H <sub>2</sub> O <sub>2</sub>	Bisphenol A 520 µM	- UPW; - WW effluent (pH 7.43; DOC 10.74 mg L <sup>-1</sup> ; conductivity 1180 µS cm <sup>-1</sup> ; Cl <sup>-</sup> 111.9 mg L <sup>-1</sup> ; NO <sub>3</sub> <sup>-</sup> 47.5 mg L <sup>-1</sup> ; SO <sub>4</sub> <sup>2-</sup> 121.8 mg L <sup>-1</sup> ), Germany.	- Stirred batch photoreactor; - V 750 mL; T 298 K; - Optical path length 4 cm; - Irradiation source: UV immersed LP Heraeus Hg lamp TN 15/35 with a nominal output of 15 W (λ <sub>max</sub> = 254 nm), located at the centre axis of the reactor, in a quartz sleeve; - 0, 250, 500, 750 µM H <sub>2</sub> O <sub>2</sub> .	The matrix played an important role on the photodegradation yield. The removal rate of bisphenol A by photolysis was slightly higher in WW than in UPW, probably due to the ROS produced in the effluent. On the contrary, the removal rate by UV/H <sub>2</sub> O <sub>2</sub> was lower in the WW.	[4]
UV/H <sub>2</sub> O <sub>2</sub>	Benzoylcegonine 2.8×10 <sup>-5</sup> ± 4.0×10 <sup>-6</sup> mol L <sup>-1</sup>	- UPW (pH 6.0; conductivity 2.5 µS cm <sup>-1</sup> ; TOC 0.248 mg L <sup>-1</sup> ; NO <sub>3</sub> <sup>-</sup> 1.0 mg L <sup>-1</sup> ); - SW (pH 7.8; conductivity 930 µS cm <sup>-1</sup> ; TOC 46.37 mg L <sup>-1</sup> ; NO <sub>3</sub> <sup>-</sup> 25.8 mg L <sup>-1</sup> ; NO <sub>2</sub> <sup>-</sup> 0.17 mg L <sup>-1</sup> ), Grand Union Canal, UK; - SWW (pH 6.0; conductivity 80 µS cm <sup>-1</sup> ; TOC 20.79 mg L <sup>-1</sup> ; NO <sub>3</sub> <sup>-</sup> 1.0 mg L <sup>-1</sup> ); - WW effluent (pH 7.8; conductivity 960 µS cm <sup>-1</sup> ; TOC 43.25 mg L <sup>-1</sup> ; NO <sub>3</sub> <sup>-</sup> 52.4 mg L <sup>-1</sup> ; NO <sub>2</sub> <sup>-</sup> 0.17 mg L <sup>-1</sup> ), Leicestershire, UK.	- Microcapillary film array photoreactor; - Irradiation source: UV monochromatic lamp (Germicidal G8T5, 8W) emitting at 253.7 nm; - [H <sub>2</sub> O <sub>2</sub> ]/[BE] ~ 500.	The removal of benzoylcegonine was affected by the matrix, mainly due to the presence of different xenobiotics and natural compounds that can act as HO <sup>•</sup> scavengers and as inner filters. Moreover, the presence of NO <sub>3</sub> <sup>-</sup> in higher concentration in WW promoted the removal, in comparison to SW.	[39]
UV/H <sub>2</sub> O <sub>2</sub>	Benzoylcegonine 0.6–18.5 mg L <sup>-1</sup>	- UPW (pH 6.0; conductivity 2.5 µS cm <sup>-1</sup> ; TOC 0.248 mg L <sup>-1</sup> ; NO <sub>3</sub> <sup>-</sup> 1.0 mg L <sup>-1</sup> ); - SW (pH 7.8; conductivity 930 µS cm <sup>-1</sup> ; TOC 46.37 mg L <sup>-1</sup> ; NO <sub>3</sub> <sup>-</sup> 25.8 mg L <sup>-1</sup> ; NO <sub>2</sub> <sup>-</sup> 0.17 mg L <sup>-1</sup> ), Grand Union Canal, UK; - SWW (pH 6.0; conductivity 80 µS cm <sup>-1</sup> ; TOC 20.79 mg L <sup>-1</sup> ; NO <sub>3</sub> <sup>-</sup> 1.0 mg L <sup>-1</sup> ); - WW effluent (pH 7.8; conductivity 960 µS cm <sup>-1</sup> ; TOC 43.25 mg L <sup>-1</sup> ; NO <sub>3</sub> <sup>-</sup> 52.4 mg L <sup>-1</sup> ; NO <sub>2</sub> <sup>-</sup> 0.17 mg L <sup>-1</sup> ), Leicestershire, UK.	- Microcapillary film array photoreactor; - Irradiation source: UV monochromatic lamp (Germicidal G8T5, 8W) emitting at 253.7 nm; - H <sub>2</sub> O <sub>2</sub> concentration: 10 <sup>-4</sup> - 10 <sup>-3</sup> M..	The removal efficiency was affected by organic and inorganic compounds present in the matrices.	[40]
UV/H <sub>2</sub> O <sub>2</sub>	Atrazine, sulfamethoxazole and N-nitrosodimethylamine 0.5 – 11 µM	- 3 lake waters, Switzerland and Norway; - WW effluent (DOM 3.9 mg C L <sup>-1</sup> ; alkalinity 6.5 mg CaCO <sub>3</sub> L <sup>-1</sup> ), Switzerland.	- 500 mL cylindrical glass vessel filled with 350 mL of solution; - Irradiation source: UV immersed LP Heraeus Hg lamp TN 15/35 with a nominal output of 15 W (λ <sub>max</sub> 254 nm), with a quartz cooling jacket; - MP Hg arc lamp (Heraeus Noble-light model TQ718, nominal power 500 – 700 W) and a UV W-55 glass band pass filter (λ 308 – 410 nm) in the cooling jacket.	The degradation rate was higher in waters with lower DOM concentration and/or lower HO <sup>•</sup> scavenging rates. The reactivity of DOM was different in different waters with the same DOC concentration.	[13]

<b>UV UV/H<sub>2</sub>O<sub>2</sub></b>	Carbamazepine, clarithromycin, diclofenac, metoprolol, benzotriazole, mecoprop ng L <sup>-1</sup> to µg L <sup>-1</sup> levels	- WW effluents with different secondary treatment, namely activated sludge (pH 7.8; TOC 37 mg L <sup>-1</sup> ; COD 63 mg L <sup>-1</sup> ; alkalinity 273 mg CaCO <sub>3</sub> L <sup>-1</sup> ; Fe <sub>total</sub> 0.9 mg L <sup>-1</sup> ; TSS 12 mg L <sup>-1</sup> ); moving bed bioreactor (pH 7.4; TOC 20.2 mg L <sup>-1</sup> ; COD 35 mg L <sup>-1</sup> ; alkalinity 85 mg CaCO <sub>3</sub> L <sup>-1</sup> ; Fe <sub>total</sub> 1.6 mg L <sup>-1</sup> ; TSS 14 mg L <sup>-1</sup> ) and coagulation flocculation (pH 7.9; TOC 57.2 mg L <sup>-1</sup> ; COD 90 mg L <sup>-1</sup> ; alkalinity 231 mg CaCO <sub>3</sub> L <sup>-1</sup> ; Fe <sub>total</sub> 1.9 mg L <sup>-1</sup> ; TSS 30 mg L <sup>-1</sup> ), Lausanne, Switzerland.	- 300 mL double-wall, water-jacketed glass batch stirred reactors; - UV-C irradiation source: 36 W, low-pressure amalgam lamp (λ <sub>max</sub> 254 nm); - H <sub>2</sub> O <sub>2</sub> : 25 mg L <sup>-1</sup> .	Regardless the type of secondary treatment, the degradation rates were higher when using UV/H <sub>2</sub> O <sub>2</sub> than UV-C. Both UV-based processes removed 80% of the selected MPs. Comparing matrices, the higher removal of both pollutants and TOC was achieved when using effluents resulting from moving bed bioreactor, following by activated sludge and coagulation flocculation. The UV/H <sub>2</sub> O <sub>2</sub> process led to a higher degradation rate of the MPs and TOC abatement.	[20]
<b>UV</b>	Hydrochlorothiazide 1 µM	- UPW; - SW from a public reservoir, Spain; - WW effluent (pH 8.0; TOC 23.3 mg L <sup>-1</sup> ; alkalinity 250 mg CaCO <sub>3</sub> L <sup>-1</sup> ), Spain.	- 500 mL cylindrical glass vessel filled with 350 mL of solution; - Irradiation source: UV immersed LP Heraeus Hg lamp TN 15/35 with a nominal output of 15 W (λ <sub>max</sub> 254 nm), located at the centre axis of the reactor, in a quartz sleeve; - T 20 °C.	Photodegradation led to a lower removal rate in the WW, intermediate in the SW and higher in UPW, which can be explained by the DOM present in the studied matrices, absorbing part of UV radiation.	[23]
<b>UV</b>	Azathioprine, cyclophosphamide, cytarabine, doxorubicin, methotrexate, 5-fluorouracil, flutamide and mitotane 100 µg L <sup>-1</sup>	- DI (pH 6.0; turbidity <0.1 NTU; TOC 0.08 mg L <sup>-1</sup> ; Total alkalinity <5.0 mg L <sup>-1</sup> ; NO <sub>3</sub> <sup>-</sup> <0.05 mg L <sup>-1</sup> ; SO <sub>4</sub> <sup>2-</sup> <0.05 mg L <sup>-1</sup> , Cl <sup>-</sup> <5.0 mg L <sup>-1</sup> ); - Treated water from water treatment plant (pH 8.0; turbidity 0.2 NTU; TOC 0.8 mg L <sup>-1</sup> ; alkalinity 13.0 mg L <sup>-1</sup> ; NO <sub>3</sub> <sup>-</sup> 3.2 mg L <sup>-1</sup> ; SO <sub>4</sub> <sup>2-</sup> 21.6 mg L <sup>-1</sup> , Cl <sup>-</sup> 10.0 mg L <sup>-1</sup> ); - WW effluent (pH 6.7; turbidity 5.3 NTU; TOC 10.6 mg L <sup>-1</sup> ; alkalinity 54.9 mg L <sup>-1</sup> ; NO <sub>3</sub> <sup>-</sup> 6.3 mg L <sup>-1</sup> ; SO <sub>4</sub> <sup>2-</sup> 45.1 mg L <sup>-1</sup> , Cl <sup>-</sup> 145.5 mg L <sup>-1</sup> ).	- Cylindrical photoreactor (1 L) - Irradiation source: 5 W Philips UV lamp (λ = 254 nm); Addition of HA, HCO <sub>3</sub> <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , Cl <sup>-</sup> , and SO <sub>4</sub> <sup>2-</sup> .	The presence of HA decreased the degradation rates of the target pollutants. NO <sub>3</sub> <sup>-</sup> (0.5 to 5 mg L <sup>-1</sup> ) promoted their photodegradation; whereas HCO <sub>3</sub> <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup> and Cl <sup>-</sup> did not affect it. The performance of the UV treatment was not reduced when applied to treated water since the TOC content of this matrix was very low. However, the degradation efficiency decreased in the WW effluent, with a much higher TOC content (10.6 mg L <sup>-1</sup> ). Furthermore, the addition of S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> and H <sub>2</sub> O <sub>2</sub> increased the degradation efficiency.	[24]
<b>UV UV/H<sub>2</sub>O<sub>2</sub></b>	E1, E2, EE2 1.3-1.5 mg L <sup>-1</sup>	- DW; - WW effluent (pH 7.5-7.8; DOC 6.1-11 mg L <sup>-1</sup> ; COD 18.5-21.7 mg L <sup>-1</sup> ; BOD <sub>5</sub> 3-5.8 mg L <sup>-1</sup> ; SS 2.0-4.7 mg L <sup>-1</sup> ; NH <sub>4</sub> <sup>+</sup> 0.6-4.24 mg L <sup>-1</sup> ; NO <sub>2</sub> <sup>-</sup> 0.09-0.54 mg L <sup>-1</sup> ; NO <sub>3</sub> <sup>-</sup> 3.68-4.54 mg L <sup>-1</sup> ), France.	- Commercial UVC reactor (COMAP WT) and a 55 W LP lamp (λ <sub>max</sub> 254 nm); - Reactor: 81.5 cm long, 5.4 cm diameter, 1 cm distance between the lamp sleeve and the inner side of the chamber; - V 1.12 L; T 20 °C.; - H <sub>2</sub> O <sub>2</sub> : 10, 40 and 90 mg L <sup>-1</sup> .	UV photolysis was more efficient to degrade E1 than E2 and EE2 in both matrices, being the degradation rate constants in the same order of magnitude, regardless the matrix. This low impact of the matrix on degradation rates was attributed to: (i) ROS formed by the action of UV on organic components of the matrices, probably balancing the low transmittance of the WW; and (ii) NO <sub>3</sub> <sup>-</sup> content, known to act as HO <sup>•</sup> precursor. UV/H <sub>2</sub> O <sub>2</sub> process highly increased the removals of all hormones, but it was significantly affected by the water matrix, with lower degradation rate constants obtained in treated WW. The NOM competing for UV irradiation, and scavengers competing for HO <sup>•</sup> (e.g., humic substances, Cl <sup>-</sup> , HCO <sub>3</sub> <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup> , and NO <sub>3</sub> <sup>-</sup> ) were suggested as main factors impacting the removals.	[25]

UV	O-phenylphenol, methyl paraben, propyl paraben, triclosan, bisphenol A 0.5 mg L <sup>-1</sup>	- UPW; - River water (pH 6.8; DOC 1.42 mg L <sup>-1</sup> ; TC 3.70 mg L <sup>-1</sup> ; NO <sub>3</sub> <sup>-</sup> 8.40 mg L <sup>-1</sup> ; Cl <sup>-</sup> 8.37 mg L <sup>-1</sup> ; PO <sub>4</sub> <sup>3-</sup> < 0.044 mg L <sup>-1</sup> ; SO <sub>4</sub> <sup>2-</sup> 7.0 mg L <sup>-1</sup> ), Northwest of Spain; - WW effluent (pH 7.1; DOC 3.61 mg L <sup>-1</sup> ; TC 12.8 mg L <sup>-1</sup> ; NO <sub>3</sub> <sup>-</sup> 4.7 mg L <sup>-1</sup> ; Cl <sup>-</sup> 23.1 mg L <sup>-1</sup> ; PO <sub>4</sub> <sup>3-</sup> 1.32 mg L <sup>-1</sup> ; SO <sub>4</sub> <sup>2-</sup> 30.4 mg L <sup>-1</sup> ).	- Homemade photoreactor with 20 mL of selected water matrix exposed; - UV Irradiation source: two 8 W LP lamps (254 nm); - Effect of NO <sub>3</sub> <sup>-</sup> addition (25 mg L <sup>-1</sup> ).	Overall, the removal efficiencies were in the following order: UP > SW > WW. NO <sub>3</sub> <sup>-</sup> had a positive effect in the removal of the investigated pollutants under sunlight and UV radiation, mainly by the enhancement of transformation routes involving HO <sup>•</sup> . In ultrapure and river water, NO <sub>3</sub> <sup>-</sup> addition reduced the compounds stability, while not significant changes were found in WW. However, reactive species could be partially consumed by DOC, reducing the removal efficiency.	[29]
UV	Monensin, salinomycin, narasin 0.5 mg L <sup>-1</sup>	- DI; - WW effluent (pH 7.4; Cl <sup>-</sup> 23.1 mg L <sup>-1</sup> ; DOC 0.435 mg L <sup>-1</sup> ; NO <sub>3</sub> <sup>-</sup> 1.45 mM; HCO <sub>3</sub> <sup>-</sup> 0.120 mM; CO <sub>3</sub> <sup>2-</sup> 0.000141 mM).	- Cylindrical quartz reactor (100 mL) kept in a photochamber; - Irradiation source: 4-W LP UV lamp ( $\lambda = 254$ nm); - Addition of DOM, NO <sub>3</sub> <sup>-</sup> .	The photodegradation rate of monensin was significantly increased in WW in comparison with deionized water while the photodegradation of salinomycin was not enhanced. The overall photodegradation of studied compounds in real water matrices is a result of both direct and indirect photolysis. NO <sub>3</sub> <sup>-</sup> and DOM increased the photodegradation of monensin and salinomycin. An exception was found for the degradation of salinomycin in the presence of one type of DOM.	[30]
UV	Caffeine, carbamazepine, diuron, simazine, sulfamethoxazole, triclosan, 2,4-dichlorophenoxyacetic acid 150 $\mu$ g L <sup>-1</sup>	- UPW; - WW effluent (pH 7.85±0.21; DOC 11.55±2.05 mg L <sup>-1</sup> ; COD 33.00±5.65 mg L <sup>-1</sup> ; NO <sub>3</sub> <sup>-</sup> 26.25±0.64 mg L <sup>-1</sup> ; UVA <sub>254</sub> 0.36±0.02 cm <sup>-1</sup> ; UVA <sub>254</sub> /DOC 3.10±0.28 m <sup>-1</sup> mg <sup>-1</sup> ), Victoria, Australia	- Sealed quartz test tubes (20 mL); - Irradiation source: natural (average solar irradiance 7.7-9.2 KW m <sup>-2</sup> ) and simulated sunlight xenon arc lamp with an UV range of 290–400 nm; - Effect of HA (DOC of 0, 2 and 4 mg L <sup>-1</sup> ) or NO <sub>3</sub> <sup>-</sup> (10 mg L <sup>-1</sup> and 20 mg L <sup>-1</sup> ) addition.	The photodegradation rates of the studied compounds were significantly greater in the WW than in the UPW, indicating they primarily degraded via indirect photolysis. However, sulfamethoxazole and triclosan were mainly degraded via direct photolysis. NO <sub>3</sub> <sup>-</sup> could act as photosensitizer and produce HO <sup>•</sup> , promoting the photodegradation of the MPs. The addition of NO <sub>3</sub> <sup>-</sup> promoted the photolysis of all compounds, with minor effect on those which indirect photolysis was not the main degradation pathway. HA enhanced the degradation of caffeine, diuron and sulfamethoxazole, inhibiting the photolysis of the other compounds.	[15]
UV UV/H <sub>2</sub> O <sub>2</sub>	Monensin, salinomycin, narasin, nigericin 0.8 – 3.0 $\mu$ M	- Deionized water (buffered at pH 7.0); - SW (SW); - WW effluent (pH 7.4; DOC 0.435 mg L <sup>-1</sup> ; Cl <sup>-</sup> 0.41 mM; NO <sub>3</sub> <sup>-</sup> 1.45 mM; PO <sub>4</sub> <sup>3-</sup> 0.95 mM; HCO <sub>3</sub> <sup>-</sup> 0.00011 mM; CO <sub>3</sub> <sup>2-</sup> 0.12 mM).	- 60 mL cylindrical quartz reactor with a 4-W LP UV lamp ( $\lambda_{\max}$ 254 nm); - Incident light intensity 2.0 mW·cm <sup>-2</sup> ( $\approx$ to a photo fluence rate of $3.36 \times 10^{-6}$ Einstein·L <sup>-1</sup> ·s <sup>-1</sup> ); - Fluences from 0 to $6.05 \times 10^{-4}$ Einstein·L <sup>-1</sup> ; - 30 mg L <sup>-1</sup> H <sub>2</sub> O <sub>2</sub> ; - T 22 °C.	Under UV irradiation, the degradation of the antibiotics in SW and WW was faster than in buffered DI. In this case, the degradation occurred by direct UV photolysis, whereas indirect photolysis contributed to the faster degradation in the actual matrices. Matrix components such as NO <sub>3</sub> <sup>-</sup> , Cl <sup>-</sup> and DOM may produce certain radicals and reactive transient species under UV irradiation, reacting quickly. However, the degradation rates by UV/H <sub>2</sub> O <sub>2</sub> were lower in SW and WW than in DI. The authors attributed this behaviour to matrix effects, mostly HO <sup>•</sup> scavengers and competitors for UV absorption. Since the direct photolysis was significantly slower than the reaction of the compounds with HO <sup>•</sup> , the direct photolysis by UV can be considered negligible in the UV/H <sub>2</sub> O <sub>2</sub> process.	[34]

<b>UV UV/H<sub>2</sub>O<sub>2</sub></b>	Sulfamethoxazole, sulfamethazine, sulfadiazine, trimethoprim, bisphenol A, diclofenac 4 μM	- UPW; - Lake water (pH 6.84; DOC 5.1 mg L <sup>-1</sup> ; alkalinity 24.4 mg CaCO <sub>3</sub> L <sup>-1</sup> ; NO <sub>3</sub> <sup>-</sup> 1.9 mg L <sup>-1</sup> ; NO <sub>2</sub> <sup>-</sup> < 0.25 mg L <sup>-1</sup> ; Cl <sup>-</sup> 5.8 mg L <sup>-1</sup> ; Br <sup>-</sup> < 0.25 mg L <sup>-1</sup> ; SO <sub>4</sub> <sup>2-</sup> 4.6 mg L <sup>-1</sup> ); - WW effluent (pH 6.84; DOC 7.3 mg L <sup>-1</sup> ; alkalinity 73.4 mg CaCO <sub>3</sub> L <sup>-1</sup> ; NO <sub>3</sub> <sup>-</sup> 4.9 mg L <sup>-1</sup> ; NO <sub>2</sub> <sup>-</sup> < 0.25 mg L <sup>-1</sup> ; Cl <sup>-</sup> 59.2 mg L <sup>-1</sup> ; Br <sup>-</sup> < 0.25 mg L <sup>-1</sup> ; SO <sub>4</sub> <sup>2-</sup> 47.5 mg L <sup>-1</sup> ).	- Bench scale quasi-collimated beam apparatus equipped with 4 LP UV lamps; - pH in UPW experiments: 3.6, 7.85, 9.7 (only for UV); - pH in water matrices experiments: 7.85; - H <sub>2</sub> O <sub>2</sub> : 2, 6, 10 mg L <sup>-1</sup> .	UV/H <sub>2</sub> O <sub>2</sub> treatment led to removals ranging from 43% for trimethoprim to 98% for diclofenac in lake water. In WW, the removals were lower (31-97%), suggesting a superior scavenging rate of HO <sup>•</sup> , namely DOC, alkalinity, Cl <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup> and NO <sub>3</sub> <sup>-</sup> . [38]
<b>UV</b>	Sulfamethoxazole 1.0, 2.0, 5.0 and 10 mg L <sup>-1</sup>	- UPW; - WW effluent (pH 7.0; DOC 16 mg L <sup>-1</sup> ; COD 21.2 mg L <sup>-1</sup> ; turbidity 2.0 NTU; N <sub>total</sub> 23 mg L <sup>-1</sup> ; P <sub>total</sub> 0.4 mg L <sup>-1</sup> ), Shanghai, China.	- 0.8 L a cylindrical glass-jacketed reactor ; - 10 W power input LP Hg lamp (Shanghai, China) (λ <sub>max</sub> 254 nm); - Effect of organic anions (Cl <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup> , NO <sub>3</sub> <sup>-</sup> , HCO <sub>3</sub> <sup>-</sup> ) and HA.	The removal of sulfamethoxazole (10 mg L <sup>-1</sup> ) in UPW was completed in 30 min, but the degradation rate decreased in WW, with almost total removal after 60 min. The degradation was slightly improved in water matrices containing 1.0 mM of Cl <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup> and NO <sub>3</sub> <sup>-</sup> , and 5 mg L <sup>-1</sup> of HA. In turn, HA at higher concentrations and HCO <sub>3</sub> <sup>-</sup> reduced the degradation rate. [41]
<b>UV UV/H<sub>2</sub>O<sub>2</sub></b>	Erythromycin, doxycycline, clindamycin, ciprofloxacin, penicillin-G, trimethoprim 0.68-1.72 μM	- UPW; - WW effluent 1 (pH 6.84; DOC 5.8 mg L <sup>-1</sup> ; alkalinity 123 mg CaCO <sub>3</sub> L <sup>-1</sup> ; NO <sub>3</sub> <sup>-</sup> 4.04 mg L <sup>-1</sup> ; NO <sub>2</sub> <sup>-</sup> < 0.015 mg L <sup>-1</sup> ); - WW effluent 1 (pH 6.58; DOC 4.9 mg L <sup>-1</sup> ; alkalinity 88 mg CaCO <sub>3</sub> L <sup>-1</sup> ; NO <sub>3</sub> <sup>-</sup> 10.3 mg L <sup>-1</sup> ; NO <sub>2</sub> <sup>-</sup> 0.021 mg L <sup>-1</sup> ).	- MP lamp system consisting of a 1-kW lamp emitting a polychromatic spectrum > 200 nm; - LP lamp system consisting of four 15-W lamps emitting monochromatic light at λ 253.7 nm; - H <sub>2</sub> O <sub>2</sub> : 10 mg L <sup>-1</sup> .	Photolysis and UV/ H <sub>2</sub> O <sub>2</sub> experiments showed the matrix influence. UV-photosensitized reactions were recorded for clindamycin. In UV/H <sub>2</sub> O <sub>2</sub> process, erythromycin and doxycycline originated some active intermediates at low treatment doses of UV <sub>254</sub> and only in WW effluents, suggesting that these by-products does not result from direct reaction with HO <sup>•</sup> . The reactions seem to be controlled by some components of the matrix by the following mechanisms: (i) reaction initiated when HO <sup>•</sup> interact with the pollutant in the presence of other matrix components; (ii) result of dark reactions of photoproducts; or (iii) result from photosensitized reactions in complex matrices under UV, namely with <sup>1</sup> O <sub>2</sub> or <sup>3</sup> DOM*. [19]
<b>UV UV/H<sub>2</sub>O<sub>2</sub></b>	Oxytetracycline, doxycycline, ciprofloxacin 5 μM	- UPW; - SW; - DW; - WW effluent (pH 7.84; DOC 5.0 mg L <sup>-1</sup> ; alkalinity 1.58 mM HCO <sub>3</sub> <sup>-</sup> ; NO <sub>3</sub> <sup>-</sup> 132 mg L <sup>-1</sup> ; Cl <sup>-</sup> 107.3 mg L <sup>-1</sup> ; F <sup>-</sup> 0.4 mg L <sup>-1</sup> ; SO <sub>4</sub> <sup>2-</sup> 60.7 mg L <sup>-1</sup> ).	- 11W LP Hg lamp emitting monochromatic light at λ 254 nm; - H <sub>2</sub> O <sub>2</sub> : 1mM.	The performance of UV/H <sub>2</sub> O <sub>2</sub> process was influenced by water matrix. For all target antibiotics, the DW was the matrix which led to faster degradation and the opposite occurred in WW due to the higher background HO <sup>•</sup> radical scavenging in this matrix. [35]
<b>UV UV/H<sub>2</sub>O<sub>2</sub></b>	1-H-Benzotriazole, N,N-diethyl-m-toluamide (DEET), Chlorophene, 3-Methylindole, Nortripty-line HCl 1 μM	- UPW; - Lake water (pH 7.4; TOC 5.2 mg L <sup>-1</sup> ; COD 18 mg L <sup>-1</sup> ; conductivity 80.2 μS cm <sup>-1</sup> ; alkalinity 30 mg CaCO <sub>3</sub> L <sup>-1</sup> ; N <sub>total</sub> 1.51 mg L <sup>-1</sup> ; P <sub>total</sub> 0.041 mg L <sup>-1</sup> ); - WW effluent (pH 7.9-8.3; TOC 2.8-11.1 mg L <sup>-1</sup> ; COD 7-56 mg L <sup>-1</sup> ; conductivity 550-570 μS cm <sup>-1</sup> ; alkalinity 325-335 mg CaCO <sub>3</sub> L <sup>-1</sup> ; N <sub>total</sub> 21.3-35.5 mg L <sup>-1</sup> ; P <sub>total</sub> 0.156-1.76 mg L <sup>-1</sup> ), Spain.	- Irradiation source: UV immersed LP Heraeus Hg lamp TN 15/35 with a nominal output of 15 W (λ <sub>max</sub> 254 nm); - H <sub>2</sub> O <sub>2</sub> : 1 and 5 x 10 <sup>-5</sup> M; - Natural pH of each water ; - Temperature of 20 °C.	In the simultaneous photodegradation by UV and UV/H <sub>2</sub> O <sub>2</sub> , the removal rate of all compounds decreased with the relative organic matter contents of the different water matrices. [42]

<p><b>UV</b> <b>UV/H<sub>2</sub>O<sub>2</sub></b></p>	<p>Benalaxyl, cyprodinil, dimethomorph, fenhexamide, iprovalicarb, kresoxim-methyl, metalaxyl, myclobutanil, tebuconazole 10 µg L<sup>-1</sup></p>	<p>- Tap water; - Swimming pool water; - River water; - WW effluent (composition not provided).</p>	<p>- Middle-scale photoreactor with water recirculation to simulate real conditions; - Irradiation source: UVC 6W lamp (λ = 254 nm) - H<sub>2</sub>O<sub>2</sub>: 20 mg L<sup>-1</sup>.</p>	<p>Under UVC radiation, degradation occurred in all water samples and was quite similar despite of the studied matrices, removing approximately &gt;50% (except for benalaxyl, iprovalicarb and myclobutanil) after 30 min. Regarding the removal efficiency by UVC/H<sub>2</sub>O<sub>2</sub>, an average removal of 75% was verified for all the water matrices in less than 6 min. The addition of H<sub>2</sub>O<sub>2</sub> under UVC light allowed an improvement of the reaction kinetics.</p> <p>[43]</p>
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**Abbreviations:** BOD<sub>5</sub>, biochemical oxygen demand; COD, chemical oxygen demand; DI, distilled water; DOC, dissolved organic carbon; DOM, dissolved organic matter; DW, drinking water; E1, estrone; E2, 17-beta-estradiol; EE2, 17-alpha-ethinylestradiol; HA, humic acids; LP, low pressure; MP, micropollutants; NOM, natural organic matter; NTU, nephelometric turbidity unit; ROS, reactive oxidation species; SS, suspended solids; SW, surface water; SWW, synthetic wastewater; TC, total carbon; TOC, total organic carbon; TSS, total suspended solids; UPW, ultrapure water; WW, wastewater.



**Table S2.** Reaction rate constants ( $k$ ).

Reaction	$k$	Reference	
9	$\text{H}_2\text{O}_2 + \text{HO}^\bullet \rightarrow \text{HO}_2^\bullet + \text{H}_2\text{O}$	$3.3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$	[171]
10	$\text{H}_2\text{O}_2 + \text{HO}_2^\bullet \rightarrow \text{HO}^\bullet + \text{O}_2 + \text{H}_2\text{O}$	$3 \text{ M}^{-1} \text{ s}^{-1}$	[172]
15	$\text{HO}^\bullet + \text{HCO}_3^- \rightarrow \text{H}_2\text{O} + \text{CO}_3^{\bullet-}$	$8.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$	[173]
16	$\text{HO}^\bullet + \text{CO}_3^{2-} \rightarrow \text{HO}^\bullet + \text{CO}_3^{\bullet-}$	$3.9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$	[173]
17	$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{HO}^- + \text{HO}^\bullet$	$76 \text{ M}^{-1} \text{ s}^{-1}$	[37]
18	$\text{Fe}^{2+} + \text{HO}^\bullet \rightarrow \text{Fe}^{3+} + \text{HO}^-$	$3.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$	[118]
19	$\text{HO}^\bullet + \text{RH} \rightarrow \text{H}_2\text{O} + \text{R}^\bullet$	$10^7 \text{ M}^{-1} \text{ s}^{-1}$	[118]
21	$\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + \text{HO}_2^\bullet + \text{H}^+$	$0.001 - 0.01 \text{ M}^{-1} \text{ s}^{-1}$	[174]
41	$\text{O}_2^- + \text{H}^+ \rightarrow \text{HO}_2^-$	$2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	[175]
44	$\text{O}_3 + \text{HO}^- \rightarrow \text{HO}_2^- + \text{O}_2$ (basic pH)	$70 \text{ M}^{-1} \text{ s}^{-1}$	[153]
45	$\text{O}_3 + \text{HO}_2^- \rightarrow \text{HO}^\bullet + \text{O}_2^- + \text{O}_2$	$2.8 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$	[153]
46	$\text{O}_3 + \text{O}_2^- \rightarrow \text{O}_3^- + \text{O}_2$	$1.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	[153]
47	$\text{O}_3^- + \text{H}^+ \leftrightarrow \text{HO}_3^\bullet$ (pH < 8)	$k_+ = 5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ $k_- = 3.3 \times 10^2 \text{ s}^{-1}$	[153]
48	$\text{HO}_3^\bullet \rightarrow \text{HO}^\bullet + \text{O}_2$ (pH < 8)	$1.4 \times 10^5 \text{ s}^{-1}$	[153]
49	$\text{O}_3^- \leftrightarrow \text{O}^- + \text{O}_2$ (pH > 8)	$k_+ = 2.1 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ $k_- = 3.3 \times 10^9 \text{ s}^{-1}$	[153]
50	$\text{O}^- + \text{H}_2\text{O} \rightarrow \text{HO}^\bullet + \text{HO}^-$ (pH > 8)	$10^8 \text{ s}^{-1}$	[153]
51	$\text{HO}^\bullet + \text{O}_3 \rightarrow \text{HO}_2^\bullet + \text{O}_2$	$1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1} - 2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	[153]
57	$\text{O}_3^- + \text{H}^+ \rightarrow \text{HO}_3^\bullet$	$5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$	[176]
58	$\text{HO}_3^\bullet \rightarrow \text{O}_2 + \text{HO}^\bullet$	$1.4 \times 10^5 \text{ s}^{-1}$	[176]
59	$\text{HO}^\bullet + \text{O}_3 \rightarrow \text{O}_2 + \text{HO}_2^\bullet$	$2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	[175]

**Table S3.** Matrix effects occurring in studies dealing with Fenton-based processes, published since 2005. Unless otherwise stated, the experimental conditions refer to the tested conditions for the evaluation of matrix effects.

AOT	Target pollutant Concentration	Matrices	Experimental conditions	Main conclusions	Reference
<b>Fenton-like</b>	Bisphenol A 285-14200 $\mu\text{g L}^{-1}$	- UPW; - DW; - GW; - SW; - WW effluent (pH 8; TOC 7 $\text{mg L}^{-1}$ ; conductivity 311 $\mu\text{S cm}^{-1}$ ; $\text{Cl}^-$ 0.5 $\text{mg L}^{-1}$ ; $\text{NO}_3^-$ 57 $\text{mg L}^{-1}$ ; $\text{HCO}_3^-$ 182 $\text{mg L}^{-1}$ ; $\text{SO}_4^{2-}$ 30 $\text{mg L}^{-1}$ ).	- Glass cylindrical reaction vessel; - 20 mL of an aqueous solution containing Bisphenol A; - Magnetic stirring, open air equilibrium; - Catalyst: sodium persulphate (SPS) and a magnetic carbon xerogel, consisting of interconnected carbon microspheres with embedded iron and cobalt microparticles.	The elimination rate in UPW was always lower than in any other matrices. This resulted from an interplay among many effects, namely: (i) the presence of HA and low molecular weight organic acids (e.g., oxalate) able to form complexes with iron species, promoting the Fenton-like reactions; and (ii) the presence of organic/inorganic species that could lead to competitive adsorption onto the xerogel surface, as well as scavenging effects. The experiments performed in spiked UPW showed that organics and $\text{HCO}_3^-$ hindered the degradation, by acting as scavengers of $\text{SO}_4^{\cdot-}$ and $\text{HO}^\bullet$ , whereas $\text{Cl}^-$ (> 50 $\text{mg/L}$ ) had a positive effect, maybe due to the formation $\text{Cl}_2^{\cdot-}$ .	[14]
<b>Bio-electro-Fenton</b>	Ketoprofen, diclofenac, ibuprofen and naproxen 40 $\mu\text{g L}^{-1}$	- DI; - WW after primary clarifier (COD 186 $\text{mg l}^{-1}$ ; pH 7.9; conductivity 1.3 $\mu\text{S cm}^{-1}$ ; $\text{NH}_4^+\text{-N}$ 0.08 $\text{g L}^{-1}$ ; $\text{PO}_4^{3-}\text{-P}$ 0.01 $\text{g L}^{-1}$ ; $\text{Cl}^-$ 0.1 $\text{g L}^{-1}$ ; $\text{SO}_4^{2-}$ 0.03 $\text{g L}^{-1}$ ), Copenhagen, Denmark.	- Lab-scale rectangular bio-electrochemical system; - Reactors were maintained with 90 mL of WW; - Voltage: 0.5 V; - pH 2; - Airflow rate: 8 $\text{mL min}^{-1}$ ; - $\text{FeSO}_4$ : 5 mM.	Lower removal rates were found when actual WW was used as matrix. Regarding ketoprofen, diclofenac and naproxen the $k_{\text{app}}$ were 30-65% lower, which can be explained by the presence of organic matter present in WW competing with the targeted compounds for $\text{HO}^\bullet$ . Fenton reactions can be inhibited by inorganic ions. Ferric ion can form complexes with $\text{PO}_4^{3-}$ , $\text{SO}_4^{2-}$ , $\text{Cl}^-$ and $\text{F}^-$ can reduce the reactivity of ferric ion.	[44]
<b>Fenton Fe(II)-activated persulfate</b>	Trimethoprim 0.05 mM	- DI; - SWW; - WW effluent, Beijing.	- Glass bottle (150 mL) fill with 100 mL; - $\text{Fe}^{2+}$ : 0.05 mM; - $\text{H}_2\text{O}_2$ : 1 mM. - pH 3.	Complete degradation of trimethoprim was obtained when using DI. A decrease in the treatment efficiency was found in actual WW, with 35.8% and 43.6% removal for Fenton and the Fe (II)-activated persulfate processes, respectively. Furthermore, the decomposition efficiencies for $\text{H}_2\text{O}_2$ was lower in comparison to DI and SWW, which may be due the formation of Fe(II) complexes with organic matter present in actual WW, decreasing the amount of Fe(II) available for reaction with $\text{H}_2\text{O}_2$ . The removal efficiency in the presence of persulfate decreased in WW, possibly due to the reaction between the sulphate radicals and organic MPs.	[45]
<b>Fenton Photo-Fenton</b>	Prednisolone 100 $\text{mg L}^{-1}$	- DI;	- Cylindrical glass reactor (550 mL); - Irradiation source: LED (40 W, $\lambda_{\text{max}}=360$ nm);	Matrix constituents affected the mineralization rates, with only 10% removal after 1 hour treatment, while	[46]

<b>UV UV/H<sub>2</sub>O<sub>2</sub></b>		- WW effluent (pH 6.9; COD 35 mg O <sub>2</sub> L <sup>-1</sup> ; TOC 52.7 mg L <sup>-1</sup> ; BOD <sub>5</sub> 2 mg O <sub>2</sub> L <sup>-1</sup> ; SS 12 mg L <sup>-1</sup> ), Spain.	- Solution pH 3; - Fe <sup>2+</sup> : 3 mM; - H <sub>2</sub> O <sub>2</sub> : 3 mM.	50% was obtained in DI. The presence of inorganic and organic compounds in the WW may reduce the concentration of oxidant species by reacting with HO <sup>•</sup> .	
<b>Solar irradiation Fenton Solar photo-Fenton</b>	Carbamazepine, clarithromycin, diclofenac, metoprolol, benzotriazole, mecoprop ng L <sup>-1</sup> to μg L <sup>-1</sup> levels	- WW effluents with different secondary treatment, namely activated sludge (pH 7.8; TOC 37 mg L <sup>-1</sup> ; COD 63 mg L <sup>-1</sup> ; alkalinity 273 mg CaCO <sub>3</sub> L <sup>-1</sup> ; Fe <sub>total</sub> 0.9 mg L <sup>-1</sup> ; TSS 12 mg L <sup>-1</sup> ), moving bed bioreactor (pH 7.4; TOC 20.2 mg L <sup>-1</sup> ; COD 35 mg L <sup>-1</sup> ; alkalinity 85 mg CaCO <sub>3</sub> L <sup>-1</sup> ; Fe <sub>total</sub> 1.6 mg L <sup>-1</sup> ; TSS 14 mg L <sup>-1</sup> ) and coagulation flocculation (pH 7.9; TOC 57.2 mg L <sup>-1</sup> ; COD 90 mg L <sup>-1</sup> ; alkalinity 231 mg CaCO <sub>3</sub> L <sup>-1</sup> ; Fe <sub>total</sub> 1.9 mg L <sup>-1</sup> ; TSS 30 mg L <sup>-1</sup> ), Lausanne, Switzerland.	- 100-mL brown bottles; - Irradiation source: solar simulator; - H <sub>2</sub> O <sub>2</sub> : 25 mg L <sup>-1</sup> ; - Fe <sup>2+</sup> : 5 mg L <sup>-1</sup> .	Regardless the type of secondary treatment, the order of degradation rates was photo-Fenton > solar irradiation > Fenton. In general, the higher abatement of both pollutants and TOC was reached when using effluents from moving bed bioreactor, following by activated sludge. Although the moving bed bioreactor effluents led to a higher removal by Fenton process than the other matrices, the consumption of peroxide was inferior due to the lower alkalinity, showing the HCO <sub>3</sub> <sup>-</sup> effect.	[20]
<b>Photo-Fenton</b>	Tetracycline 24 mg L <sup>-1</sup>	- UPW; - SW; - WW effluent (pH 8.0; TOC 10.6 mg L <sup>-1</sup> ; IC 52.4 mg L <sup>-1</sup> ; COD 136 mg L <sup>-1</sup> ; BOD 30.0 mg L <sup>-1</sup> ; DO 5.0 mg L <sup>-1</sup> ; Cl <sup>-</sup> 54.4 mg L <sup>-1</sup> ; NO <sub>3</sub> <sup>-</sup> 0.73 mg L <sup>-1</sup> ; turbidity 134 NTU; TDS 510 mg L <sup>-1</sup> ), Brazil.	- Iron (0.2 mM) source: Fe(NO <sub>3</sub> ) <sub>3</sub> or potassium ferrioxalate; - H <sub>2</sub> O <sub>2</sub> : 3, 10 mM; <i>Black-light irradiation</i> - Upflow reactor; V 280 mL; - Irradiation source: 15W black-light lamp (λ <sub>max</sub> 365 nm), with an irradiance of 19 W m <sup>-2</sup> ; - Recirculation of the solution at a flow rate of 80 mL min <sup>-1</sup> , after addition of iron, pH adjustment to 2.5 and addition of H <sub>2</sub> O <sub>2</sub> ; <i>Solar irradiation</i> - Transparent glass vessel; V 500 mL; - Direct sunlight, during summer between 10 a.m. and 14 p.m., in Brazil (22°S 48°W); - Irradiance: 15 to 20 W m <sup>-2</sup> .	The SW matrix did not decrease the degradation efficiency, in comparison to UPW, under either black-light or solar irradiation. In the case of WW under solar irradiation in the presence of ferrioxalate, no influence of the matrix was also observed. However, lower efficiency was obtained under black-light, indicating the interference of the matrix components on the efficiency of the process. This effect could be originated by the high TOC and/or IC content of 52.4 mg L <sup>-1</sup> at pH 8. The increase of H <sub>2</sub> O <sub>2</sub> resulted in an even lower efficiency, suggesting the influence of other matrix constituents.	[37]
<b>Photo-Fenton</b>	62 MPs 3-66,379 ng L <sup>-1</sup>	- WW effluent (pH 7.6–8.3; TOC 16-18 mg L <sup>-1</sup> ; IC 69-116 mg L <sup>-1</sup> ; COD 20-29 mg L <sup>-1</sup> ), Almería, Spain. - Stripped WW: 0.4–0.5 g H <sub>2</sub> SO <sub>4</sub> L <sup>-1</sup> effluent) was added to reduce HCO <sub>3</sub> <sup>-</sup> /CO <sub>3</sub> <sup>-</sup> content to less than 5 mg L <sup>-1</sup> as IC, with no significant decrease on the pH.	- CPC plant under natural solar irradiation; - Fe(II): 5 mg L <sup>-1</sup> ; - H <sub>2</sub> O <sub>2</sub> : 50 mg L <sup>-1</sup> ; - Complexing agents (HA and EDDS); - pH: 3 (classical photo-Fenton), 6.5 (modified photo-Fenton).	Modified photo-Fenton with HA at neutral pH resulted in a longer treatment time required to reach a similar degradation to that observed on conventional photo-Fenton. Modified photo-Fenton with EDDS showed promising results, with lower consumption of H <sub>2</sub> O <sub>2</sub> and keeping the pH.	[47]
<b>Photo-Fenton</b>	Acetaminophen, antipyrine, atrazine, caffeine, carbamazepine, diclofenac, flumequine, hydroxybiphenyl, ibuprofen, isoproturon,	- WW effluent (pH 7.6–8.3; TC 87-132 mg L <sup>-1</sup> ; IC 69-116 mg L <sup>-1</sup> ; COD 20-19 mg L <sup>-1</sup> ), Almería, Spain. - Stripped WW: 0.4–0.5 g H <sub>2</sub> SO <sub>4</sub> L <sup>-1</sup> effluent was added to reduce HCO <sub>3</sub> <sup>-</sup> /CO <sub>3</sub> <sup>-</sup> content to less than 5 mg L <sup>-1</sup> as IC, with no significant decrease on the pH.	CPC solar plant; Solution of Fe:EDDS (molar ratio 1:2 or 1:1); H <sub>2</sub> O <sub>2</sub> : 50 mg L <sup>-1</sup> .	The removal rate by photo-Fenton was only slightly lower in the WW effluent than in the stripped effluent, since the first radical formed with Fe:EDDS during Fenton-like or photoactivated Fe is the O <sub>2</sub> <sup>•-</sup> . The reactivity of HCO <sub>3</sub> <sup>-</sup> with the O <sub>2</sub> <sup>•-</sup> is much lower than with the HO <sup>•</sup> , turning its influence negligible.	[48]

	ketorolac, ofloxacin, progesterone, sulfamethoxazole, and triclosan 100 µg L <sup>-1</sup>			
<b>Photo-Fenton</b>	Acetaminophen, antipyrine, atrazine, caffeine, carbamazepine, diclofenac, flumequine, hydroxybiphenyl, ibuprofen, isoproturon, ketorolac, ofloxacin, progesterone, sulfamethoxazole and triclosan 5 and 100 µg L <sup>-1</sup>	- WW effluent (pH 7.6–8.3; DOC 10-24 mg L <sup>-1</sup> ; IC 91-120 mg L <sup>-1</sup> ; COD 26-63 mg L <sup>-1</sup> ), Almería, Spain. - Stripped WW: 0.4–0.5 g H <sub>2</sub> SO <sub>4</sub> L <sup>-1</sup> effluent) was added to reduce HCO <sub>3</sub> <sup>-</sup> /CO <sub>3</sub> <sup>-</sup> content to less than 1 mg L <sup>-1</sup> as IC.	Modified solar photo-Fenton; - 5mg L <sup>-1</sup> of Fe(II); - 50 mg L <sup>-1</sup> of H <sub>2</sub> O <sub>2</sub> ; - pH ≈7; - Addition of 35 mg L <sup>-1</sup> oxalic acid; - Addition of HA (10, 25, 50 mg L <sup>-1</sup> ); - Mixing 31% of WWTP influent and 69% effluent.	The use of ferrioxalate, humic substances and mixing the WWTP effluent with a percentage of influent, were attempted to form photoactive Fe(III) complexes. Both oxalate- and HA-enhanced processes provided higher degradation of MPs, but mixing influent was not successful. [49]
<b>Photo-Fenton</b>	Ofloxacin 10 mg L <sup>-1</sup>	- Demineralized water; - Simulated natural freshwater; - Simulated municipal WW; - WW effluent (pH 7.8; DOC 10.72 mg L <sup>-1</sup> ; COD 63.7 mg L <sup>-1</sup> ; conductivity 3.05 µS cm <sup>-1</sup> ; Cl <sup>-</sup> 0.54 mg L <sup>-1</sup> ; NO <sub>3</sub> <sup>-</sup> 0.02 mg L <sup>-1</sup> ; SO <sub>4</sub> <sup>2-</sup> 1.05 mg L <sup>-1</sup> ; Na <sup>+</sup> 0.37 mg L <sup>-1</sup> ; NH <sub>4</sub> <sup>+</sup> 0.11 mg L <sup>-1</sup> ; K <sup>+</sup> 0.045 mg L <sup>-1</sup> ; Ca <sup>2+</sup> 0.12 mg L <sup>-1</sup> ; Mg <sup>2+</sup> 0.064 mg L <sup>-1</sup> ), Almería, Spain.	- CPC plant under natural solar irradiation; - pH 2.8–2.9, - Fe(II): 2 mg L <sup>-1</sup> ; - H <sub>2</sub> O <sub>2</sub> : 2.5 mg L <sup>-1</sup> .	The process was efficient to remove ofloxacin. DOC removal and the formation of by-products were dependent on the chemical composition of the matrix, with a lower mineralization of ofloxacin observed in the WW, due to the higher concentration of inorganic (i.e. Cl <sup>-</sup> and SO <sub>4</sub> <sup>2-</sup> ) and organic species in the more complex matrix. The presence of inorganic ions in the simulated natural freshwater also affected the mineralization. [50]
<b>Photo-Fenton</b>	Trimethoprim 10 mg L <sup>-1</sup>	- Demineralized water; - Simulated natural freshwater; - SWW; - WW effluent (pH 7.8; DOC 10.72 mg L <sup>-1</sup> ; COD 63.7 mg L <sup>-1</sup> ; conductivity 3.05 µS cm <sup>-1</sup> ; Cl <sup>-</sup> 0.54 mg L <sup>-1</sup> ; NO <sub>3</sub> <sup>-</sup> 0.02 mg L <sup>-1</sup> ; SO <sub>4</sub> <sup>2-</sup> 1.05 mg L <sup>-1</sup> ; Na <sup>+</sup> 0.37 mg L <sup>-1</sup> ; NH <sub>4</sub> <sup>+</sup> 0.11 mg L <sup>-1</sup> ; K <sup>+</sup> 0.045 mg L <sup>-1</sup> ; Ca <sup>2+</sup> 0.12 mg L <sup>-1</sup> ; Mg <sup>2+</sup> 0.064 mg L <sup>-1</sup> ), Almería, Spain.	- CPC plant under natural solar irradiation; - pH 2.8–2.9, - Fe(II): 2 mg L <sup>-1</sup> ; - H <sub>2</sub> O <sub>2</sub> : 2.5 mg L <sup>-1</sup> .	In comparison to demineralized water and simulated natural freshwater, the higher organic carbon and salt content in simulated/real effluents reduced the mineralization per dose of H <sub>2</sub> O <sub>2</sub> . A slightly higher amount of H <sub>2</sub> O <sub>2</sub> was required in the case of simulated freshwater. The organic/inorganic content of WW competed with the target pollutant and interfered with its degradation pathways. [12]
<b>Fenton</b>	Nonionic surfactants (6 alcohol ethoxylates and 4 alkylphenol ethoxylates) 1.4 mg L <sup>-1</sup>	- UPW; - WW effluent (pH 7.6; TOC 13 mg L <sup>-1</sup> ; COD 42 mg L <sup>-1</sup> ; conductivity 540 µS cm <sup>-1</sup> ; Cl <sup>-</sup> 124 mg L <sup>-1</sup> ; HCO <sub>3</sub> <sup>-</sup> 232 mg L <sup>-1</sup> ; Na <sup>+</sup> 74 mg L <sup>-1</sup> ; Ca <sup>2+</sup> 77 mg L <sup>-1</sup> ; Mg <sup>2+</sup> 11 mg L <sup>-1</sup> ), Como, Italy.	- 29 ml of solution in 40 ml glass vials to which acidic Fe(II) sulphate solution and H <sub>2</sub> O <sub>2</sub> were added; - H <sub>2</sub> O <sub>2</sub> /Fe ratio: 1.4; - Fe <sup>2+</sup> : 14 mg L <sup>-1</sup> (WW) and 10.5 mg L <sup>-1</sup> (UPW); - H <sub>2</sub> O <sub>2</sub> : 12 mg L <sup>-1</sup> (WW) and 9 mg L <sup>-1</sup> (UPW); - pH range: 3–4.	The efficiency of Fenton process decreased when using the real effluents and higher doses of reactants were required in order to achieve the same removal reached in UPW, maintaining the H <sub>2</sub> O <sub>2</sub> /Fe ratio. [51]

<b>Photo-Fenton</b>	Sulfamethoxazole and clarithromycin 100 µg L <sup>-1</sup>	- DI; - Simulated effluents; - WW effluent (pH 7.4; DOC 16.5 mg L <sup>-1</sup> ; conductivity 602 µS cm <sup>-1</sup> ; Cl <sup>-</sup> 295.7 mg L <sup>-1</sup> ; NO <sub>3</sub> <sup>-</sup> 42.0 mg L <sup>-1</sup> ; SO <sub>4</sub> <sup>2-</sup> 128.6 mg L <sup>-1</sup> ; PO <sub>4</sub> <sup>3-</sup> 6.2 mg L <sup>-1</sup> ; Na <sup>+</sup> 172.2 mg L <sup>-1</sup> ; NH <sub>4</sub> <sup>+</sup> 22.6 mg L <sup>-1</sup> ; K <sup>+</sup> 24.8 mg L <sup>-1</sup> ; Ca <sup>2+</sup> 79.8 mg L <sup>-1</sup> ; Mg <sup>2+</sup> 26.1 mg L <sup>-1</sup> ; turbidity 10.7 NTU), Almería, Spain.	CPC plant under solar irradiation; Fe <sup>3+</sup> : 5 mg L <sup>-1</sup> ; H <sub>2</sub> O <sub>2</sub> : 50 mg L <sup>-1</sup> .	Sulfamethoxazole was completely removed from all matrices by Solar Fenton, with a removal of 93% in actual effluents (t <sub>30 W,n</sub> = 250 min) and a complete removal in simulated effluents (t <sub>30 W,n</sub> = 198 min) and DI (t <sub>30 W,n</sub> = 85 min). A lower removal (77%) was observed for clarithromycin at the end of the treatment time (t <sub>30 W,n</sub> = 252 min), but it was totally eliminated in the other matrices. The lower removal in the real effluents was related to the high concentrations of DOM and inorganic ions, specifically Cl <sup>-</sup> and SO <sub>4</sub> <sup>2-</sup> anions that can complex iron and scavenge HO <sup>•</sup> , forming less oxidative radicals (Cl <sub>2</sub> <sup>-</sup> and SO <sub>4</sub> <sup>-</sup> ), compared to HO <sup>•</sup> .	[52]
<b>Photo-Fenton</b>	Acetaminophen, antipyrine, atrazine, caffeine, carbamazepine, diclofenac, flumequine, hydroxybiphenyl, ibuprofen, isoproturon, ketorolac, ofloxacin, progesterone, sulfamethoxazole and triclosan 100 µg L <sup>-1</sup>	- Synthetic water; - Simulated effluent; - WW effluent (DOC 25 mg L <sup>-1</sup> ; IC 106 mg L <sup>-1</sup> ; COD 60 mg L <sup>-1</sup> ), Almería, Spain.	CPC reactor under solar irradiation; H <sub>2</sub> O <sub>2</sub> : 0–50 mg L <sup>-1</sup> ; Iron: 5 mg L <sup>-1</sup> ; Unchanged pH; Addition of 406 mg L <sup>-1</sup> H <sub>2</sub> SO <sub>4</sub> to reach an IC < 20 mg L <sup>-1</sup> .	The MPs were successfully degraded to negligible concentrations with mild solar photo-Fenton at low iron concentrations (5 mg L <sup>-1</sup> ) and 50 mg L <sup>-1</sup> of H <sub>2</sub> O <sub>2</sub> , without adjusting the pH. The degradation was dependent on the type of matrix and scavengers present in the matrix, such as CO <sub>3</sub> <sup>2-</sup> and HCO <sub>3</sub> <sup>-</sup> . The removal was faster in the WW effluent than in the simulated one, but the DOC decrease was similar, which suggests that HA present in the actual matrix might produce solvated electrons and HO <sup>•</sup> upon irradiation.	[53]
<b>Fenton</b>	Hydroquinone 100 mg L <sup>-1</sup>	- DI; - WW effluent 2 (pH 7.6, TOC 88.9 mg L <sup>-1</sup> ; COD 308.7 mg L <sup>-1</sup> ; TN 12.14 mg L <sup>-1</sup> ; TP 13.22 mg L <sup>-1</sup> ; TSS 22.0 mg L <sup>-1</sup> ; NO <sub>3</sub> <sup>-</sup> < 0.18 mg L <sup>-1</sup> ; NO <sub>2</sub> <sup>-</sup> 0.007 mg L <sup>-1</sup> ), Portugal.	- Bubble column reactor (10 L) fill with 5 L; - Solution pH 3; - Fe <sup>2+</sup> : 45 mg L <sup>-1</sup> ; - H <sub>2</sub> O <sub>2</sub> : 500 mg L <sup>-1</sup> .	No reduction in terms of MP removal from WW and mineralization was observed, in comparison to the solution prepared in DI.	[54]
<b>Fenton</b>	51 MPs ng L <sup>-1</sup> - µg L <sup>-1</sup> levels	- WW effluent 1 (pH ≈ 7, DOC 3-5 mg L <sup>-1</sup> ; COD 25 mg L <sup>-1</sup> ; BOD <sub>5</sub> < 5 mg L <sup>-1</sup> ; TN 20-30 mg L <sup>-1</sup> ; TP 10-14 mg L <sup>-1</sup> ; TSS 35 mg L <sup>-1</sup> ; (49-51 MPs detected up to 3770 ng L <sup>-1</sup> ), Mexico; - WW effluent 2 (pH ≈ 7, DOC 2-4 mg L <sup>-1</sup> ; COD 20-35 mg L <sup>-1</sup> ; BOD <sub>5</sub> < 5 mg L <sup>-1</sup> ; TN 6-8 mg L <sup>-1</sup> ; TP 4-10 mg L <sup>-1</sup> ; TSS 9 mg L <sup>-1</sup> ; 11-16 MPs detected up to 210 ng L <sup>-1</sup> ), Mexico.	- Jar Test stirred at 220 rpm during 2 min, followed by slow stirring at 20 rpm during 10 min, and a final step of settling during 60 min; - Natural pH; - Fe(II): 30 mg L <sup>-1</sup> ; - H <sub>2</sub> O <sub>2</sub> : 25 mg L <sup>-1</sup> .	The use of Fenton as post-treatment of secondary effluents from WWTPs increased the removal efficiencies of various contaminants up to 100%, but some compounds such as metformin (44%) and dehydronifedipine (29-71%, depending on the effluent), were not completely removed. The Fenton process was more efficient to treat the WW effluent 2, since WW effluent 1 had a higher content of the main chemical parameters and MPs analysed.	[55]
<b>Fenton</b>	E1, E2, EE2, carbamazepine, triclosan and acetylsalicylic acid ng L <sup>-1</sup> to µg L <sup>-1</sup> levels	- WW effluents from 3 different locations; United Kingdom.	- Continuous stir tank reactor (31.34 dm <sup>3</sup> ) containing the modified polyacrylonitrile (PAN) catalyst, corresponding to 1.31 moles of iron catalyst; - Residence time 3 h; - Flow rate 10.6 L h <sup>-1</sup> ; - H <sub>2</sub> O <sub>2</sub> mass flow rate 4.7 mg min <sup>-1</sup> ;	A modified PAN catalyst system was effective in the removal of the target pollutants in WW, at ambient temperature and natural pH: > 80% of the estrogens were removed; > 84% of triclosan; 46-84.5% of carbamazepine; depending on the sampling location and consequent different characteristics of the WW effluents.	[56]

<b>UV/H<sub>2</sub>O<sub>2</sub></b>	Gabapentin,	- UPW;	- Room temperature; natural pH.	
<b>Photo-Fenton</b>	metformin,	- Lake water (pH 8.02; TOC 2.96 mg L <sup>-1</sup> ;	- UVC light LP Hg lamp ( $\lambda_{\max}$ 365 nm);	The lower removal was observed in WWTP effluents and lake water, which was suggested to be due to light absorption at 253.7 nm and competition for HO <sup>•</sup> by scavengers occurring in water (e.g., CO <sub>3</sub> <sup>2-</sup> , Cl <sup>-</sup> , or humic-like substances). The high Cl <sup>-</sup> content in the WWTP effluent was suggested to originate coordinating effect over ferric ions. [57]
	metoprolol, atenolol, clarithromycin, primidone, methylbenzotriazole, and benzotriazole 2 $\mu$ M	conductivity 285 $\mu$ S cm <sup>-1</sup> ; Cl <sup>-</sup> 12.39 mg L <sup>-1</sup> ; NO <sub>3</sub> <sup>-</sup> 2.26 mg L <sup>-1</sup> ; SO <sub>4</sub> <sup>2-</sup> 47.07 mg L <sup>-1</sup> ; NH <sub>4</sub> <sup>+</sup> 0.19 mg L <sup>-1</sup> ); - WW effluents (pH 7.47; TOC 9.31 mg L <sup>-1</sup> ; conductivity 1068 $\mu$ S cm <sup>-1</sup> ; Cl <sup>-</sup> 156.8 mg L <sup>-1</sup> ; NO <sub>3</sub> <sup>-</sup> 69.65 mg L <sup>-1</sup> ; SO <sub>4</sub> <sup>2-</sup> 63.47 mg L <sup>-1</sup> ; NH <sub>4</sub> <sup>+</sup> 4.91 mg L <sup>-1</sup> ), Lausanne, Switzerland.	- Solar UV-simulator: irradiation source 1.8 kW Xe lamp; - Fe(II): 30 $\mu$ M; - H <sub>2</sub> O <sub>2</sub> : 300 $\mu$ M.	

**Abbreviations:** BOD, biochemical oxygen demand; COD, chemical oxygen demand; CPC, compound parabolic concentrator; DI, distilled water; DO, dissolved oxygen; DW, drinking water; E1, estrone; E2, 17-beta-estradiol; EE2, 17-alpha-ethinylestradiol; EDDS, ethylenediamine-N,N'-disuccinic acid; GW, groundwater; HA, humic acids, IC, inorganic carbon; MP, micropollutants; NTU, nephelometric turbidity unit; PAN, polyacrylonitrile; PS, persulphate; SS, suspended solids; SW, surface water; SWW, synthetic wastewater; TC, total carbon; TDS, total dissolved solids; TOC, total organic carbon; TSS, total suspended solids; UPW, ultrapure water; WW, wastewater; WWTP, wastewater treatment plant.

**Table S4.** Matrix effects occurring in studies dealing with photocatalysis, published since 2005. Unless otherwise stated, the experimental conditions refer to the tested conditions for the evaluation of matrix effects.

AOT	Target pollutant Concentration	Matrices	Experimental conditions	Main conclusions	Reference
Photocatalysis	Diclofenac 5–20 mg L <sup>-1</sup>	- DI; - GW (characterization not provided), Cyprus; - WW effluent (characterization not provided), Cyprus.	- Immersion well reactor; - V 350 mL; - T 23 °C; pH 6; - Irradiation source: 9 W UV-A lamp (350–400 nm); - TiO <sub>2</sub> :TOC ratio: 79 (GW) and 32 (WW); - H <sub>2</sub> O <sub>2</sub> :TOC ratio: 0.8 (GW) and 0 (WW).	UV-A/TiO <sub>2</sub> was efficient for the degradation and mineralization of diclofenac in treated municipal effluents. NOM and other species present in the effluent reduced the degradation in comparison with DI. The effect of water matrix on mineralization was negligible since the TOC reduction was 45±5% regardless the matrix and the addition or not of H <sub>2</sub> O <sub>2</sub> . TOC analysis showed that macromolecules (e.g., humic and fulvic acids, biopolymers) were stable to the AOT.	[32]
Photocatalysis	Clofibric acid 1 mg L <sup>-1</sup>	- DI; - WW effluent (pH 7.54; conductivity 818 μS cm <sup>-1</sup> ; TOC 27.1mg L <sup>-1</sup> ).	- 150 mL reaction cells; - Irradiation source: UV-A lamp (λ 365nm, 0.89 mW cm <sup>-2</sup> ); - Catalyst: 500 mg L <sup>-1</sup> of Aeroxide P25 and P90 and titania–P25/silica particles; - Addition of inorganic (NaCl, FeCl <sub>3</sub> , FeCl <sub>2</sub> , AlCl <sub>3</sub> , CaCl <sub>2</sub> , Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> , Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> , Na <sub>2</sub> SO <sub>4</sub> , NaHCO <sub>3</sub> , and Na <sub>2</sub> CO <sub>3</sub> ) or organic compounds (HA, surfactant).	Generally, the removal efficiency decreased by adding inorganic salts to UPW, especially SO <sub>4</sub> <sup>2-</sup> and CO <sub>3</sub> <sup>2-</sup> ions, which are good scavengers of ROS, leading to more than 70% of deactivation. Overall, the environmental waters led to a higher deactivation (> 90%).	[58]
Photocatalysis	Acetaminophen, antipyrine, atrazine, carbamazepine, diclofenac, flumequine, hydroxybiphenyl, ibuprofen, isoproturon, ketorolac, ofloxacin, progesterone, sulfamethoxazole, triclosan 100 μg L <sup>-1</sup>	- Simulated water; - SWW; - WW effluent (DOC 13 mg L <sup>-1</sup> ), Almería, Spain.	- CPC solar pilot plant; - Catalyst: TiO <sub>2</sub> immobilized on a glass substrate; - Natural pH.	MPs were removed using immobilized TiO <sub>2</sub> under solar irradiation in the following order of efficiency removal: simulated water > simulated WW > WW effluent. The photocatalyst remained active even after five cycles of reuse and degraded most of the MPs in the actual WW, however the time required was longer.	[59]

<b>Photocatalysis UV/H<sub>2</sub>O<sub>2</sub></b>	Alprazolam, clonazepam, diazepam, lorazepam, and Carbamazepine 100 µg L <sup>-1</sup>	- UPW; - WW effluent (pH 7.55; COD 37.2 mg L <sup>-1</sup> ; IC 3.72 mg L <sup>-1</sup> ; TOC 37.14 mg L <sup>-1</sup> ; N <sub>total</sub> 17.18 mg L <sup>-1</sup> ; conductivity 506.0 µS cm <sup>-3</sup> ; turbidity 11.13 NTU; DO 6.1 mg L <sup>-1</sup> ; alkalinity 133.0 mg L <sup>-1</sup> ; TS 281.0 mg L <sup>-1</sup> ; VSS 121.0 mg L <sup>-1</sup> ; Total fixed solids 160.0 mg L <sup>-1</sup> ; Cl <sup>-</sup> 54.3 mg L <sup>-1</sup> ; NO <sub>3</sub> <sup>-</sup> 1.8 mg L <sup>-1</sup> ; F <sup>-</sup> 0.6 mg L <sup>-1</sup> ; PO <sub>4</sub> <sup>3-</sup> 26.4 mg L <sup>-1</sup> ; SO <sub>4</sub> <sup>2-</sup> 28.4 mg L <sup>-1</sup> ), Rio de Janeiro, Brazil.	- Batch magnetically stirred reactor (500 mL); -Irradiation source: Polychromatic high pressure 125 W mercury vapor lamp ( $\lambda_{max}$ = 365nm) and solar radiation; - Catalyst: 0.1, 0.05, and 0.005 g L <sup>-1</sup> TiO <sub>2</sub> ; - H <sub>2</sub> O <sub>2</sub> : 250, 200, 100, 50, 25, and 10 mg L <sup>-1</sup> .	A strong matrix effect was found when WW effluents were used, with a decrease in efficiency of approximately 50%. This effect might be due to the presence of radical scavenger species such as, DOC, CO <sub>3</sub> <sup>2-</sup> and anions. These species can also absorb UV light decreasing the activation of TiO <sub>2</sub> and H <sub>2</sub> O <sub>2</sub> . Moreover, anions can compete for the absorption site on the catalyst. Water matrix played a considerable role on the degradation efficiency, decreasing with an increase of water matrix complexity. HA decreased greatly the degradation of propyl paraben, since it has high light absorbing capacity and can also occupy the active sites of the catalyst. Other organics can also compete for oxidizing species. A slightly negative effect was found for HCO <sub>3</sub> <sup>-</sup> and Cl <sup>-</sup> . Moreover, the performance was enhanced in the presence of persulfate.	[60]
<b>Photocatalysis</b>	Propyl paraben 420 µg L <sup>-1</sup>	- UPW (pH 6, , conductivity 0.56 µS cm <sup>-1</sup> ); - Bottled water (pH 7.5, conductivity 396 µS cm <sup>-1</sup> , HCO <sub>3</sub> <sup>-</sup> 15 mg L <sup>-1</sup> , SO <sub>4</sub> <sup>2-</sup> 15 mg L <sup>-1</sup> , Cl <sup>-</sup> 9.8 mg L <sup>-1</sup> ); - River water (pH 7.5, conductivity 491 µS cm <sup>-1</sup> , TOC 2.7 mg L <sup>-1</sup> , SO <sub>4</sub> <sup>2-</sup> 274 mg L <sup>-1</sup> , Cl <sup>-</sup> 5 mg L <sup>-1</sup> ), Athens, Greece; - Diluted WW (50% water); - WW effluent (pH 8, TOC 7 mg L <sup>-1</sup> , TSS 1.1 mg L <sup>-1</sup> , COD 21 mg L <sup>-1</sup> , conductivity 311 µS cm <sup>-1</sup> , SO <sub>4</sub> <sup>2-</sup> 30 mg L <sup>-1</sup> , Cl <sup>-</sup> 0.44 mg L <sup>-1</sup> ), Patras, Greece.	- Glass cylindrical vessel (120 mL); - Catalyst: 500 mg L <sup>-1</sup> of Al-doped TiO <sub>2</sub> ; - Solar simulator equipped with a 100 W xenon ozone-free lamp.	Water matrix played a considerable role on the degradation efficiency, decreasing with an increase of water matrix complexity. HA decreased greatly the degradation of propyl paraben, since it has high light absorbing capacity and can also occupy the active sites of the catalyst. Other organics can also compete for oxidizing species. A slightly negative effect was found for HCO <sub>3</sub> <sup>-</sup> and Cl <sup>-</sup> . Moreover, the performance was enhanced in the presence of persulfate.	[61]
<b>Photocatalysis</b>	Diclofenac, naproxen, iopamidol, imidacloprid, bisphenol A and 2,4 dichlorophenol 2 mg L <sup>-1</sup>	- UPW; - WW effluent (pH 6.5, COD 35 mg L <sup>-1</sup> ), Italy.	- Pyrex glass cells (5 mL); - ZnO based materials and enzyme hybrid materials (1 g L <sup>-1</sup> ); - Irradiation source: 40 Watt Philips TLK/05 lamp ( $\lambda_{max}$ = 365 nm); - Soybean peroxidase (1 × 10 <sup>-8</sup> M); - H <sub>2</sub> O <sub>2</sub> : 1 × 10 <sup>-4</sup> M.	A complete removal of all studied compounds was found for both matrices, however a loss of efficiency was found when using WW, mainly due to the presence of DOM and inorganic ions.	[62]
<b>Photocatalysis</b>	E1 1000 µg L <sup>-1</sup>	- UPW; - SWW (pH 7.41; conductivity 56.3 µS cm <sup>-1</sup> ; DOC 5.40 mg L <sup>-1</sup> ; IC 3.71 mg L <sup>-1</sup> ; COD 23.6 mg L <sup>-1</sup> ; alkalinity 6.0 mg CaCO <sub>3</sub> L <sup>-1</sup> ; Cl <sup>-</sup> 1.47 mg L <sup>-1</sup> ; SO <sub>4</sub> <sup>2-</sup> 6.95 mg L <sup>-1</sup> ; PO <sub>4</sub> <sup>3-</sup> 3.82 mg L <sup>-1</sup> ; NO <sub>3</sub> <sup>-</sup> 0.34 mg L <sup>-1</sup> ; NO <sub>2</sub> <sup>-</sup> 0.04 mg L <sup>-1</sup> ; Br <sup>-</sup> 0.65 mg L <sup>-1</sup> ). - WW effluent (pH 7.55, conductivity 621 µS cm <sup>-1</sup> ; DOC 8.04 mg L <sup>-1</sup> ; IC 39.23 mg L <sup>-1</sup> ; COD 26.2 mg L <sup>-1</sup> ; alkalinity 27.5 mg CaCO <sub>3</sub> L <sup>-1</sup> ; Cl <sup>-</sup> 32.68 mg L <sup>-1</sup> ; SO <sub>4</sub> <sup>2-</sup> 33.03 mg L <sup>-1</sup> ; PO <sub>4</sub> <sup>3-</sup> 0.21 mg L <sup>-1</sup> ; NO <sub>3</sub> <sup>-</sup> 36.30 mg L <sup>-1</sup> ; NO <sub>2</sub> <sup>-</sup> n.d.; Br <sup>-</sup> 0.54 mg L <sup>-1</sup> ), Sidney.	- 11W UV LED ( $\lambda$ = 365 410 or 523 nm) placed 5 cm above the liquid surface of the reactor; - 500 mL; - 50 mg L <sup>-1</sup> of catalyst (gold-modified TiO <sub>2</sub> (Au-TiO <sub>2</sub> ) or TiO <sub>2</sub> P25).	The Au-TiO <sub>2</sub> catalyst showed better photocatalytic activity than P25 TiO <sub>2</sub> , for all the water matrices under all light sources. The removal rate of E1 decreased in the order: ultrapure > synthetic water ≈ WW. The differences between UPW and actual matrices were attributed to the NOM whereas the lower removal in WW was ascribed to the higher content of anions in comparison to synthetic water.	[63]
<b>Photocatalysis</b>	Bisphenol A, EE2 100-300 µg L <sup>-1</sup>	- UPW; - WW effluent (pH 8; conductivity 820µS cm <sup>-1</sup> ; DOC 7.8 mg L <sup>-1</sup> ; COD 24 mg L <sup>-1</sup> ; Cl <sup>-</sup> 220 mg L <sup>-1</sup> ; SO <sub>4</sub> <sup>2-</sup> 60 mg L <sup>-1</sup> ;	- 150 mL reaction cells filled with 60 mL; - 150 W xenon lamp (solar radiation simulator: 5% UV-A radiation, 0.1% UV-	Degradation in WW was estimated as one order of magnitude lower than those obtained for UPW, which was attributed to the scavenging of HO <sup>•</sup> by	[64]



		HCO <sub>3</sub> <sup>-</sup> 188 mg L <sup>-1</sup> ; NO <sub>3</sub> <sup>-</sup> 26 mg L <sup>-1</sup> ; NO <sub>2</sub> <sup>-</sup> 57 mg L <sup>-1</sup> , Greece.	B radiation, equipped with a 280 nm cut-off); - Incident photon flux 58 × 10 <sup>-8</sup> einstein L <sup>-1</sup> s <sup>-1</sup> ; - [0.5% Pt/TiO <sub>2</sub> ] = 500 mg L <sup>-1</sup> (ten titania catalysts were synthesized, characterized and tested); - T 25 °C; Matrix inherent pH (i.e., ca. 8 for WW and 6.2 for UPW). - CPC solar pilot plant;	inorganic anions present in WW and also to the NOM that could compete with the spiked contaminants for oxidizing species.	
<b>Photocatalysis</b>	Bisphenol A 100 µg L <sup>-1</sup>	- DI; - Synthetic freshwater (pH 7.58; TOC 3.4 mg L <sup>-1</sup> ; conductivity 241 µS cm <sup>-1</sup> ; Na <sup>+</sup> 1.09 mM; Ca <sup>2+</sup> 0.34 mM; Mg <sup>2+</sup> 0.44 mM; K <sup>+</sup> 0.07 mM; Cl <sup>-</sup> 0.06 mM; SO <sub>4</sub> <sup>2-</sup> 1.18 mM); - SWW secondary effluent (pH 7.75; TOC 17.76 mg L <sup>-1</sup> ; conductivity 301 µS cm <sup>-1</sup> ; Na <sup>+</sup> 1.23 mM; Ca <sup>2+</sup> 0.34 mM; Mg <sup>2+</sup> 0.45 mM; K <sup>+</sup> 0.17 mM; NH <sub>4</sub> <sup>+</sup> 0.32 mM; PO <sub>4</sub> <sup>3-</sup> 0.03 mM; Cl <sup>-</sup> 0.04 mM; SO <sub>4</sub> <sup>2-</sup> 1.38 mM); - Real municipal WWTP secondary effluent (pH 8.54; TOC 24.0 mg L <sup>-1</sup> ; conductivity 564 µS cm <sup>-1</sup> ; Na <sup>+</sup> 22.3 mM; Ca <sup>2+</sup> 65.6 mM; Mg <sup>2+</sup> 4.82 mM; K <sup>+</sup> 0.68 mM; NH <sub>4</sub> <sup>+</sup> 1.38 mM; PO <sub>4</sub> <sup>3-</sup> 12.92 mM; Cl <sup>-</sup> 13.0 mM; SO <sub>4</sub> <sup>2-</sup> 1.85 mM), Almeria, Spain.	- Catalyst: TiO <sub>2</sub> immobilized in glass spheres (~0.6 mg of TiO <sub>2</sub> was supported on the surface of each glass sphere);	Water matrix affected drastically the photocatalytic degradation of bisphenol A, remaining in water approximately 30%. This results could be explained by the presence of substances, such as, organics, CO <sub>3</sub> <sup>2-</sup> and Cl <sup>-</sup> in the matrix, acting as radical scavengers.	[65]
<b>Photocatalysis</b>	Amoxicillin (10 mg L <sup>-1</sup> ), carbamazepine (5 mg L <sup>-1</sup> ), diclofenac (2.5 mg L <sup>-1</sup> )	- DI; - WW effluent (pH 8.1; TOC 4.51 mg L <sup>-1</sup> ; BOD <sub>5</sub> 10 mg L <sup>-1</sup> ; TSS 11 mg L <sup>-1</sup> ), Italy.	- 125 W black-light fluorescent lamp (300–420 nm); - Catalyst: 0.2–0.8 g L <sup>-1</sup> of TiO <sub>2</sub> .	The half-life of diclofenac was lower than that of carbamazepine. The mineralization of the spiked urban WW was lower than that of the spiked DI due to interference of scavengers (e.g., CO <sub>3</sub> <sup>2-</sup> ) and other oxidizable compounds, typically occurring in WWs.	[66]
<b>Photocatalysis</b>	EE2 100 µg L <sup>-1</sup>	- UPW - DW (pH 7.9; conductivity 5.5 µS cm <sup>-1</sup> ; HCO <sub>3</sub> <sup>-</sup> 152 mg L <sup>-1</sup> ); - WW effluent (pH 8.0; COD 24 mg L <sup>-1</sup> ; DOC 8.4 mg L <sup>-1</sup> ; conductivity 820 µS cm <sup>-1</sup> ; Cl <sup>-</sup> 172 mg L <sup>-1</sup> ; NO <sub>3</sub> <sup>-</sup> 37 mg L <sup>-1</sup> ; NO <sub>2</sub> <sup>-</sup> 37 mg L <sup>-1</sup> ; SO <sub>4</sub> <sup>2-</sup> 54 mg L <sup>-1</sup> ; HCO <sub>3</sub> <sup>-</sup> 194 mg L <sup>-1</sup> ).	- Immersion well, batch type, lab scale photoreactor; - Irradiation source: 9 W UV-A lamp (350–400 nm); - Catalyst load: 750 mg L <sup>-1</sup> of TiO <sub>2</sub> .	Water matrix showed a negative effect on conversion and reaction rate. To achieve a complete removal of EE2 in WW, the treatment was three times longer in comparison with UPW and twice longer needed for WW diluted with an equal volume of UPW, mainly due to the reactions involving the residual organic fraction present in WW and oxidizing agents. Moreover, HCO <sub>3</sub> <sup>-</sup> , Cl <sup>-</sup> and SO <sub>4</sub> <sup>2-</sup> present in WW and DW can act as scavengers of HO <sup>•</sup> . Similar removal values to those obtained for diluted WW were found for DW samples.	[67]

<b>Photocatalysis</b>	EE2 100 µg L <sup>-1</sup>	<ul style="list-style-type: none"> <li>- UPW (pH 6.1; conductivity 5.5 µS cm<sup>-1</sup>)</li> <li>- DW (pH 7.9; conductivity 308 µS cm<sup>-1</sup>; HCO<sub>3</sub><sup>-</sup> 152 mg L<sup>-1</sup>);</li> <li>- WW effluent (pH 7.5, COD 24 mg L<sup>-1</sup>, DOC 8.4 mg L<sup>-1</sup>; conductivity 810 µS cm<sup>-1</sup>; NO<sub>3</sub><sup>-</sup> 37 mg L<sup>-1</sup>; NO<sub>2</sub><sup>-</sup> 37 mg L<sup>-1</sup>; Cl<sup>-</sup> 172 mg L<sup>-1</sup>; SO<sub>4</sub><sup>2-</sup> 54 mg L<sup>-1</sup>; HCO<sub>3</sub><sup>-</sup> 194 mg L<sup>-1</sup>), W. Crete, Greece;</li> <li>- Diluted WW effluent.</li> </ul>	<ul style="list-style-type: none"> <li>- Cylindrical glass cell with a useful volume of 300 ml;</li> <li>- Solar irradiation simulator (5% UV-A radiation and 0.1% UV-B radiation) equipped with a 150 W xenon ozone-free lamp and an AirMass 1.5 Global Filter;</li> <li>- Catalyst load: 250 mg L<sup>-1</sup> of TiO<sub>2</sub>.</li> </ul>	<p>Solar-driven heterogeneous photocatalysis was efficient on the removal of estrogen hormones in distinct water matrices. However, the removal efficiency decreased in the following order: UPW &gt; DW &gt; diluted WW &gt; WW. The organic and inorganic constituents typically found in WW and DW impeded degradation presumably due to the scavenging of oxidizing species. Moreover, the presence of HA affected in a greater extent the removal efficiency in comparison to a mixture of anions in UPW experiments.</p>	[68]
<b>Photocatalysis</b>	EE2 100–500 µg L <sup>-1</sup>	<ul style="list-style-type: none"> <li>- UPW;</li> <li>- WW effluent (pH 8; DOC 7.8 mg L<sup>-1</sup>; COD 24 mg L<sup>-1</sup>; Cl<sup>-</sup> 220 mg L<sup>-1</sup>; SO<sub>4</sub><sup>2-</sup> 60 mg L<sup>-1</sup>; HCO<sub>3</sub><sup>-</sup> 188 mg L<sup>-1</sup>; conductivity 820 µS cm<sup>-1</sup>), Greece.</li> </ul>	<ul style="list-style-type: none"> <li>- Cylindrical Pyrex cell with a useful volume of 300 ml;</li> <li>- Solar irradiation simulator (5% UV-A radiation and 0.1% UV-B radiation) equipped with a 150 W xenon ozone-free lamp and an AirMass 1.5 Global Filter;</li> <li>- Catalyst load: 50–500 mg L<sup>-1</sup> ZnO.</li> </ul>	<p>Among the five different operating variables, the water matrix was the only with a negative effect on the removal efficiency. Since usually estrogens are found in WW effluents, water matrix can have an important role on their treatment, mainly by the presence of organic and inorganic matter. Furthermore, HO<sup>•</sup> may be scavenged by HCO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> present in WW.</p>	[69]
<b>Photocatalysis</b>	Ibuprofen 6 µg L <sup>-1</sup> 6, 60, 213 mg L <sup>-1</sup>	<ul style="list-style-type: none"> <li>- UPW;</li> <li>- WW effluent (pH 7.3; DOC 215 mg L<sup>-1</sup>; conductivity 610 µS cm<sup>-1</sup>; Cl<sup>-</sup> 58 mg L<sup>-1</sup>; SO<sub>4</sub><sup>2-</sup> 34 mg L<sup>-1</sup>; NO<sub>3</sub><sup>-</sup> 19 mg L<sup>-1</sup>; NO<sub>2</sub><sup>-</sup> 30 mg L<sup>-1</sup>; PO<sub>4</sub><sup>3-</sup> 7 mg L<sup>-1</sup>; Na<sup>+</sup> 40 mg L<sup>-1</sup>; NH<sub>4</sub><sup>+</sup> 22 mg L<sup>-1</sup>; K<sup>+</sup> 10 mg L<sup>-1</sup>; Ca<sup>2+</sup> 21 mg L<sup>-1</sup>); Portugal.</li> <li>- Pharmaceutical WW (pH 7.9; DOC 170 mg L<sup>-1</sup>; conductivity 3770 µS cm<sup>-1</sup>; Cl<sup>-</sup> 978 mg L<sup>-1</sup>; SO<sub>4</sub><sup>2-</sup> 661 mg L<sup>-1</sup>; Na<sup>+</sup> 310 mg L<sup>-1</sup>; Mg<sup>2+</sup> 27 mg L<sup>-1</sup>), Sfax, Tunisia.</li> </ul>	<ul style="list-style-type: none"> <li>- Spiked WW and UPW (250 mL): Photoreactor equipped with four 10 W UV high intensity LEDs (λ<sub>max</sub> 382 nm);</li> <li>- Catalyst load: 0.5, 1.0, 1.5 g L<sup>-1</sup> TiO<sub>2</sub>;</li> <li>- Pharmaceutical WW and WW effluent (7.5 mL): Quartz cylindrical reactor equipped with a single LED;</li> <li>- Catalyst load: 0.5, 1.0, 2.0, 2.5, 3.0, 4.0 g L<sup>-1</sup> TiO<sub>2</sub>.</li> </ul>	<p>Lower ibuprofen removals were found when treating WW effluents and pharmaceutical WW in comparison to UPW. Moreover, ibuprofen was more difficult to be removed in the case of WW effluent mainly due to the higher DOC, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup> and PO<sub>4</sub><sup>3-</sup>.</p>	[70]

<b>Photocatalysis</b>	Tetracycline 55 mg L <sup>-1</sup>	<ul style="list-style-type: none"> <li>- UPW (pH 6.6; DOC 8.4 mg L<sup>-1</sup>; conductivity 0.067 μS cm<sup>-1</sup>; transmittance (at 254 nm) 100%);</li> <li>- DW (pH 7.8; conductivity 334 μS cm<sup>-1</sup>; Cl<sup>-</sup> 5.8 mg L<sup>-1</sup>; NO<sub>3</sub><sup>-</sup> &lt;5 mg L<sup>-1</sup>; NO<sub>2</sub><sup>-</sup> &lt;0.1 mg L<sup>-1</sup>; SO<sub>4</sub><sup>2-</sup> 47 mg L<sup>-1</sup>; HCO<sub>3</sub><sup>-</sup> 63 mg L<sup>-1</sup>; Ca<sup>2+</sup> 68 mg L<sup>-1</sup>; Mg<sup>2+</sup> 11.5 mg L<sup>-1</sup>; transmittance (at 254 nm) 97.6%);</li> <li>- WW effluent (pH 8; conductivity 855 μS cm<sup>-1</sup>; COD 24 mg L<sup>-1</sup>; Cl<sup>-</sup> 92 mg L<sup>-1</sup>; NO<sub>3</sub><sup>-</sup> 23 mg L<sup>-1</sup>; NO<sub>2</sub><sup>-</sup> 48 mg L<sup>-1</sup>; SO<sub>4</sub><sup>2-</sup> 74 mg L<sup>-1</sup>; HCO<sub>3</sub><sup>-</sup> 156 mg L<sup>-1</sup>; Ca<sup>2+</sup> 88 mg L<sup>-1</sup>; Mg<sup>2+</sup> 54 mg L<sup>-1</sup>; transmittance (at 254 nm) 61.6%).</li> </ul>	<ul style="list-style-type: none"> <li>- Photocatalytic reactor (500 mL);</li> <li>- Irradiation source: 18 W lamp emitting at 254 nm;</li> <li>- Catalyst load: 1 g L<sup>-1</sup> of TiO<sub>2</sub>.</li> </ul>	<p>The removal efficiency of tetracycline was higher in DW in comparison with UPW, which could be explained by the presence of dissolved organic matter acting as photosensitizer with the generation of reactive species. However, the removal decreased when WW was used as matrix. The organic matter could act as a filter for UV radiation and HO<sup>•</sup> can be scavenged by the high concentration of HCO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup> present in the WW effluent.</p>	[71]
<b>Photocatalysis</b>	Azo dye congo red, carbamazepine 10 mg L <sup>-1</sup>	<ul style="list-style-type: none"> <li>- DI;</li> <li>- Saline water (pH 7.5; conductivity 1300 818 μS cm<sup>-1</sup>, NaCl 1 g L<sup>-1</sup>, KH<sub>2</sub>PO<sub>4</sub> 6 mg P L<sup>-1</sup>);</li> <li>- WW effluent (pH 7.5; conductivity 1700 818 μS cm<sup>-1</sup>, COD 30 mg L<sup>-1</sup>; PO<sub>4</sub><sup>3-</sup> 6 mg P L<sup>-1</sup>; NO<sub>3</sub><sup>-</sup> 30 mg N L<sup>-1</sup>), collected from a lab-scale MBR system fed on real municipal primary effluent.</li> </ul>	<ul style="list-style-type: none"> <li>- Glass cylinder (1 L) photo-reactor, equipped with an axial quartz tube holding the UV lamp;</li> <li>- Catalysts: Hydrogen titanate nanofiber and commercial TiO<sub>2</sub> (P25);</li> <li>- 8W lamp (λ 360nm).</li> </ul>	<p>The photocatalytic activity of both catalysts was similar in saline water and effluent, but the degradation of the target compounds had an opposite trend regarding the matrix effects. Matrix effect on the dark adsorption of congo red was higher in real effluents than in saline water, while carbamazepine had negligible adsorption, explained by the different polarity, which causes different adsorption and interaction with the catalyst surface. Anions affected slightly the removal rates, whereas calcium had a pronounced negative effect on the photocatalytic performance using nanofiber catalyst.</p>	[72]
<b>Photocatalysis</b>	Acetaminophen, thiabendazole, acetamiprid 100 μg L <sup>-1</sup>	<ul style="list-style-type: none"> <li>- DI;</li> <li>- Synthetic freshwater;</li> <li>- SWW;</li> <li>- WW effluent (pH 8.4; conductivity 2670 μS cm<sup>-1</sup>, DOC 21.10 mg L<sup>-1</sup>; IC 60.4 mg L<sup>-1</sup>; Cl<sup>-</sup> 12.9 mg L<sup>-1</sup>; SO<sub>4</sub><sup>2-</sup> 1.85 mg L<sup>-1</sup>; Na<sup>+</sup> 23.0 mg L<sup>-1</sup>; NH<sub>4</sub><sup>+</sup> 0.06 mg L<sup>-1</sup>; K<sup>+</sup> 0.68 mg L<sup>-1</sup>; Ca<sup>2+</sup> 65.7 mg L<sup>-1</sup>; Mg<sup>2+</sup> 4.82 mg L<sup>-1</sup>), Spain.</li> </ul>	<ul style="list-style-type: none"> <li>- CPC solar pilot plant;</li> <li>- Solar simulator equipped with a Xenon lamp and a 290 nm cut-off filter;</li> <li>- Catalyst: TiO<sub>2</sub>-coated glass beads.</li> </ul>	<p>The matrix effect led to a reduction of degradation rate due to the presence of other substances in the matrix (organics, CO<sub>3</sub><sup>2-</sup>, etc.), which can be adsorbed onto the catalyst surface (blocking and/or competing for reaction sites) and/or compete for HO<sup>•</sup> in the bulk.</p>	[73]

<b>Photocatalysis</b>	Metoprolol 50 mg L <sup>-1</sup>	- UPW; - WW effluent (pH 7.56; TOC 18.8 mg C L <sup>-1</sup> ; COD 44.6 mg L <sup>-1</sup> ; BOD <sub>5</sub> 8.4 mg L <sup>-1</sup> ; UV <sub>254</sub> 0.235 cm <sup>-1</sup> ; turbidity 10.4 NTU; alkalinity 471 mg CaCO <sub>3</sub> L <sup>-1</sup> ; TSS 18.8 mg L <sup>-1</sup> ; VSS 14.6 mg L <sup>-1</sup> ; Cl <sup>-</sup> 745 mg L <sup>-1</sup> ; NO <sub>3</sub> <sup>-</sup> 3.0 mg L <sup>-1</sup> ; NO <sub>2</sub> <sup>-</sup> n.d.; PO <sub>4</sub> <sup>3-</sup> 15 mg L <sup>-1</sup> ; SO <sub>4</sub> <sup>2-</sup> 232 mg L <sup>-1</sup> ; NH <sub>4</sub> <sup>+</sup> 57.1 mg L <sup>-1</sup> ; Na <sup>+</sup> 495 mg L <sup>-1</sup> ; K <sup>+</sup> 45.9 mg L <sup>-1</sup> ; Ca <sup>2+</sup> 138 mg L <sup>-1</sup> ; Mg <sup>2+</sup> 59.6 mg L <sup>-1</sup> ), Spain.	- Solar simulator equipped with a Xenon lamp and an optical filter (cut-off < 280 nm); - Photon flux 2.99 × 10 <sup>-6</sup> Einstein s <sup>-1</sup> (290–400 nm); Duran tubular photoreactor (24 cm length, 2.11 cm diameter, 0.078 L illuminated volume) placed at the bottom of the solarbox in the axis of a parabolic mirror; Recirculation at a flow rate of 0.65 L min <sup>-1</sup> ; - Catalyst: boron-modified TiO <sub>2</sub> (5% w/w of B); - V 1.0 L; T 25 °C.	The optimal photocatalyst concentration was higher in WW due to the competition of organic matter for active species generated and for adsorption in the photocatalyst surface. Inorganic ions may also interfere, by deactivation of the catalyst surface.	[74]
<b>Photocatalysis</b>	Carbamazepine 5 mg L <sup>-1</sup>	- WW effluent from a lab-scale MBR used to treat primary WWs from a WWTP (COD 13.5-22 mg L <sup>-1</sup> ; PO <sub>4</sub> <sup>3-</sup> 21.7-23.8 mg L <sup>-1</sup> ; NO <sub>3</sub> <sup>-</sup> 210-238 mg L <sup>-1</sup> ), South Australia	- Sequential batch annular slurry photoreactor; - Low-intensity (11 W) UV-C lamp; - Catalysts: immobilized TiO <sub>2</sub> , namely anatase titanate nanofiber and mesoporous TiO <sub>2</sub> impregnated kaolinite; - Presence of effluent organic matter and inorganic ions.	The sequential batch annular slurry photoreactor system was successfully applied for the elimination of carbamazepine from WW, but high molecular weight effluent organic matter competed for the photocatalytic reaction. The presence of inorganic ions interfered with the surface fouling of immobilized photocatalysts, reducing their photoactivity.	[75]
<b>Photocatalysis</b>	Ofloxacin, atenolol 10 mg L <sup>-1</sup>	- UPW; - GW; - WW effluent (pH 8.22; TOC 11 mg L <sup>-1</sup> ; COD 6 mg L <sup>-1</sup> ; turbidity 1.9 NTU; conductivity 1424 μS cm <sup>-1</sup> ; TSS 4.5 mg L <sup>-1</sup> ; N <sub>total</sub> 3.7 mg L <sup>-1</sup> ; P <sub>total</sub> 2.96 mg L <sup>-1</sup> ; N-NH <sub>4</sub> <sup>+</sup> 0.16 mg L <sup>-1</sup> ; Cl <sup>-</sup> 196 mg L <sup>-1</sup> ), Cyprus.	- 9W lamp emitting predominantly at 350–400 nm; -Catalyst: 0.25 g L <sup>-1</sup> of TiO <sub>2</sub> .	The extent of mineralization followed the decreasing order: UPW > GW > WW. This could be attributed to the corresponding TOC increment and other species present in the actual matrices, which are able to scavenge radicals or other reactive moieties.	[76]
<b>Photocatalysis</b>	Diclofenac, fluoxetine mg L <sup>-1</sup> levels	- DI; - WW effluent (pH 6.15; TOC 5.15 mg L <sup>-1</sup> ; DOC 4.65 mg L <sup>-1</sup> ; SS 11 mg L <sup>-1</sup> ), Portugal.	- XX-15 BLB UV lamp (λ 365 nm), - Catalysts: Single-phase Hydroxyapatite (HAp) and HAp-titania (TiHAp) materials (1 wt% TiO <sub>2</sub> ); - DI: spiked with 2-8 mg L <sup>-1</sup> ; catalyst load between 1 and 4 g L <sup>-1</sup> ; Effluents: spiked with 5 mg L <sup>-1</sup> of both contaminants; 4 g L <sup>-1</sup> of TiHAp.	The HAp-titania photocatalyst was effective when using actual treated WW, but the removal efficiency decreased by 20% for diclofenac and by 4% for fluoxetine, probably due to the suspended solids present in the WW. The degradation rate using centrifuged WW was comparable to that observed in DI.	[77]
<b>Photocatalysis</b>	Sulfamethoxazole 10 mg L <sup>-1</sup>	- UPW; - GW; - WW effluent (pH 8.22; TOC 11 mg L <sup>-1</sup> ; COD 6 mg L <sup>-1</sup> ; turbidity 1.9 NTU; conductivity 1424 μS cm <sup>-1</sup> ; TSS 4.5 mg L <sup>-1</sup> ; N <sub>total</sub> 3.7 mg L <sup>-1</sup> ; P <sub>total</sub> 2.96 mg L <sup>-1</sup> ; N-NH <sub>4</sub> <sup>+</sup> 0.16 mg L <sup>-1</sup> ; Cl <sup>-</sup> 196 mg L <sup>-1</sup> ), Cyprus.	- 9W lamp emitting predominantly at 350–400 nm; -Catalyst: 0.5 g L <sup>-1</sup> of TiO <sub>2</sub> .	The degradation was favoured at acidic pH. Comparing to UPW, the matrix effects on degradation were negligible, even for WW with high TOC and GW with high content of HCO <sub>3</sub> <sup>-</sup> , both known scavengers of radicals. At near-neutral pH, the	[78]

				presence of co-existing substances in environmental samples slightly affected the degradation of the pharmaceutical, suggesting that the ionic strengths of both environmental matrices had a role on promoting the agglomeration of TiO <sub>2</sub> particles, decreasing the effective surface area.	
<b>Photocatalysis</b>	Sulfonamides (sulfathiazole, sulfamethoxazole, sulfadiazine) 5 mg L <sup>-1</sup>	- DI; - Influent (with and without preliminary filtration and coagulation); - WW effluents (pH 7.10-7.66; conductivity 1204-1722 μS cm <sup>-1</sup> ; COD 137-774 mg L <sup>-1</sup> ; BOD <sub>5</sub> 60-89 mg L <sup>-1</sup> ; turbidity 4-50), Poland.	- 4 UV lamps emitting at λ <sub>max</sub> 366 nm; -Catalyst: 0.5 g L <sup>-1</sup> of TiO <sub>2</sub> and/or 1 mM of FeCl <sub>3</sub> ; - pH 3.	The optimum photocatalytic system was TiO <sub>2</sub> /FeCl <sub>3</sub> under acid pH. The degradation rate was significantly lower in WW than in DI. Similar results were obtained using the model WW. Preliminary microfiltration and coagulation of the influents did not improved the photocatalytic efficiency, in comparison to untreated influents.	[79]
<b>Photocatalysis</b>	Carbamazepine 133 ng L <sup>-1</sup>	- Deionized water; - WW effluent from a sequential batch reactor (SBR) activated sludge process with phosphate precipitation by Fe <sup>3+</sup> (pH 7.7; TOC 10 mg L <sup>-1</sup> , electrical conductivity 803 μmho cm <sup>-1</sup> ; IC 26.3 mg CaCO <sub>3</sub> L <sup>-1</sup> )	- Temperature: between 21 and 25 °C; - Catalyst: 100 mg L <sup>-1</sup> of TiO <sub>2</sub> ; - pH 7.3; - Presence and absence of powdered activated carbon.	The photocatalytic efficiency was matrix and pH dependent. Carbamazepine present in the WW (pH 7.3) was not completely removed by photocatalysis with a UV dose of about 6 kJ L <sup>-1</sup> . In contrast, spiking carbamazepine at 10 mg L <sup>-1</sup> in deionized water and in acidic effluent led to an efficient removal with the same UV dose. Under alkaline conditions, the UV dose needed for the same removal from the spiked effluent was 10 times higher.	[80]
<b>Photocatalysis</b>	Diclofenac, carbamazepine, ibuprofen and propranolol 5 mg L <sup>-1</sup>	- DI; - WW effluent (pH 7.3; DOC 12.2 mg L <sup>-1</sup> ; COD 35.2 mg L <sup>-1</sup> ; BOD <sub>5</sub> 6 mg L <sup>-1</sup> ; Cl <sup>-</sup> 49.5 mg L <sup>-1</sup> ; SO <sub>4</sub> <sup>2-</sup> 24.4 mg L <sup>-1</sup> ; NO <sub>3</sub> <sup>-</sup> 4.5 mg L <sup>-1</sup> ; TN 7.2 mg L <sup>-1</sup> ; TP 0.55 mg L <sup>-1</sup> ), The Netherlands.	- Simulated solar irradiation (96 h): Xenon high-intensity discharge lamps (55 W) emitting at λ range of 300–800 nm; - Stirring at 75 rpm; - Catalyst: 25 g of immobilized TiO <sub>2</sub> .	Photolysis efficiency was enhanced by the DOM present in WW effluent, organic matter, which might absorb light to excite triplet states of DOM ( <sup>3</sup> DOM*) and further to reactive radicals. NO <sub>3</sub> <sup>-</sup> could also play a role by adsorption of light < 350 nm and production of HO*, accelerating the indirect photolysis. Photocatalysis led to superior removal efficiencies for all pharmaceuticals. However, carbamazepine and ibuprofen were degraded at less extent in WW, probably due a proposed partial or selective reduction of the oxidized intermediates back to parent compounds.	[81]

<b>Photocatalysis</b>	Carbamazepine, gabapentin, lamotrigine, oxcarbazepine, venlafaxine, bisoprolol, celiprolol, talinolol, bezafibrate, tramadol, candesartan, eprosartan, irbesartan and valsartan 0.35-11.30 $\mu\text{g L}^{-1}$ levels	- UPW; - WW effluent (pH 7.5; COD 37 $\text{mg L}^{-1}$ ; BOD <sub>5</sub> 4 $\text{mg L}^{-1}$ ; TN 12.0 $\text{mg L}^{-1}$ ; NO <sub>3</sub> <sup>-</sup> 7.4 $\text{mg L}^{-1}$ ; NO <sub>2</sub> <sup>-</sup> 0.03 $\text{mg L}^{-1}$ ; NH <sub>4</sub> <sup>+</sup> 0.31 $\text{mg L}^{-1}$ ; TP 0.86 $\text{mg L}^{-1}$ ; PO <sub>4</sub> <sup>3-</sup> 0.56 $\text{mg L}^{-1}$ ), Dresden, Germany.	- UVA radiation: six 8W Hg fluorescent tubes (365 nm); - Catalyst load: 1 $\text{g L}^{-1}$ of TiO <sub>2</sub> P25 or ZnO.	UVA/TiO <sub>2</sub> and UVA/ZnO systems led to a significant degradation of the analysed pharmaceuticals and in the particular case of carbamazepine, for which the matrix effect was also studied. Similar results were obtained when comparing UPW and WW for each photocatalytic system, but ZnO nanoparticles showed a better performance.	[82]
<b>Photocatalysis–DCMD (direct contact membrane distillation)</b>	Diclofenac, naproxen and ibuprofen 100 $\mu\text{g L}^{-1}$	- UPW; - DW; - Primary WW effluents; - Secondary WW effluents, Poland.	- Photoreactor equipped with an UV-C germicidal lamp ( $\lambda_{\text{max}}$ 254 nm) located between a feed tank and a membrane module; - Catalyst load: 0.5 $\text{g L}^{-1}$ of TiO <sub>2</sub> ; - DCMD: hydrophobic polypropylene membranes, with an area of 0.014 $\text{m}^2$ and nominal pore size of 0.2 $\mu\text{m}$ ; - Feed and distillate solution temperatures: 60 and 20 °C.	A PMR using DCMD and UV-C radiation was applied to WWTP effluents. In general the removal efficiency by the hybrid process was in the following decreasing order, except for diclofenac: UPW > tap water > secondary effluent > primary effluent. Diclofenac was faster removed in the primary vs secondary effluents, possibly due to adsorption of the drug on the suspended matter present in the WW.	[83]
<b>Photocatalysis</b>	Carbamazepine 50 $\mu\text{M}$	- DW; - WW effluents.	- Carbamazepine/peroxymonosulphate (PMS) molar ratio: from 1 to 30; - Cobalt salts tested: CoCl <sub>2</sub> ·6H <sub>2</sub> O and Co(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O.	Sulphate radical yielded a faster degradation of carbamazepine compared to HO <sup>•</sup> , in both real and DI. The WW matrix had an important effect on the inhibition of degradation by both PMS/Co(II) and Fenton systems. The Cl <sup>-</sup> ions were involved in the inhibition effect, but the organic matter could also affect the oxidation kinetic decrease.	[84]
<b>Photocatalysis</b>	Diatrizoate (744±28 $\mu\text{g L}^{-1}$ ), acetaminophen (736±36 $\mu\text{g L}^{-1}$ ), carbamazepine (738±31 $\mu\text{g L}^{-1}$ ), atenolol (757±67 $\mu\text{g L}^{-1}$ )	- WW effluent (pH 7.7±0.3; conductivity 1.3±0.2 $\text{mS cm}^{-1}$ ; DOC 6±2 $\text{mg L}^{-1}$ ; COD 18±6 $\text{mg L}^{-1}$ ; BOD <sub>5</sub> 3.4±1.7 $\text{mg L}^{-1}$ ; UV <sub>254</sub> 15±3 $\text{m}^{-1}$ ; Cl <sup>-</sup> 267±35 $\text{mg L}^{-1}$ ; SO <sub>4</sub> <sup>2-</sup> 89±13 $\text{mg L}^{-1}$ ; NO <sub>3</sub> <sup>-</sup> 7±3 $\text{mg L}^{-1}$ ; NO <sub>2</sub> <sup>-</sup> 0.08±0.06 $\text{mg L}^{-1}$ ; HCO <sub>3</sub> <sup>-</sup> 259±64 $\text{mg L}^{-1}$ ; Na <sup>+</sup> 152±14 $\text{mg L}^{-1}$ ; Ca <sup>2+</sup> 160±17 $\text{mg L}^{-1}$ ; Mg <sup>2+</sup> 6.6±0.8 $\text{mg L}^{-1}$ ; K <sup>+</sup> 22±3 $\text{mg L}^{-1}$ ), France.	- Modular tube reactor; - Irradiation source: UV-A lamp ( $\lambda$ 365 nm, 3-40 $\text{W}_{\text{UV}} \text{m}^{-2}$ ); - Recirculation flow rate: 1.5 $\text{L min}^{-1}$ ; - Catalyst: 2 $\text{g L}^{-1}$ TiO <sub>2</sub> .	Organic matter, phosphate and bicarbonate ions affected negatively the process efficiency by HO <sup>•</sup> scavenging. Consequently, the kinetic constant of mineralization decreased. Degradation of target compounds ranged from 20% to 80%, decreasing for higher volumetric reduction factor.	[85]
<b>Photocatalysis (TiO<sub>2</sub> and persulfate)</b>	Trimethoprim 1 $\text{mg L}^{-1}$	- WW effluent (pH 7.30; conductivity 2.15 $\text{mS cm}^{-1}$ ; turbidity 4.2 NTU; TOC 13.9 $\text{mg L}^{-1}$ ; IC 59.5 $\text{mg L}^{-1}$ ; Cl <sup>-</sup> 477.4 $\text{mg L}^{-1}$ ; SO <sub>4</sub> <sup>2-</sup> 157.5 $\text{mg L}^{-1}$ ; NO <sub>3</sub> <sup>-</sup> 47 $\text{mg L}^{-1}$ ; Na <sup>+</sup> 269.5 $\text{mg L}^{-1}$ ; Ca <sup>2+</sup> 81 $\text{mg L}^{-1}$ ; Mg <sup>2+</sup> 54.4 $\text{mg L}^{-1}$ ; NH <sub>4</sub> <sup>+</sup> 25.1 $\text{mg L}^{-1}$ ). - Natural water (pH 7.55; conductivity 1.1 $\text{mS cm}^{-1}$ ; TOC 2.6 $\text{mg L}^{-1}$ ; IC 89.4 $\text{mg L}^{-1}$ ; Cl <sup>-</sup> 148 $\text{mg L}^{-1}$ ; SO <sub>4</sub> <sup>2-</sup> 159.4	- CPC solar pilot plant; - V 39 L; - Catalyst: 200 $\text{mg L}^{-1}$ TiO <sub>2</sub> ; - HA: 10 $\text{mg L}^{-1}$ ; - Sodium persulphate: 0.125-0.5 mM; - pH 4-7.5;	The removal occurred by the combination of heterogeneous photocatalysis, photolysis and persulphate oxidation. Trimethoprim degradation rate decreased as the complexity of the matrix increases. The addition of sodium persulphate	[86]

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mg L<sup>-1</sup>; NO<sub>3</sub><sup>-</sup> 3 mg L<sup>-1</sup>; Na<sup>+</sup> 231.2 mg L<sup>-1</sup>; Ca<sup>2+</sup> 24.7 mg L<sup>-1</sup>; Mg<sup>2+</sup> 26 mg L<sup>-1</sup>);  
- Well water (pH 8.1; conductivity 2.4 mS cm<sup>-1</sup>; TOC 5.2 mg L<sup>-1</sup>; IC 179 mg L<sup>-1</sup>; Cl<sup>-</sup> 296 mg L<sup>-1</sup>; SO<sub>4</sub><sup>2-</sup> 319 mg L<sup>-1</sup>; NO<sub>3</sub><sup>-</sup> 6 mg L<sup>-1</sup>; Na<sup>+</sup> 462 mg L<sup>-1</sup>; Ca<sup>2+</sup> 49 mg L<sup>-1</sup>; Mg<sup>2+</sup> 52 mg L<sup>-1</sup>).

reduced the effect of scavenger species (chloride, sulphate and bicarbonate). HA competes for reactive species in the reaction mixture.

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**Abbreviations:** BOD<sub>5</sub>, biochemical oxygen demand; COD, chemical oxygen demand; CPC, compound parabolic concentrator; DCMD, direct contact membrane distillation; DI, distilled water; DO, dissolved oxygen; DOC, dissolved organic carbon; DW, drinking water; E1, estrone; EE2, 17-alpha-ethinylestradiol; GW, groundwater; HA, humic acids, Hap, hydroxyapatite; IC, inorganic carbon; MP, micropollutants; NOM, natural organic matter; NTU, nephelometric turbidity unit; PMS, peroxymonosulphate; PMR, photocatalytic membrane reactor; SS, suspended solids; SW, surface water; SWW, synthetic wastewater; TOC, total organic carbon; TS, total solids; TSS, total suspended solids; UPW, ultrapure water; VSS, volatile suspended solids; WW, wastewater; WWTP, wastewater treatment plant.

**Table S5.** Matrix effects occurring in studies dealing with ozone-based processes, published since 2005. Unless otherwise stated, the experimental conditions refer to the tested conditions for the evaluation of matrix effects.

AOT	Target pollutant Concentration	Matrices	Experimental conditions	Main conclusions	Reference
<b>O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub></b>	Atrazine, sulfamethoxazole, N-nitrosodimethylamine 0.5 – 11 µM	- 3 Lake waters, Switzerland and Norway; - WW effluent (DOM 3.9 mg C L <sup>-1</sup> ; alkalinity 6.5 mg CaCO <sub>3</sub> L <sup>-1</sup> ), Switzerland.	- 500 mL batch reactor; - T 20 °C; - pH 8.0; - Spiked O <sub>3</sub> stock solution; - Addition of H <sub>2</sub> O <sub>2</sub> (2:1, O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub> ) prior to O <sub>3</sub> addition.	The O <sub>3</sub> dose needed was higher for WW. The addition of H <sub>2</sub> O <sub>2</sub> enhanced the removal and reduced bromate formation. Generally, the waters with lower DOM concentration and/or lower HO <sup>•</sup> scavenging rates had a higher transformation. The reactivity of DOM was different in waters with the same DOC concentration. The content on CO <sub>3</sub> <sup>2-</sup> /HCO <sub>3</sub> <sup>-</sup> led to an inhibitory effect of O <sub>3</sub> decay.	[13]
<b>O<sub>3</sub></b>	Hydrochlorothiazide 1 µM	- UPW; - SW from a public reservoir (pH 7.3; TOC 4.3 mg L <sup>-1</sup> ; alkalinity 30 mg CaCO <sub>3</sub> L <sup>-1</sup> ), Spain; - WW effluent (pH 8.0; TOC 23.3 mg L <sup>-1</sup> ; alkalinity 250 mg CaCO <sub>3</sub> L <sup>-1</sup> ), Spain.	- 500 mL flask reactor; - Spiked O <sub>3</sub> stock solution (concentration 0 – 10 mg L <sup>-1</sup> ); - T 20 °C.	Ozonation led to a removal rate of the compound in the following order: WW < SW < UPW. This fact is attributed to the dissolved organic matter (DOM) in the matrices under study, which could consume part of the oxidant. A lower O <sub>3</sub> dose was enough to eliminate the pharmaceutical from SW, in comparison to that required for WW.	[23]
<b>UV O<sub>3</sub> O<sub>3</sub>/UV Photocatalysis Catalytic ozonation Photocatalytic ozonation</b>	Diclofenac, sulfamethoxazole, caffeine 10 mg L <sup>-1</sup>	- UPW; - WW effluent (pH 7-8; TOC 35 mg L <sup>-1</sup> ; IC 23 mg L <sup>-1</sup> ; COD 58-84 mg L <sup>-1</sup> ; BOD 30-60 mg L <sup>-1</sup> ), Spain.	- 1L tubular glass photoreactor (450 mm height, 80 mm diameter) filled with 900 mL of solution; - pH 7.0 (UPW); - Irradiation source: HP Heraeus Hg lamp (bandwidth range 238–579 nm with three λ <sub>max</sub> emitting at 254, 313 and 366) immersed in a glass well placed at the middle of the reactor, UVB radiation was cut off; - TiO <sub>2</sub> concentration: 1.5 g L <sup>-1</sup> ; - O <sub>3</sub> : inlet concentration 10 mg L <sup>-1</sup> and flow rate 30 L h <sup>-1</sup> .	Diclofenac elimination rate with UVA radiation was higher in WW than that in UPW, possibly due to some substance present in the effluent acting as photosensitizing agent. The removal rates of all compounds and TOC by the other AOTs were slightly slower in WW. For all the pharmaceuticals, no significant differences were verified on their removal by single O <sub>3</sub> with/without the presence of HCO <sub>3</sub> <sup>-</sup> /CO <sub>3</sub> <sup>2-</sup> , suggesting that direct attack by O <sub>3</sub> is the main mechanism.	[28]
<b>O<sub>3</sub></b>	Metoprolol, naproxen, amoxicillin, phenacetin 1 µM	- GW, Spain; - SW from a public reservoir, Spain; - 3 WW effluents (pH 7.8-8.1; TOC 13.2-23.3 mg L <sup>-1</sup> ; COD 28.2-49.7 mg L <sup>-1</sup> ; conductivity 637-905 µS cm <sup>-1</sup> ; alkalinity 93-325 mg CaCO <sub>3</sub> L <sup>-1</sup> ), Spain.	- Each run was initiated by injecting a variable volume of the O <sub>3</sub> stock solution to achieve a dose of O <sub>3</sub> varying between 0.5 and 5 mg L <sup>-1</sup> for the secondary effluents, and between 0.1 and 2 mg L <sup>-1</sup> for the natural waters; - T 20 °C; - pH 7 by using the phosphoric acid/phosphate buffer; - Initial concentrations of p-chlorobenzoic acid of 1.0 µM.	The removal of pharmaceuticals in the WW was lower than in the SW, which was in turn lower than in GW. The amount of dissolved organic matter present in each water explains this trend (COD and TOC: GW < SW < WW effluents). The organic matter content consumed part of the oxidant in competition with the pharmaceuticals.	[87]



<b>UV Photocatalysis (TiO<sub>2</sub> and persulphate (PS)) Photo-Fenton UV/PS/Fe</b>	Acetamiprid 100 µg L <sup>-1</sup>	<ul style="list-style-type: none"> <li>- DI;</li> <li>- Synthetic WW;</li> <li>- WW effluent (pH 8.6; DOC 18.5 mg L<sup>-1</sup>; IC 44 mg L<sup>-1</sup>; COD 71 mg L<sup>-1</sup>; NO<sub>3</sub><sup>-</sup> 2.1 mg L<sup>-1</sup>; NO<sub>2</sub><sup>-</sup> 0.02 mg L<sup>-1</sup>; PO<sub>4</sub><sup>3-</sup> 4.1 mg L<sup>-1</sup>; SO<sub>4</sub><sup>2-</sup> 58 mg L<sup>-1</sup>).</li> </ul>	<ul style="list-style-type: none"> <li>- Three 30W UV-C LP lamps (254 nm);</li> <li>- Catalysts: TiO<sub>2</sub> at 50, 100, 200 mg L<sup>-1</sup> and persulphate at 25, 50, 100 mg L<sup>-1</sup>;</li> <li>- H<sub>2</sub>O<sub>2</sub>: 25, 50, 100 mg L<sup>-1</sup>;</li> <li>- pH natural (2.8 for UV/H<sub>2</sub>O<sub>2</sub>/Fe);</li> <li>- Effect of organic matter: addition of HA, lignin-derivative and lauryl sulphate.</li> </ul>	<p>All processes at neutral pH were able to effectively remove acetamiprid, being the photo-Fenton the most efficient for all water matrices. UV/PS and UV/PS/Fe systems also showed good efficiencies. The matrix effect retarded the removal rates, due to the high alkalinity and organic matter content of both synthetic and actual effluents. HA interfered with UV photolysis at high concentration due to the absorptivity of UV radiation. In turn, they had no impact on UV/H<sub>2</sub>O<sub>2</sub>/Fe and UV/PS/Fe processes. AOTs using iron probably originated Fe(II) complexes with lignin, acting as filter due to the high absorptivity. The lauryl sulphate did not promoted the formation such complexes at natural pH, leading to similar removal rates for all processes.</p>	[88]
<b>Photocatalysis Photo-Fenton O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub></b>	Carbamazepine, diclofenac 10-1000 µg L <sup>-1</sup>	<ul style="list-style-type: none"> <li>- DI;</li> <li>- WW effluent (pH 7.45; COD 119 mg L<sup>-1</sup>; BOD 250 mg L<sup>-1</sup>; N<sub>total</sub> 30 mg L<sup>-1</sup>; P<sub>total</sub> 0.38 mg L<sup>-1</sup>; SS 267 mg L<sup>-1</sup>).</li> </ul>	<ul style="list-style-type: none"> <li>- T 25 °C and pH 7.0, except for photo-Fenton (pH 3.0);</li> <li><i>Photo-Fenton</i></li> <li>- Three 4 W near-UV-A (black light) fluorescent lamps with a radiation peak at 352 nm;</li> <li>- Fe<sup>2+</sup>: 10 mg L<sup>-1</sup>;</li> <li>- H<sub>2</sub>O<sub>2</sub>: 100 mg L<sup>-1</sup>;</li> <li><i>O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub></i></li> <li>- O<sub>3</sub>: inlet concentration 0.36 mg L<sup>-1</sup> and flow rate 3.0 L h<sup>-1</sup>;</li> <li>- H<sub>2</sub>O<sub>2</sub>: 20 mg L<sup>-1</sup>;</li> <li><i>Heterogeneous photocatalysis</i></li> <li>- TiO<sub>2</sub>: 200 mg L<sup>-1</sup>.</li> </ul>	<p>The order of the inhibition caused by matrix components was as follows: O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> &gt; UV/TiO<sub>2</sub> &gt; UV/H<sub>2</sub>O<sub>2</sub>/Fe. For UV/H<sub>2</sub>O<sub>2</sub>/Fe, the Fenton reaction was favoured by the presence of co-existing substances, possibly providing additional iron ions, while the photo-reduction was inhibited by the complex-forming reaction and/or light scattering. For UV/TiO<sub>2</sub>, substances present in the matrix could inhibit the removal via scavenger effects, light scattering and adsorption. In the O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> process, the matrix affected the mass transfer of O<sub>3</sub> from the gas to the liquid phase, in addition to the scavenger effects on both HO<sup>•</sup> and dissolved O<sub>3</sub>.</p>	[16]
<b>O<sub>3</sub></b>	Tetrabromobisphenol 100 mg L <sup>-1</sup>	<ul style="list-style-type: none"> <li>- UPW spiked with anions and HA;</li> <li>- River water (pH 7.49; DOC 9.10 mg L<sup>-1</sup>);</li> <li>- Raw WW (pH 7.74; DOC 45.31 mg L<sup>-1</sup>);</li> <li>- WW effluent (pH 7.65; DOC 17.04 mg L<sup>-1</sup>).</li> </ul>	<ul style="list-style-type: none"> <li>- 100 mL conical flasks filled with 50 mL of pollutant solution;</li> <li>- O<sub>3</sub> flow rate of 36 mL min<sup>-1</sup>;</li> <li>- inlet O<sub>3</sub> concentration in the gas phase was measured as 140.6 mg L<sup>-1</sup>;</li> <li>- Effect of inorganic ions (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, HCO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>) at 0.5 and 5.0 mmol L<sup>-1</sup>;</li> <li>- Effect of HA at 5.0 and 50.0 mg L<sup>-1</sup>.</li> </ul>	<p>Tetrabromobisphenol A was completely removed after 6 min of ozonation at pH 8.0. The anions (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, HCO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>) and HA did not significantly affect its degradation. Additionally, no significant difference in the abatement of the pollutant was found employing ozonation to treat the different water matrices. The little influence of WW components in the oxidation rate is probably due to the excessive O<sub>3</sub> and HO<sup>•</sup> in solution.</p>	[89]
<b>O<sub>3</sub></b>	Flumequine 20 µg L <sup>-1</sup> -20 mg L <sup>-1</sup>	<ul style="list-style-type: none"> <li>- UPW;</li> <li>- River water;</li> <li>- WW influent;</li> <li>- WW effluent (characterization not provided).</li> </ul>	<ul style="list-style-type: none"> <li>- 100 mL semi-batch glass reactor filled with 50 mL of solution stirred at 450 rpm; T 25 °C;</li> <li>- O<sub>3</sub> continuously bubbled into the reactor bottom at a constant flow rate (36 mL min<sup>-1</sup>) through a glass tube (0.5m) with a sintered end;</li> <li>- Inlet O<sub>3</sub> concentration in the gas phase: 140.6 mg L<sup>-1</sup>;</li> </ul>	<p>The different ions and types of water (UPW, river water, WW influent and effluent) did not influenced the reaction efficiency significantly. However, the DOM extract composed by river sediment behaved as inhibitor and two DOM extracts, namely rice straw and pig manure, promoted the oxidation of the target pollutants</p>	[90]

<b>O<sub>3</sub></b> <b>O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub></b>	Metoprolol, naproxen, amoxicillin, phenacetin 1 μM	- UPW; - 2 WW effluents.	- Effect of inorganic ions (Cl <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup> , HCO <sub>3</sub> <sup>-</sup> , K <sup>+</sup> , Ca <sup>2+</sup> , Mg <sup>2+</sup> ) or extracts of DOM (HA, rice straw, river sediment, pig manure). - 500 mL cylindrical glass reactor; - T 25 °C; - Natural pH; - O <sub>3</sub> : 16 mg h <sup>-1</sup> .	For both processes, the removal rate was lower in the WW effluents than in UPW, due to the presence of DOM in WW, which consumes part of the oxidant, competing with the target substances. The two WW had different DOM contents, giving higher degradation rates for that with less amount of DOM, for both processes. To achieve the same removal, higher oxidant doses would be required.	[91]
<b>Photocatalytic ozonation</b>	Diclofenac 10 <sup>-4</sup> and 10 <sup>-6</sup> M	- UPW; - WW effluent (pH 7–8; TOC 33 mg L <sup>-1</sup> ; IC 28 mg L <sup>-1</sup> ; COD 60 mg L <sup>-1</sup> ; BOD 33 mg L <sup>-1</sup> ), Spain.	- Cylindrical borosilicate glass photo-reactor (0.45 m height, 0.08 m diameter); - HP Hg lamp (UV-Vis λ > 300 nm); - T 20 °C; - pH 7.0; - Inlet O <sub>3</sub> gas concentration: 10 mg L <sup>-1</sup> ; - Gas flow rate: 30 L h <sup>-1</sup> ; - Catalyst: 1.5 g L <sup>-1</sup> of TiO <sub>2</sub> .	Diclofenac (initial concentration 10 <sup>-4</sup> M) was completely removed within 6 min and 60–75% of TOC removals were observed after 60 min, regardless of the matrix. However, for lower initial concentration of diclofenac (10 <sup>-6</sup> M) in WW, TOC removal largely depended on the organic–inorganic WW content.	[92]
<b>O<sub>3</sub></b>	42 APIs 1 μg L <sup>-1</sup>	- 6 WW effluents (pH 6.6–7.2; TOC 5.2–13.7 mg L <sup>-1</sup> ; COD 29–90 mg L <sup>-1</sup> ; NH <sub>4</sub> <sup>+</sup> 0.77–5.98 mg L <sup>-1</sup> ; alkalinity 154–256 mg CaCO <sub>3</sub> L <sup>-1</sup> ), Sweden.	- 150 mL flask reactor; - Spiked O <sub>3</sub> stock solution (concentration 0.5 – 12 mg L <sup>-1</sup> ).	A large variability was observed in the required O <sub>3</sub> dose to attain elimination of different APIs in the same effluent and for the same API between effluents. The removal was lower when COD and alkalinity were higher, requiring higher O <sub>3</sub> doses.	[93]
<b>O<sub>3</sub></b>	Ofloxacin 22 mg L <sup>-1</sup>	- WW effluent (pH 7.4; DOC 8.4 mg L <sup>-1</sup> ; COD 28 mg L <sup>-1</sup> ; turbidity 7.0 NTU; conductivity 750 μS cm <sup>-1</sup> ; TSS 11 mg L <sup>-1</sup> ; Na <sup>+</sup> 65 mg L <sup>-1</sup> ; NH <sub>4</sub> <sup>+</sup> 4.1 mg L <sup>-1</sup> ; K <sup>+</sup> 15 mg L <sup>-1</sup> ; Mg <sup>2+</sup> 18 mg L <sup>-1</sup> ; Ca <sup>2+</sup> 52 mg L <sup>-1</sup> ; NO <sub>3</sub> <sup>-</sup> 59 mg L <sup>-1</sup> ; PO <sub>4</sub> <sup>3-</sup> 3.3 mg L <sup>-1</sup> ; SO <sub>4</sub> <sup>2-</sup> 81 mg L <sup>-1</sup> ; Cl <sup>-</sup> 86 mg L <sup>-1</sup> ), Spain. - Synthetic matrix prepared in UPW spiked with NaHCO <sub>3</sub> to equal the alkalinity and pH values of the WW effluent.	- Cylindrical reactor (51 cm height and 6.0 cm internal diameter) with a total working volume of 1.44 L, operating in continuous co-current mode; - Average retention time of 10.3 min; - Water flow rate: 142 mL min <sup>-1</sup> ; - Gas flow was 390 mL min <sup>-1</sup> with different inlet O <sub>3</sub> concentrations; - Inlet O <sub>3</sub> dosage: 4.2 – 145 mg O <sub>3</sub> L <sup>-1</sup> ; - Samples taken once the stationary state was reached.	For similar O <sub>3</sub> exposures, ofloxacin was removed at a higher extent in synthetic WW, in comparison to WW effluent, showing the competition between the DOM and ofloxacin for O <sub>3</sub> and suggesting that O <sub>3</sub> and/or HO <sup>•</sup> preferably attack certain moieties of DOM present in WW. A higher O <sub>3</sub> dose was required to achieve the complete abatement of the pharmaceutical.	[94]
<b>O<sub>3</sub></b>	Benzalkonium chloride 10 mg L <sup>-1</sup>	- WW influent before biological treatment (pH 8.3; DOC 61.2 mg L <sup>-1</sup> ; COD 121 mg L <sup>-1</sup> ; turbidity 145 NTU; conductivity 1,234 μS cm <sup>-1</sup> ; TSS 108 mg L <sup>-1</sup> ; Na <sup>+</sup> 110 mg L <sup>-1</sup> ; NH <sub>4</sub> <sup>+</sup> 53.8 mg L <sup>-1</sup> ; K <sup>+</sup> 26.2 mg L <sup>-1</sup> ; Mg <sup>2+</sup> 19.3 mg L <sup>-1</sup> ; Ca <sup>2+</sup> 41.4 mg L <sup>-1</sup> ; NO <sub>3</sub> <sup>-</sup> 0.10 mg L <sup>-1</sup> ; PO <sub>4</sub> <sup>3-</sup> 14.9 mg L <sup>-1</sup> ; SO <sub>4</sub> <sup>2-</sup> 56.0 mg L <sup>-1</sup> ; Cl <sup>-</sup> 127 mg L <sup>-1</sup> ), Spain; - Synthetic matrix prepared in UPW spiked with NaHCO <sub>3</sub> to equal the alkalinity and pH values of the wastewater effluent.	- Cylindrical reactor with a total working volume of 1.44 L, operating in continuous co-current mode; - Average retention time of 10.3 min; - Water flow rate: 142 mL min <sup>-1</sup> ; - Gas flow was 390 mL min <sup>-1</sup> with different inlet O <sub>3</sub> concentrations: - Inlet O <sub>3</sub> dosage: 5 – 300 mg O <sub>3</sub> L <sup>-1</sup> ; - Samples taken once the stationary state was reached.	Water matrix strongly influenced benzalkonium chloride depletion, in comparison to synthetic WW, mainly due to the high DOC content. An instantaneous ozone demand of 77 mg L <sup>-1</sup> was required in non-spiked raw wastewater. The presence of NiO nanoparticles affected the ozone dose required. The consumed ozone in WW was approximately fivefold the corresponding value in synthetic WW.	[95]
<b>O<sub>3</sub></b>	Propiconazole, atrazine, 2,4 dichlorophenoxyacetic	- Reverse osmosis water; - SWW; - WW effluent.	- Ozone dose: 0, 0.2, 0.7, 1.9, 4.9, 9.9 and 14.8 mg O <sub>3</sub> L <sup>-1</sup> in reverse osmosis water;	As the matrix complexity increased, lower removals of the studied compounds were found. Moreover, in some cases the effect was greater in	[96]

	acid, tebuconazole, climbazole, myclobutanil, irgarol, terbutryn, dicamba, mecoprop and diuron 5, 20 mg L <sup>-1</sup>		- Ozone dose: 0 - 38.2 mg O <sub>3</sub> L <sup>-1</sup> in synthetic wastewater and wastewater effluent.	SWW in comparison with WW effluent, mainly due to the higher COD values, the presence of HCO <sub>3</sub> <sup>-</sup> , PO <sub>4</sub> <sup>3-</sup> and Cl <sup>-</sup> . Furthermore, dicamba and 2,4-dichlorophenoxyacetic acid, followed by atrazine, were the most recalcitrant compounds.
<b>O<sub>3</sub> Catalytic ozonation</b>	Mesoxalic and oxalic acids 50 mg L <sup>-1</sup>	- WW effluent (pH 7.7; TOC 8.1 mg L <sup>-1</sup> ; COD 27 mg L <sup>-1</sup> ; turbidity 5.3 NTU; conductivity 667 μS cm <sup>-1</sup> ; TSS 7.3 mg L <sup>-1</sup> ; Na <sup>+</sup> 83 mg L <sup>-1</sup> ; NH <sub>4</sub> <sup>+</sup> 3.3 mg L <sup>-1</sup> ; K <sup>+</sup> 15 mg L <sup>-1</sup> ; Mg <sup>2+</sup> 20 mg L <sup>-1</sup> ; Ca <sup>2+</sup> 32 mg L <sup>-1</sup> ; NO <sub>3</sub> <sup>-</sup> 36 mg L <sup>-1</sup> ; PO <sub>4</sub> <sup>3-</sup> 1.2 mg L <sup>-1</sup> ; SO <sub>4</sub> <sup>2-</sup> 82 mg L <sup>-1</sup> ; Cl <sup>-</sup> 83 mg L <sup>-1</sup> ), Spain.	- T 25 °C; - pH 8; - Catalyst: copper oxide supported on mesoporous silica SBA-15; - Influence of HCO <sub>3</sub> <sup>-</sup> (250 mg L <sup>-1</sup> ), PO <sub>4</sub> <sup>3-</sup> (1 mg L <sup>-1</sup> ), Cl <sup>-</sup> (100 mg L <sup>-1</sup> ), and SO <sub>4</sub> <sup>2-</sup> (108 mg L <sup>-1</sup> ); - Influence of suspended solids.	The removal rate by ozonation was almost inhibited by the suspended solids and strongly dependent on the presence of inorganic anions, suggesting a scavenging effect of HO <sup>•</sup> , in the following order: HCO <sub>3</sub> <sup>-</sup> ≈ Cl <sup>-</sup> > PO <sub>4</sub> <sup>3-</sup> >> SO <sub>4</sub> <sup>2-</sup> . Catalytic ozonation was more efficient to degrade organic acids, being almost unaffected by the presence of the inorganic anions or suspended solids, only PO <sub>4</sub> <sup>3-</sup> having a noticeable effect on oxalic acid depletion. [97]
<b>O<sub>3</sub> O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub></b>	Sulfamethoxazole, diclofenac 30 mg L <sup>-1</sup>	- Synthetic matrix prepared in DI (pH 7; NaHPO <sub>4</sub> 1.44 g L <sup>-1</sup> ; NaH <sub>2</sub> PO <sub>4</sub> 0.24 g L <sup>-1</sup> ; NaOH 0.5 M; COD 88.5±4.0 mg O <sub>2</sub> L <sup>-1</sup> ). - WW effluent (pH 7.58; COD 188.2±13.2 mg L <sup>-1</sup> ).	- 0.5 L magnetically stirred reactor operating in semi-continuous mode; - Inlet O <sub>3</sub> concentration: 20 g Nm <sup>-3</sup> ; - H <sub>2</sub> O <sub>2</sub> concentration: 5 mM; - Gas flow rate: 0.2 L min <sup>-1</sup> .	Significant differences were not found on the removal of sulfamethoxazole and diclofenac in both synthetic and WW matrices, which were totally removed in 45 and 60 min, respectively. On the other hand, the removal of COD was much lower, with higher ozone and H <sub>2</sub> O <sub>2</sub> consumption, when WW was used, which might be explained by the presence of ions, such as CO <sub>3</sub> <sup>2-</sup> , HCO <sub>3</sub> <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup> , PO <sub>4</sub> <sup>3-</sup> , among others. [98]
<b>O<sub>3</sub> O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub></b>	33 pharmaceuticals ng L <sup>-1</sup> levels	- 2 WW effluents: urban WW composed by domestic and industrial WW (pH 7.54-8.01; TOC 5.7-15.7 mg L <sup>-1</sup> ; COD 35-72 mg L <sup>-1</sup> ; BOD <sub>5</sub> 3.0-18 mg L <sup>-1</sup> ; conductivity 407-614 μS cm <sup>-1</sup> ; TSS ≈0-12.4 mg L <sup>-1</sup> ; alkalinity 345-539 mg CaCO <sub>3</sub> L <sup>-1</sup> ; Cl <sup>-</sup> 61-81 mg L <sup>-1</sup> ; SO <sub>4</sub> <sup>2-</sup> 91-133 mg L <sup>-1</sup> ) and domestic WW (pH 7.52-8.38; TOC 8.4-17.5 mg L <sup>-1</sup> ; COD 44-182 mg L <sup>-1</sup> ; BOD <sub>5</sub> 4.7-24 mg L <sup>-1</sup> ; conductivity 368-631 μS cm <sup>-1</sup> ; TSS 0.55-23.9 mg L <sup>-1</sup> ; alkalinity 305-580 mg CaCO <sub>3</sub> L <sup>-1</sup> ; Cl <sup>-</sup> 52-63 mg L <sup>-1</sup> ; SO <sub>4</sub> <sup>2-</sup> 81-114 mg L <sup>-1</sup> ), Madrid, Spain.	-5-L glass jacketed reactor; - T 25 °C; - pH 8.0; - Gas flow rate: 360 L h <sup>-1</sup> ; - O <sub>3</sub> concentration: 46 g N m <sup>-3</sup> .	The degradation kinetics in urban and domestic WW was significantly different and TOC elimination was markedly higher for urban WW. [99]
<b>Catalytic ozonation</b>	Diclofenac, sulfamethoxazole, EE2 10 mg L <sup>-1</sup>	- WW effluent pre-treated to partially remove its CO <sub>3</sub> <sup>2-</sup> and HCO <sub>3</sub> <sup>-</sup> content by stripping (pH 7.52; TOC 8 mg L <sup>-1</sup> ; COD 64 mg L <sup>-1</sup> ; BOD <sub>5</sub> 15 mg L <sup>-1</sup> ; turbidity 15.9 NTU; conductivity 710 μS cm <sup>-1</sup> ; TSS 28 mg L <sup>-1</sup> ; N <sub>total</sub> 22.1 mg L <sup>-1</sup> ; NH <sub>4</sub> <sup>+</sup> 18.3 mg L <sup>-1</sup> ; PO <sub>4</sub> <sup>3-</sup> 5.0 mg L <sup>-1</sup> ), Spain.	- Reactor system: one gas-liquid reactor (300 mm height, 50 mm diameter) with a porous plate at its bottom to bubble an O <sub>3</sub> -O <sub>2</sub> mixture and a fixed bed reactor where 5g of catalyst were loaded; - Catalysts: commercial γ-Al <sub>2</sub> O <sub>3</sub> and synthesized Co <sub>3</sub> O <sub>4</sub> /Al <sub>2</sub> O <sub>3</sub> ;	Regardless of the water matrix and the presence/absence of any catalyst, the elimination of the pharmaceuticals occurred through fast direct reactions with O <sub>3</sub> in less than 10 min. Catalytic ozonation, particularly in the presence of the synthesized Co <sub>3</sub> O <sub>4</sub> /Al <sub>2</sub> O <sub>3</sub> , improved the COD and TOC removals obtained when single ozonation was applied. The ozonation developed through fast initial COD removal followed by a second slower [100]

<b>Photocatalytic ozonation</b>	Diclofenac, amoxicillin 0.1 mM	- UPW; - WW effluent (characterization not provided), Portugal.	- O <sub>3</sub> : 50 g Nm <sup>-3</sup> and 150 Ncm <sup>3</sup> min <sup>-1</sup> ; - MP Hg vapour lamp (UV-Vis λ > 300 nm); - Catalyst: 0.5 g L <sup>-1</sup> of TiO <sub>2</sub> .	stage, which could be greatly improved by the Co <sub>3</sub> O <sub>4</sub> /Al <sub>2</sub> O <sub>3</sub> catalyst. The removal of the investigated compounds was similar in both matrices. The oxamic acid formed in DI by photocatalytic ozonation was further degraded, whereas it was refractory to the photocatalytic ozonation in the case of spiked WW effluents, where the concentration of this carboxylic acid increased during 45 min and then remained constant.	[101]
<b>O<sub>3</sub> Catalytic ozonation</b>	Formic, acetic, oxalic and maleic acids 7 mg L <sup>-1</sup>	- WW effluent (pH 7.24; TOC 5.12 mg L <sup>-1</sup> ; COD 14.3 mg L <sup>-1</sup> ; turbidity 0.4 NTU; conductivity 800 μS cm <sup>-1</sup> ; TSS 30 mg L <sup>-1</sup> ; Na <sup>+</sup> 67.5 mg L <sup>-1</sup> ; NH <sub>4</sub> <sup>+</sup> 0.34 mg L <sup>-1</sup> ; K <sup>+</sup> 13.9 mg L <sup>-1</sup> ; Mg <sup>2+</sup> 20.1 mg L <sup>-1</sup> ; Ca <sup>2+</sup> 52.8 mg L <sup>-1</sup> ; NO <sub>3</sub> <sup>-</sup> 36.8 mg L <sup>-1</sup> ; NO <sub>2</sub> <sup>-</sup> 0.49 mg L <sup>-1</sup> ; PO <sub>4</sub> <sup>3-</sup> 3.31 mg L <sup>-1</sup> ; SO <sub>4</sub> <sup>2-</sup> 68.8 mg L <sup>-1</sup> ; Cl <sup>-</sup> 88.2 mg L <sup>-1</sup> ; HCO <sub>3</sub> <sup>-</sup> 189 mg L <sup>-1</sup> ), Spain; - Synthetic matrix prepared in UPW spiked with NaHCO <sub>3</sub> to equal the alkalinity and pH values of the WW effluent.	- Cylindrical reactor (51 cm height and 6.0 cm internal diameter) with a total working volume of 1.44 L, operating in continuous co-current mode; - Average retention time: 10.3 min; - Water flow rate: 142 mL min <sup>-1</sup> ; - Gas flow was 390 mL min <sup>-1</sup> with different inlet O <sub>3</sub> concentrations; - Copper: 1-250 μg L <sup>-1</sup> (synthetic WW) and 10-500 μg L <sup>-1</sup> (WW effluent); - Samples taken once the stationary state was reached.	Catalytic ozonation was strongly influenced by the water matrix, since the complexation with organic matter reduces the availability of metal as catalyst. In WW, a five-fold copper concentration is required to achieve similar removal of oxalic acid to that obtained in the synthetic WW.	[102]
<b>O<sub>3</sub> Photocatalysis Photocatalytic ozonation</b>	Acetaminophen, norfloxacin, metoprolol, caffeine, antipyrine, sulfamethoxazole, ketorolac, hydroxyl-biphenyl, diclofenac 50 μg L <sup>-1</sup>	- UPW; - WW effluent (pH 8-8.5; TOC 25-30 mg L <sup>-1</sup> ; IC 35-40 mg L <sup>-1</sup> ; COD 40 mg L <sup>-1</sup> ), Spain.	- 1 L cylindrical borosilicate glass reactor; - 15-W black-light lamps (350–410 nm); - Catalyst: 0.25 g L <sup>-1</sup> of TiO <sub>2</sub> or 5 g L <sup>-1</sup> TiO <sub>2</sub> supported on activated carbon; - O <sub>3</sub> : inlet concentration 15 mg L <sup>-1</sup> and flow rate 30 L h <sup>-1</sup> .	The efficiency of the treatments was lower using WW as matrix in comparison to ultra-pure water, due to the effect of other organic/inorganic components occurring in the secondary effluents.	[103]
<b>O<sub>3</sub> UV UV/H<sub>2</sub>O<sub>2</sub> O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> as pre-treatment for nanofiltration</b>	Amoxicillin, hydrochlorothiazide, metoprolol, naproxen, phenacetin 1 μM	- GW, Spain; - Surface water from a public reservoir, Spain; - WW effluent (pH 7.6; TOC 15 mg L <sup>-1</sup> ; conductivity 650 μS cm <sup>-1</sup> ; alkalinity 250 mg CaCO <sub>3</sub> L <sup>-1</sup> ), Spain.	- 25 mL flask reactors; - T 20 °C; pH natural (7); - Spiked O <sub>3</sub> stock solution or 10 <sup>-3</sup> M hypochlorous acid solution; - Irradiation source: LP Heraeus Hg lamp TN 15/35 with a nominal output of 15 W (λ <sub>max</sub> 254 nm); <i>Membrane filtration</i> - Cross-flow membrane filtration unit; Transmembrane pressure: 5 bar (ultrafiltration) and 20 bar (nanofiltration).	Removal rates by chemical oxidation of water pre-treated by membrane filtration showed the following trend among each water matrix: GW > reservoir > WW. The different amount of DOM in each water matrix might consume partially the oxidant and compete with the target substances. In the case of ozonation of WW, higher initial O <sub>3</sub> dose was required to achieve similar removal efficiency of those obtained in natural waters.	[104]
<b>O<sub>3</sub> UV/H<sub>2</sub>O<sub>2</sub></b>	Organophosphate esters 50 μg L <sup>-1</sup>	- UPW; - HA solution; - WW effluent (pH 8.2; TOC 7.8 mg L <sup>-1</sup> ; COD 28.4 mg L <sup>-1</sup> ; turbidity 1.99 NTU; alkalinity 325 mg CaCO <sub>3</sub> L <sup>-1</sup> ; NH <sub>4</sub> <sup>+</sup> 13.9 mg L <sup>-1</sup> ; Mg <sup>2+</sup> 52.1 mg L <sup>-1</sup> ; Ca <sup>2+</sup> 115.4 mg L <sup>-1</sup> ; NO <sub>3</sub> <sup>-</sup> 24.9 mg L <sup>-1</sup> ; NO <sub>2</sub> <sup>-</sup> 7.35 mg L <sup>-1</sup> ; SO <sub>4</sub> <sup>2-</sup> 203.3 mg L <sup>-1</sup> ; Cl <sup>-</sup> 624.2 mg L <sup>-1</sup> ), Canada.	- 2.0 L jacketed glass reactor; - natural pH; O <sub>3</sub> - T 20 °C; - O <sub>3</sub> : 60 L h <sup>-1</sup> and 10 mg L <sup>-1</sup> ; UV/H <sub>2</sub> O <sub>2</sub> - T 25 °C;	The aromatic and aliphatic pollutants were rapidly oxidized by ozone and UV/H <sub>2</sub> O <sub>2</sub> , while the chlorinated and the ramified aliphatic compounds were more recalcitrant. For ozonation, the following decreasing order of removal was reported: HA solution > UPW > WW effluents. The acidic pH of UPW led to selective ozonation of organic compounds with electron-rich	[105]

			- 3 LP UV lamps (8 W, 26% UVC efficiency) ( $\lambda_{\max}$ 254 nm); - H <sub>2</sub> O <sub>2</sub> : 20 mg L <sup>-1</sup> .	functional groups. The reactions between O <sub>3</sub> and the electron-rich moieties of HA explain the faster degradation rates of the reactive organophosphate esters due to the production of HO <sup>•</sup> . Direct and indirect oxidation occurred in the municipal secondary effluent (pH 8-8.2). The EfOM could react with molecular O <sub>3</sub> . Some ions (e.g., Cl <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup> , NO <sub>3</sub> <sup>2-</sup> , HCO <sub>3</sub> <sup>-</sup> ) and EfOM were ascribed as radical scavengers. The reactivity of the target pollutants exhibited a similar trend in UV/H <sub>2</sub> O <sub>2</sub> to that in ozonation. The elimination efficiencies in the effluent were generally similar to those in HA solution.	
<b>O<sub>3</sub> UV UV/H<sub>2</sub>O<sub>2</sub> UV/O<sub>3</sub>, O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> O<sub>3</sub>/UV/H<sub>2</sub>O<sub>2</sub></b>	E1 3 µg L <sup>-1</sup> – 5 mg L <sup>-1</sup>	- UPW; - WW effluent (pH 7.4; TOC 9.61 mg L <sup>-1</sup> ; COD 36 mg L <sup>-1</sup> ; turbidity 10 NTU; TSS 23 mg L <sup>-1</sup> ; TDS 373 mg L <sup>-1</sup> ; Na <sup>+</sup> 83.3 mg L <sup>-1</sup> ; NH <sub>4</sub> <sup>+</sup> 2.3 mg L <sup>-1</sup> ; K <sup>+</sup> 10.4 mg L <sup>-1</sup> ; Mg <sup>2+</sup> 18.5 mg L <sup>-1</sup> ; Ca <sup>2+</sup> 83.9 mg L <sup>-1</sup> ; NO <sub>3</sub> <sup>-</sup> 18.1 mg L <sup>-1</sup> ), Canada.	- Annular reactor (750 mL); - 13 W LP UV lamp ( $\lambda_{\max}$ 253.7 nm); - O <sub>3</sub> : 0.33 – 1.31 mg L <sup>-1</sup> ; - H <sub>2</sub> O <sub>2</sub> : 20, 40 and 60 mg L <sup>-1</sup> .	The best performing treatment for E1 removal was ozonation. The removal rate decreased slightly with the background TOC in water, however, in the WW effluent with low COD values, E1 removal was only reduced by 5%.	[106]
<b>Catalytic ozonation</b>	Benzotriazole 10 mg L <sup>-1</sup>	- WW effluent (pH 6.5; conductivity 750 µS cm <sup>-1</sup> ; COD 20 mg L <sup>-1</sup> ; TP 15.4 mg L <sup>-1</sup> ; TN 15.4 mg L <sup>-1</sup> ; TDS 540 mg L <sup>-1</sup> ; Cl <sup>-</sup> 75 mg L <sup>-1</sup> ; NO <sub>3</sub> <sup>-</sup> 21.6 mg L <sup>-1</sup> ; NO <sub>2</sub> <sup>-</sup> 2.3 mg L <sup>-1</sup> ; PO <sub>4</sub> <sup>3-</sup> 9.1 mg L <sup>-1</sup> ; NH <sub>4</sub> <sup>+</sup> 10.3 mg L <sup>-1</sup> ), Iran.	- Semi-continuous reactor; - V 1.2 L; - Catalyst: 0.5 g L <sup>-1</sup> magnetic alumina nanocomposite; - Oxygen gas flow rate: 0.3 L min <sup>-1</sup> .	The catalyst addition enhanced greatly the removal rate of target compound. Experiments using secondary municipal wastewater effluent indicated that no significant decrease in the performance of the catalyst occurred.	[107]

**Abbreviations:** API, active pharmaceutical ingredient; AOT, advanced oxidation technologies; BOD<sub>5</sub>, biochemical oxygen demand; COD, chemical oxygen demand; DI, distilled water; DOC, dissolved organic carbon; DOM, dissolved organic matter; E1, estrone; EE2, 17-alpha-ethinylestradiol; GW, groundwater; HA, humic acids, HP, high pressure; IC, inorganic carbon; LP, low pressure; MP, micropollutants; NTU, nephelometric turbidity unit; PS, persulphate; SS, suspended solids; SW, surface water; SWW, synthetic wastewater; TOC, total organic carbon; TDS, total dissolved solids; TSS, total suspended solids; UPW, ultrapure water; WW, wastewater.