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Anaëlle Gabet, Hélène Métivier, Christine de Brauer, Gilles Mailhot, Marcello Brigante. Hydrogen peroxide and persulfate activation using UVA-UVB radiation: Degradation of estrogenic compounds and application in sewage treatment plant waters. *Journal of Hazardous Materials*, 2021, 405, pp.124693. 10.1016/j.jhazmat.2020.124693 . hal-03052735

HAL Id: hal-03052735

<https://uca.hal.science/hal-03052735>

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1 **Hydrogen peroxide and persulfate activation using UVA-UVB radiation:**
2 **degradation of estrogenic compounds and application in sewage treatment**
3 **plant waters**

4 Anaëlle Gabet^{1,2}, H  l  ne M  tivier², Christine de Brauer², Gilles Mailhot¹, Marcello
5 Brigante^{1,*}

6
7 ¹Universit   Clermont Auvergne, CNRS, SIGMA Clermont, Institut de Chimie de Clermont-
8 Ferrand, F-63000 Clermont-Ferrand, France

9 ² INSA Lyon, DEEP, 34 Avenue des Arts, 69621 Villeurbanne Cedex, France

10 *corresponding author: marcello.brigante@uca.fr

11

12 **Abstract**

13 In the present work, the degradation of three estrogens (17  -estradiol (E2), estrone (E1) and
14 17  -ethinylestradiol (EE2)) was investigated under photoactivation of hydrogen peroxide and
15 persulfate. Lab-scale irradiation experiments showed that both UVA and UVB radiations are
16 able to photoactivate the oxidant precursors, although UVB is more efficient to generate
17 radicals and therefore to degrade the targets. The efficiency of both oxidant precursors was
18 investigated showing higher efficiency in the system with persulfate. The pseudo-first order
19 degradation rate constants and the second order rate constants between the hydroxyl or the
20 sulfate radicals and estrogens were measured. In order to evaluate the process efficiency in
21 real treatment conditions, the degradation of the estrogens spiked into sewage treatment plant
22 effluent was studied. Measurements of second order rate constants between the radical and the
23 effluent organic matter by laser flash photolysis allowed to understand the involved
24 quenching mechanisms. A Yeast Estrogen Screen (YES) assay was used to follow the
25 decrease in estrogenic activity during the estrogen degradation. This assay permitted to ensure

26 that the studied processes are not only able to degrade the estrogens but also to remove their
27 estrogenic activity.

28

29 **Keywords:** estrogens, decontamination, wastewaters, hydroxyl radical, sulfate radical, AOPs,
30 photolysis

31

32 **1. Introduction**

33 Whilst estrogens are known to be hydrophobic and have significantly high partition
34 coefficients ($\log K_{ow} = 4$) (Pal et al., 2010), their presence in surface waters and river
35 sediments has been widely reported around the world (Anderson et al., 2012; Praveena et al.,
36 2016; Valdés et al., 2015; Zuo et al., 2013). The most commonly detected estrogens are
37 estrone (E1) and 17 β -estradiol (E2), which are naturally excreted by humans and animals, as
38 well as 17 α -ethinylestradiol (EE2), a synthetic hormone used in contraceptive pills. It has
39 been reported that these three hormones are the main estrogenic compounds found in
40 domestic sewage treatment plant (STP) effluents (Amin et al., 2018; Desbrow et al., 1998;
41 Huang et al., 2014). Laurenson et al. (2014) reported that one human being excretes on
42 average 19.00 μg of E1, 7.70 μg of E2 and 0.41 μg of EE2 per day. As a consequence, these
43 hormones tend to reach concentrations up to tens of ng L^{-1} in domestic STP wastewaters,
44 particularly in urban areas where their impact is significant. The current treatment processes
45 are not sufficient to provide appropriate degradation rates. Therefore, STP effluents which are
46 released into the environment are likely to contain E1, E2 and EE2 at concentrations up to
47 several ng L^{-1} (Amin et al., 2018; Desbrow et al., 1998; Huang et al., 2014).

48 When entering the human or animal body via external sources, these hormones are considered
49 as endocrine disrupting chemicals because their biological activity can interfere with natural
50 hormone activities. It has been reported that these estrogens have a negative impact on river

51 wildlife, particularly downstream from STPs. Purdom et al. (1994) have highlighted that the
52 exposure of rainbow trout to EE2 concentrations of approximately 1 ng L⁻¹ resulted in an
53 abnormal production of vitellogenin, a protein normally synthesized only during female
54 gestation. A study carried out on several British rivers has shown that surface water estrogens
55 can cause varying degrees of feminisation in male fish populations (Jobling et al., 1998).
56 These observations were also reported by Kidd et al. (2007) in an *in situ* study in Canada on
57 fathead minnow. They observed that concentrations around 5 ng L⁻¹ of EE2 impacted the
58 gonadal development of males. Each of these reported effects have led to a disruption in
59 reproduction, and ultimately a decline in the population of wild species within impacted areas.
60 To avoid the contamination of surface waters by estrogens, the efficacy of various quaternary
61 treatments on domestic STPs is under investigation. There are two categories of treatment,
62 physical and chemical. Physical treatments include the adsorption of micropollutants on
63 activated carbon and membrane processes (microfiltration, nanofiltration, ultrafiltration or
64 reverse osmosis) whereas chemical treatments include advanced oxidation processes (AOPs)
65 such as ozonation and UV based processes (Bui et al., 2016). The former processes are costly
66 and require specialist treatment facilities. This is a barrier to their use on small and medium
67 domestic STP effluents (< 10 000 inhabitant equivalent). In order to remove estrogen from
68 these effluents, chemical treatments are necessary.

69 Cédât et al. (2016) have highlighted the efficiency of a UVC/H₂O₂ process to remove the
70 estrogenic activity of estrogen spiked water samples. Numerous recent studies have also
71 shown the ability of sulfate radicals (SO₄^{•-}), generated through persulfate UVA or UVC
72 photo-activation, to degrade micropollutants in wastewater (Al Hakim et al., 2020; Li et al.,
73 2017; Olmez-Hanci et al., 2015; Palharim et al., 2020), including estrogens (Angkaew et al.,
74 2019). In the majority of cases, the photo-activation in AOPs is carried out with UVC
75 radiation (254 nm). However, they have several disadvantages compared to UVA and UVB

76 radiations: UVC lamps are more expensive and can be hazardous to manipulate. The use of
77 UVA or UVB radiations also aims at more sustainable processes. They are less energy-
78 consuming and could even be replaced by solar light for real-scale application. Lamps are
79 nevertheless easier to use and to control for research purposes than solar light.
80 In this work we investigated the ability of UVA and UVB activation of H_2O_2 and $\text{S}_2\text{O}_8^{2-}$
81 processes to degrade three commonly found hormones in wastewaters: 17β -estradiol, estrone
82 and 17α -ethinylestradiol. Preliminary degradation studies were carried out on 17β -estradiol in
83 milli-Q water and few parameters such as oxidant dosage were investigated. Subsequent
84 studies were conducted to establish the efficacy of the technique on STP effluent spiked with
85 the three estrogens. Moreover, estrogenic activity assays were performed during degradation
86 process to follow the harmfulness evolution during irradiation.

87

88 **2. Materials and methods**

89 *2.1. Chemicals and reagents*

90 17β -estradiol (E2), estrone (E1) and 17α -ethinylestradiol (EE2) were purchased from Sigma-
91 Aldrich, as well as hydrogen peroxide (H_2O_2) (30% in water) and sodium persulfate
92 ($\text{Na}_2\text{S}_2\text{O}_8$). Acetonitrile was supplied by Carlo Erba Reagents. Ultrapure water was obtained
93 from a milli-Q system. Wastewaters were collected at the outlet of the treatment from the “3
94 rivières” urban STP, Clermont-Ferrand, France in September (STPW1) and December
95 (STPW2) 2019. This STP is equipped with a conventional activated sludge process. STP
96 waters were filtered on a paper filter followed by a filtration on a CHROMAFIL® Xtra RC-
97 45/25 syringe filter from Macherey-Nagel. Main physico-chemical parameters after filtration
98 are reported in Table SM1.

99

100 *2.2. Irradiation experiments*

101 UVA and UVB irradiations were carried out in a 150 mL Pyrex reactor, magnetically stirred
102 and kept at room temperature (20°C) by a cooling system. The reactor was placed in a home-
103 made rectangular box equipped on the top with four polychromatic fluorescence tubes (UVA
104 F15W/350BL, Sylvania Blacklight, Germany, or UVB G15T8E, Sanyo Denki, Japan). The
105 UVA ($\lambda_{\text{max}} = 352 \text{ nm}$) and UVB ($\lambda_{\text{max}} = 308 \text{ nm}$) lamp emission spectra were measured on top
106 of the reactor using an optical fibre and a charge-coupled device spectrophotometer (Ocean
107 Optics USD 2000 + UV-vis), calibrated using a DH-2000-CAL Deuterium Tungsten Halogen
108 reference lamp (Figure SM1). UV-visible spectra of the estrogens, oxidants and STPW2 were
109 carried out with a Cary 300 scan UV-visible spectrophotometer and reported in Figures SM2,
110 SM3 and SM4. H_2O_2 concentration was followed using p-hydroxyphenylacetic acid (HPAA,
111 purity > 98%) and horseradish peroxidase (POD), according to the spectrofluorimetric
112 quantification method (Miller & Kester, 1988) with a Varian Cary Eclipse fluorescence
113 spectrophotometer setting excitation wavelengths at 320 nm and emission maximum at 408
114 nm. The formation of the dimer of HPAA was correlated with the concentration of H_2O_2
115 using standard solutions.

116 Estrogen stock solutions (1 mM) were prepared in acetonitrile and stored in the dark at 4°C.
117 Solutions of 100 mL containing 5 μM of estrogens and different oxidant precursor
118 concentrations (from 0 to 5 mM) were irradiated under polychromatic wavelengths (UVA or
119 UVB). Such concentration of estrogens do not require the use of pre-concentration techniques
120 before HPLC analysis which avoids a source of errors while using relatively low
121 concentration. 1 mL of solution was withdrawn at fixed interval times for HPLC
122 quantification of estrogen concentrations. However, small volume variations did not impact
123 the irradiation efficacy.

124

125 *2.3. Sample analysis and data processing*

126 Estrogen concentrations were followed using a Waters Acquity Ultra High Performance
127 Liquid Chromatography (UPLC) system equipped with a BEH C18 column (100 × 2.1 mm,
128 1.7 μm), coupled to a diode array detector (200-400 nm) and a fluorescence detector ($\lambda_{\text{ex}} =$
129 280 nm, $\lambda_{\text{em}} = 305$ nm). Elution flow rate was 0.6 mL min⁻¹ and eluents were a mixture of
130 milli-Q water and acetonitrile. A gradient raising the acetonitrile percentage from 30% to 70%
131 in 4 minutes and then 1 min constant at 70% was used. Injection volume was 6 μL and
132 column temperature was fixed at 40°C.

133 Concentration of estrogen during irradiation was fitted by the following first order equation:

134 $C_t/C_0 = \exp(-k't)$ where C_0 and C_t are respectively the initial concentration and the

135 concentration at time t and k' is the pseudo-first order rate constant.

136 The error bars associated to the rate data represent 3σ , derived from the scattering of the
137 experimental data around the fit curves (intra-series variability).

138

139 2.4. Laser flash photolysis

140 A time resolved spectroscopy was used to determine the second order rate constant of
141 hydroxyl and persulfate radicals with E1, E2 and EE2 but also with the organic and inorganic
142 carbon of the STPW. The second order rate constants allowed to estimate the radicals
143 selectivity between the various species in solution.

144 All experiments were carried out using the fourth harmonic ($\lambda_{\text{exc}} = 266$ nm) of a Quanta Ray
145 GCR 130-01 Nd:YAG laser system instrument and an energy of ~45 mJ/pulse. The
146 experimental setup has been described before (Wu et al., 2015). Briefly, for hydroxyl radical
147 reactivity, a competition kinetic method using thiocyanate anion was used and reactivity was
148 determined following the absorption at 450 nm of (SCN)₂⁻ transient (Huang et al., 2018). For
149 sulfate radical, the decay (k' , s⁻¹) of SO₄⁻ signal at 370 nm was plotted as a function of

150 quencher concentration (i.e. estrogen or carbon from STPW) concentration. The slope of the
151 linear correlation gives the value of the second order rate constant (k'' , $M^{-1} s^{-1}$).

152

153 2.5. Estrogenic activity removal

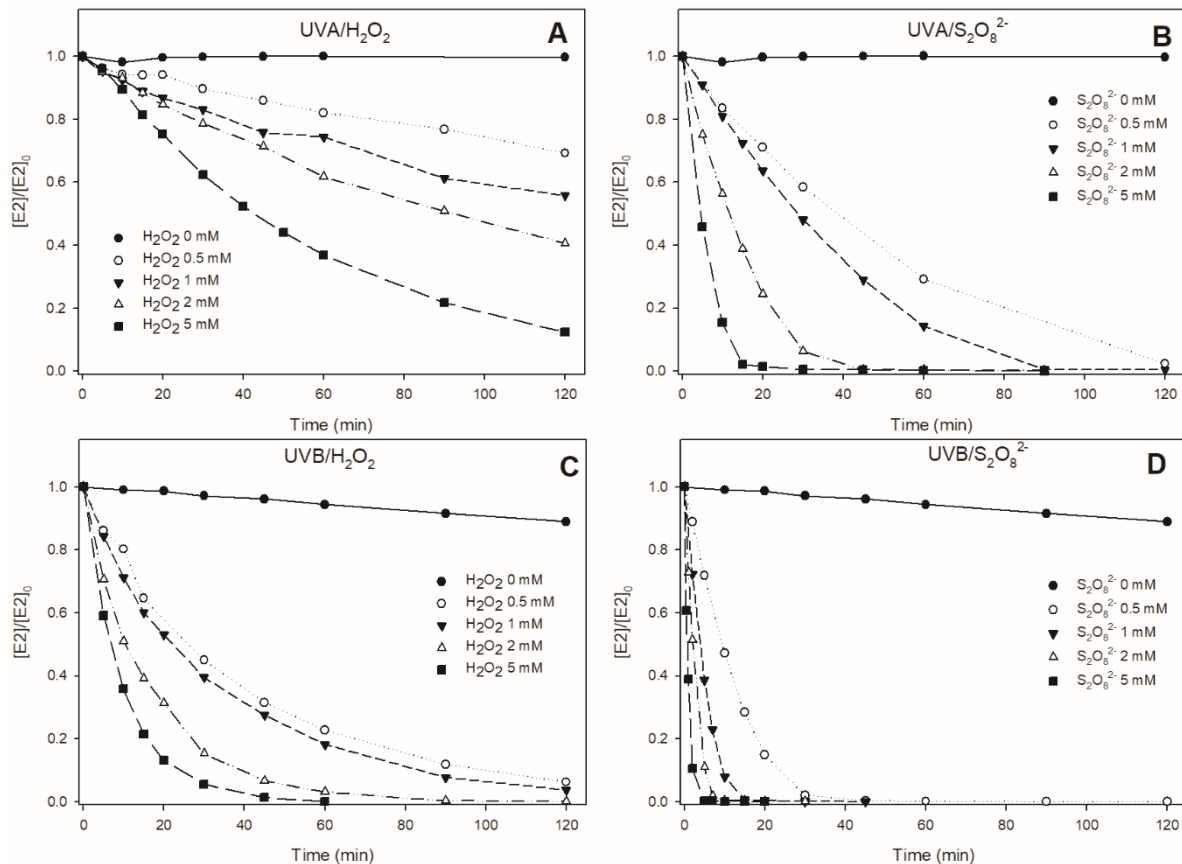
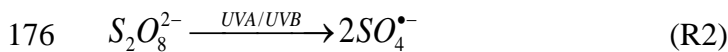
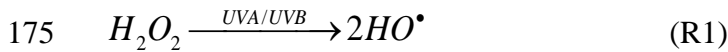
154 The Arxula Yeast Estrogen Screen assay (A-YES) ready-to-use test kit was provided by New-
155 diagnostics (Germany). This assay allows to quantify the estrogenic activity caused by
156 estrogen-active substances in aqueous samples. The results are obtained in E2 equivalent
157 concentration. It includes the use of genetically modified *Arxula adenivorans* yeast cells
158 which contain the gene for human estrogenic receptor. The estrogenic activity of the aqueous
159 solution is correlated to the chromogenic activity of the final solution (Hettwer et al., 2018).
160 The assays were carried out in 96-well plates. The calibration standards were analysed in
161 duplicates, in the range of 1 to 80 ng L⁻¹, along with two blanks. The samples were diluted to
162 fit in the studied range and analysed in triplicates.

163

164 3. Results and discussion

165 3.1. Effects of H₂O₂ and S₂O₈²⁻ under UVA and UVB radiations on the degradation of E2

166 In Figure 1, E2 degradations were followed under UVA and UVB radiations in the presence
167 of different H₂O₂ or S₂O₈²⁻ concentrations (from 0 to 5 mM). Despite no photolysis observed
168 under UVA, about 15% degradation of E2 was observed after 4 hours under UVB. In all
169 systems, E2 undergoes faster disappearance in the presence of H₂O₂ and S₂O₈²⁻. This trend
170 was attributed to the photoactivation of both radical precursors (reactions R1 and R2) leading
171 to the generation of highly oxidative species such as hydroxyl (HO[•]) and sulfate (SO₄^{•-})
172 radicals in solution. Faster degradation of E2 in the presence of UVB compared to the UVA
173 lamp was predicted considering higher absorption of both oxidant precursors at shorter
174 wavelength irradiations (Figure SM3).

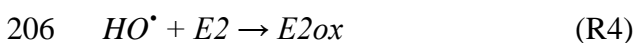
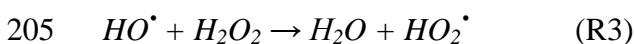


177
 178 *Figure 1. Effect of the oxidant precursor concentration (from 0 to 5 mM) on E2 (5 μM) degradation in milli-Q water at pH 6*
 179 *under various conditions: UVA/H₂O₂ (A), UVA/S₂O₈²⁻ (B), UVB/H₂O₂ (C) and UVB/S₂O₈²⁻ (D).*

180 As clearly depicted on Figure 1, S₂O₈²⁻ allows for faster degradation than H₂O₂ under both
 181 UVA and UVB radiations. Degradation of E2 up to 99% was achieved after 45 min under
 182 UVB + 5 mM H₂O₂ and after 5 min under UVB + 5 mM S₂O₈²⁻. In fact, E2 degradation can
 183 be attributed to the higher photolysis yield of radicals in the S₂O₈²⁻ system compared to H₂O₂.
 184 Oxidant precursors photolysis yield under the polychromatic UVA and UVB lights were
 185 determined following their degradations in solutions containing respectively H₂O₂ and S₂O₈²⁻
 186 as the only species. 1 mL of methanol (hydroxyl and sulfate radicals quencher) was added to
 187 the solutions (100 mL) to prevent self-quenching between the radicals and the oxidant
 188 precursors (i.e. radical reactivity) and ensure photolysis as the only degradation path. S₂O₈²⁻

189 photolysis constant ($k'_{S_2O_8^{2-}}$) were determined to be $1.93 \pm 0.09 \times 10^{-5} \text{ s}^{-1}$ under UVA radiation
 190 and $2.72 \pm 0.13 \times 10^{-5} \text{ s}^{-1}$ under UVB radiation while for H_2O_2 lower constants ($k'_{H_2O_2}$) of 1.48
 191 $\pm 0.07 \times 10^{-6} \text{ s}^{-1}$ under UVA radiation and $6.08 \pm 0.33 \times 10^{-6} \text{ s}^{-1}$ under UVB radiation were
 192 measured.

193 In Figure 2, the correlation between E2 pseudo-first order rate constant and oxidant precursor
 194 concentrations is presented. An increase of E2 degradation was observed when the
 195 concentration of radical precursors (H_2O_2 and $S_2O_8^{2-}$) increases. However, no linear
 196 correlation can be established in the different system. This effect is mainly observed on the
 197 H_2O_2 systems. It can be explained considering the competition undergone by the
 198 photogenerated radical HO^\bullet between E2 and H_2O_2 (R3 and R4). Hydrogen peroxide plays a
 199 role of hydroxyl radical scavenger, enhanced at high concentrations (Table SM2).
 200 Considering the H_2O_2 initial concentration and the second order rate constants between HO^\bullet
 201 and E2 (Table 1) ($k''_{HO^\bullet, E2} = 2.9 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$) and between HO^\bullet and H_2O_2 ($k''_{HO^\bullet, H_2O_2} = 2.7 \times$
 202 $10^7 \text{ M}^{-1} \text{ s}^{-1}$) (Buxton et al., 1988), we can estimate that in the presence of H_2O_2 at 5 mM, about
 203 48% of the hydroxyl radicals react through reaction R3 leading to the strong decrease of the
 204 reactivity towards E2 and the formation of less reactive species i.e. $HO_2^\bullet/O_2^{\bullet-}$ (pKa = 4.88).

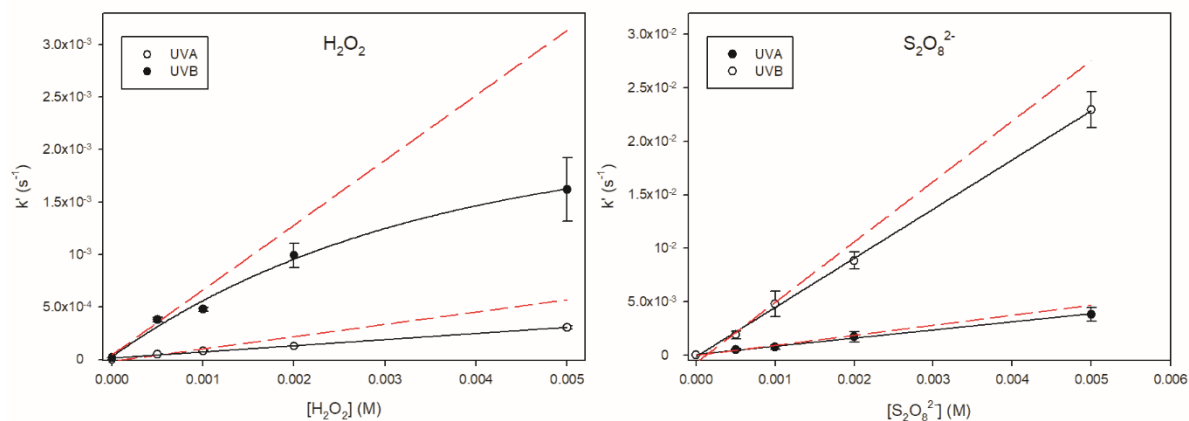


207 *Table 1. Second order rate constant of HO^\bullet and $SO_4^{\bullet-}$ with estrogens or STPW2 carbon, at neutral pH. Data are in $M^{-1} s^{-1}$ for*
 208 *estrogens and in $M_C^{-1} s^{-1}$ for STPW2. TOC constants were determined after acidification of STPW2 to pH 4 to remove the*
 209 *inorganic carbon.*

	E2	EE2	E1	STPW2 TC	STPW2 TOC
k''_{HO^\bullet}	$2.91 \pm 0.09 \times 10^{10}$	$1.81 \pm 0.02 \times 10^{10}$	$2.85 \pm 0.03 \times 10^{10}$	$2.8 \pm 0.1 \times 10^8$	$2.5 \pm 0.1 \times 10^8$
$k''_{SO_4^{\bullet-}}$	$2.66 \pm 0.03 \times 10^9$	$1.84 \pm 0.02 \times 10^9$	$4.11 \pm 0.04 \times 10^9$	$2.4 \pm 0.1 \times 10^8$	$2.2 \pm 0.2 \times 10^8$

210 On the contrary, $S_2O_8^{2-}$ scavenging effect is minor due to the lower reactivity constant
 211 between $SO_4^{\bullet-}$ and $S_2O_8^{2-}$ ($k''_{SO_4^{\bullet-}, S_2O_8^{2-}} = 6.1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$) (McElroy & Waygood, 1990)

212 whereas $k''_{SO_4^{\cdot-},E2} = 2.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. In the presence of 5 mM of $S_2O_8^{2-}$, the quenching of the
 213 photogenerated sulfate radical can be estimated to only 18%. The calculations for all oxidant
 214 precursors concentrations and competition reactivity are presented in the Supplementary
 215 material section.



216
 217 *Figure 2. E2 pseudo-first order rate constants (s^{-1}) depending on the oxidant precursor concentrations at pH 6: H_2O_2 (A) and*
 218 *$S_2O_8^{2-}$ (B), under UVA and UVB radiations. Dashed red lines estimate the curves without the oxidant precursors scavenging*
 219 *effects. The error is $\pm 3\sigma$, obtained from the scattering of the experimental data.*
 220

221 3.2. Effect of STP effluent on the degradation of E2 in the different systems

222 In this work, two STP effluents sampled at different times of the year were characterised.
 223 Similar E2 degradation rates were obtained when spiked into STPW1 and STPW2. STPW2
 224 will be considered for the rest of this study. In Table 2, E2 pseudo-first order degradation rate
 225 constants in STP effluent (STPW2) are compared to the results obtained in milli-Q water. E2
 226 removal inhibition was about 90% ($\pm 3\%$) in STPW using 2 mM of H_2O_2 or $S_2O_8^{2-}$ under both
 227 UVA or UVB. Such effect can be attributed to the presence of naturally occurring scavengers
 228 in STPW able to react with the photogenerated radicals. Chloride (Cl^-), bicarbonates (HCO_3^-)
 229 and occasionally nitrate (NO_3^-) ions are known as possible interfering species during radical
 230 based degradation processes (Tao et al., 2020; Zhang et al., 2018). The inhibition effect on E2
 231 degradation was tested for each individual ion to their concentration measured in STPW2
 232 (Table SM1) and no significant impact was observed (Figure SM5). Only in the presence of

233 chloride ions a slight inhibition (< 5%) of E2 degradation can be observed and attributed to
 234 the formation of less oxidant species such as dichloride radical ions ($\text{Cl}_2^{\cdot-}$) (Armstrong et al.,
 235 2015).

236 The composition of the organic matter in STPW2 has not been determined. Several studies
 237 highlighted that effluent compositions have a large variation range, depending on the influent
 238 characteristics but also on the type of treatment process upstream (Imai et al., 2002; Ma et al.,
 239 2001; Yu et al., 2012; Zhang et al., 2009). In this work, the organic matter reactivity has been
 240 standardised on the organic carbon reactivity.

241 Considering that the reactivity of organic carbon with hydroxyl and sulfate radicals is
 242 respectively $k''_{\text{HO}^{\cdot},\text{TOC}} = 2.5 \times 10^8 \text{ M}_C^{-1} \text{ s}^{-1}$ and $k''_{\text{SO}_4^{\cdot-},\text{TOC}} = 2.2 \times 10^8 \text{ M}_C^{-1} \text{ s}^{-1}$ (Table 1), we
 243 can estimate that about 82% and 74% of HO^{\cdot} and $\text{SO}_4^{\cdot-}$ are scavenged by organic matter of
 244 STPW2 in the H_2O_2 and $\text{S}_2\text{O}_8^{2-}$ systems respectively. The inhibition effect is not far from the
 245 experimental value reported in Table 2 and shows that the organic matter is mainly
 246 responsible for slowing down E2 degradation in STPW2. In their study on the degradation of
 247 Bisphenol A, Olmez-Hanci et al. (2015) have also determined that the natural organic matter
 248 from raw freshwaters was the main HO^{\cdot} and $\text{SO}_4^{\cdot-}$ scavengers, and Ghauch et al. (2017)
 249 reported that inorganic anions had a minor implication in the degradation inhibition.
 250 However, Ma et al. (2018) observed that carbonates were also significant scavengers, whereas
 251 the scavenging effect of chlorides depended on the studied pollutants and their concentration.

252 *Table 2. E2 pseudo-first order degradation rate constants in milli-Q water or STPW2 in the presence of H_2O_2 or $\text{S}_2\text{O}_8^{2-}$ (2*
 253 *mM) under UVA/UVB radiations at neutral pH.*

	UVA/ H_2O_2	UVA/ $\text{S}_2\text{O}_8^{2-}$	UVB/ H_2O_2	UVB/ $\text{S}_2\text{O}_8^{2-}$
k' (s^{-1}) in milliQ water	1.3×10^{-4}	1.7×10^{-3}	9.9×10^{-4}	8.8×10^{-3}
k' (s^{-1}) in STPW2 effluent	1.4×10^{-5}	1.2×10^{-4}	1.2×10^{-4}	1.1×10^{-3}
Inhibition (%)	89	93	88	87

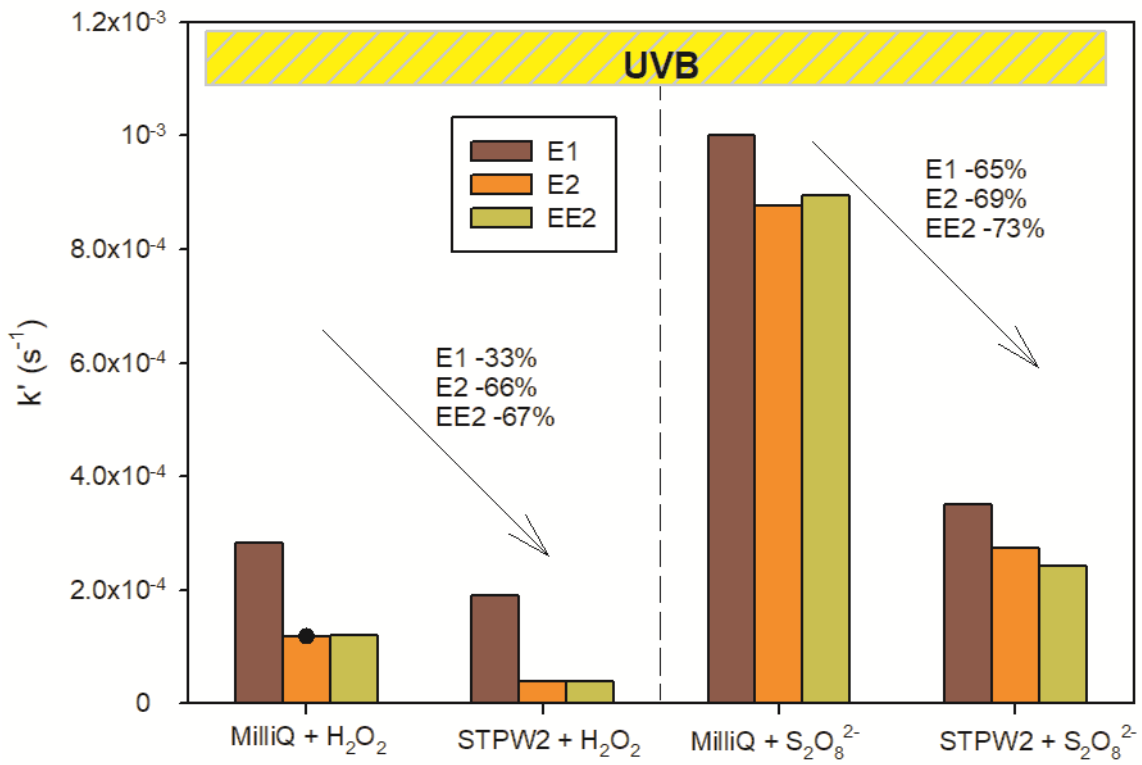
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255 *3.3. Comparison between E1, E2 and EE2 degradation under UVB radiation*

256 Figure 3 illustrates E1, E2 and EE2 degradations under UVB radiation of a mixture (5 μM
257 each) in milliQ water and in STPW2. For the same reasons as explained about E2 in section
258 3.1., E1 and EE2 degradations are faster when using $\text{S}_2\text{O}_8^{2-}$ than in the presence of H_2O_2 due
259 to the higher sulfate radical formation rate. The study was carried out with 2 mM of oxidant
260 precursors in order to minimize the oxidant precursors quenching effect (see section 3.1.). It
261 was also seen that all the hormones degradations are inhibited in a wastewater matrix.

262 In all the studied systems, E1 degradation was faster than E2 and EE2 degradations, which are
263 similar. The three hormones are subjected to photolysis and photo-induced degradation with
264 oxidant $\text{S}_2\text{O}_8^{2-}$ or H_2O_2 . As seen in Table 1, second order reaction rate constants between each
265 hormone and HO^\bullet or $\text{SO}_4^{\bullet-}$ have the same order of magnitude. Therefore, E1 faster
266 degradation is explained by its faster photolysis. In milli-Q water only, Figure 4 shows that E1
267 reached 95% degradation after 4 hours under UVB radiation while E2 and EE2 degradations
268 were around 15%.

269 This phenomenon also advantaged E1 degradation in STP water. As seen on Figure 3, its
270 degradation was less inhibited than E2 and EE2 degradations by STP water constituents,
271 particularly when using H_2O_2 (inhibition of 33%). Because hydrogen peroxide has a slower
272 degradation effect compared to persulfate, photolysis is effective in larger proportion. It also
273 allows E1 degradation to be less impacted by the inhibition effect from the STP water
274 scavengers.



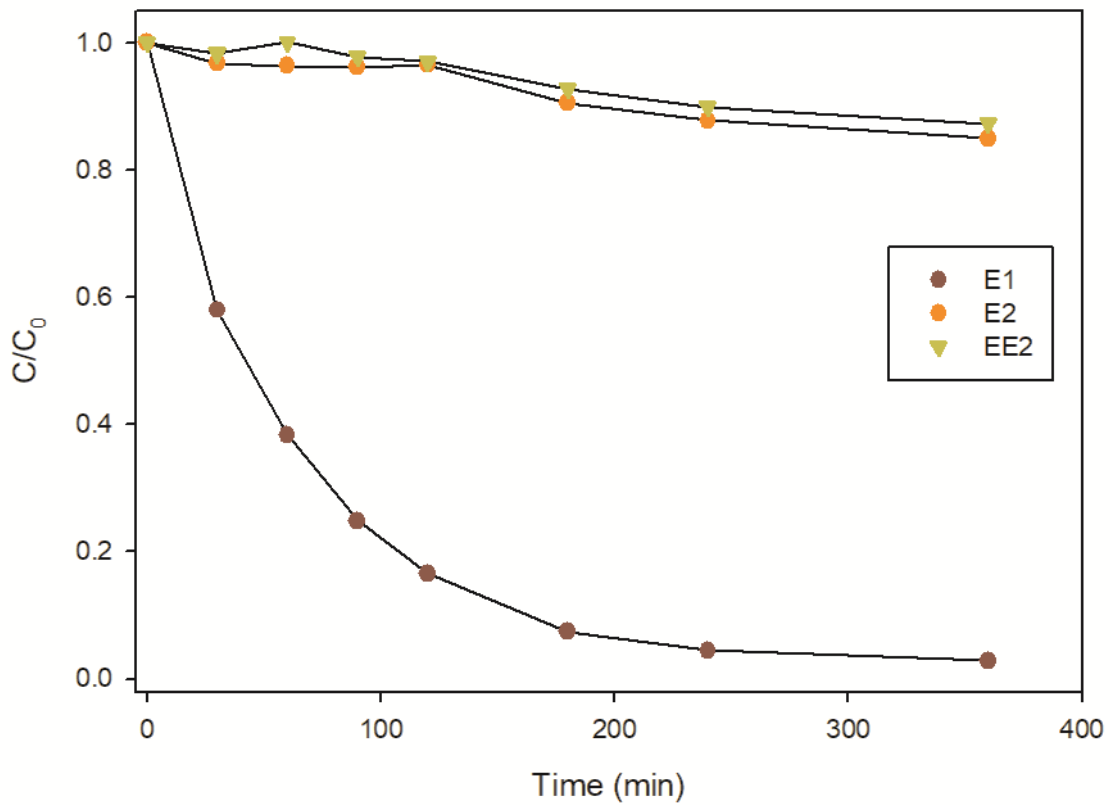
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278

Figure 3. E1, E2 and EE2 pseudo first-order degradation rate constants in a mixture (5 μM each) under UVB radiation. Comparison between the use of H₂O₂ and S₂O₈²⁻ (2 mM) as an oxidant precursor and milli-Q water (pH 6) and STP wastewater (pH 8) as a matrix. Inhibition percentages between milli-Q water and STPW2 are mentioned.



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280

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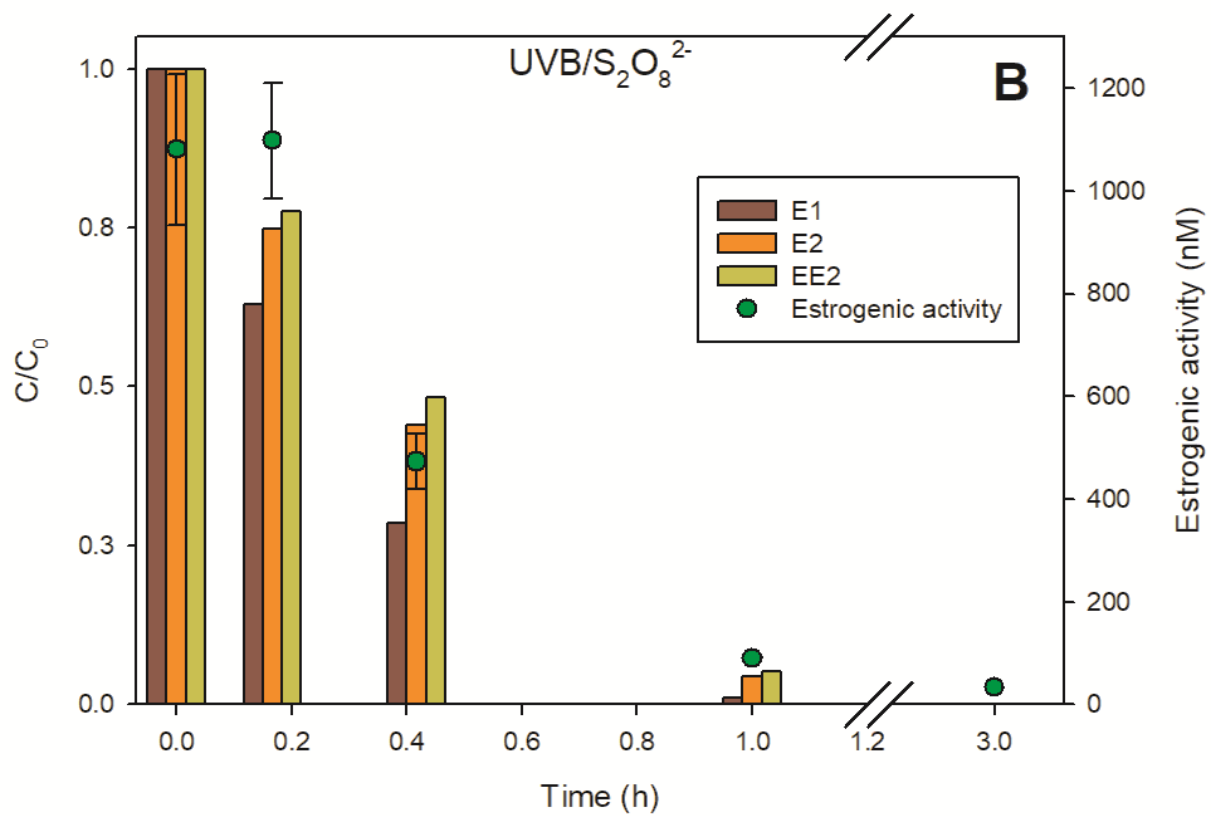
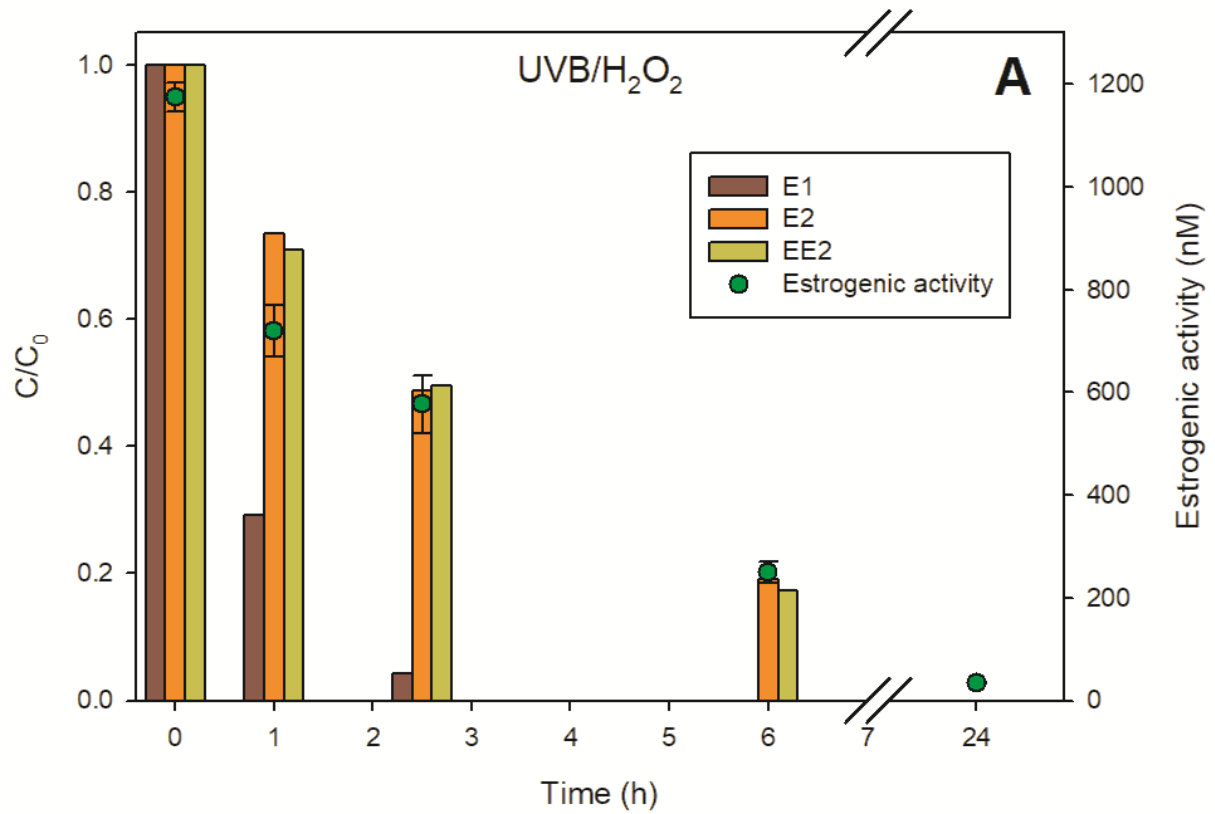
Figure 4. E1, E2 and EE2 photolysis under UVB radiation in milli-Q water (pH 6.5).

282 *3.4. Estrogenic activity removal and effect of hormone mixture under UVB radiation*

283 The aim of the YES assay was to ensure that the estrogen degradation goes along with a
284 decline in the estrogenic activity of the sample, responsible for its harmfulness. The
285 estrogenic activity of a sample was expressed in E2 equivalent concentration. The degradation
286 of a mixture of the three hormones (0.5 μM each) in milli-Q water under UVB radiation and
287 oxidant precursors (0.1 mM) was investigated. Concentrations of hormones were lower than
288 previous experiments in order to get closer to environmental concentrations, however the ratio
289 estrogen/oxidant precursor was similar to keep consistency. The estrogenic activity of the
290 mixture is reported in Figure 5 and compared to the degradation of each estrogen during UVB
291 irradiation. The use of both oxidant precursors shows a concordance between the decrease in
292 E2 and EE2 concentrations and the decline in estrogenic activity. E1 faster degradation seems
293 to have a minor effect on the estrogenic activity of the solution, which is mainly governed by
294 E2 and EE2 concentrations because of their higher estrogenic potencies. Considering that the
295 estrogenic potency of E2 is 1, those of E1 and EE2 are respectively 0.1 and 1.2 in agreement
296 with literature data (Murk et al., 2002). Theoretical estrogenic activity of the solution based
297 on the estrogenic potencies of each estrogen and on their concentrations have the same order
298 of magnitude than experimental values. Therefore, degradation products do not seem to have
299 a significant impact on the total estrogenic activity of the solutions. This could be due to a low
300 estrogenic activity of the by-products or to the fast disappearance of potentially high
301 estrogenic activity compounds.

302 However, while the estrogen concentration has fallen below 99.9% of the initial concentration
303 after 24 hours when using H_2O_2 and after 3 hours when using $\text{S}_2\text{O}_8^{2-}$, the estrogenic activity
304 remains around 30 nM which represents almost 3% of the initial estrogenic activity. It is
305 unknown whether this is due to the persisting estrogenic activity potentially caused by
306 degradation by-products, to the proximity with the limit of quantification (about 15 nM), or to

307 an experimental contamination. Anyway, after 24 hours of treatment using H_2O_2 and 3 hours
 308 using persulfate, a strong decrease of estrogenic activity, more than 97%, is obtained.



310 *Figure 5. Estrogenic activity assessment of a mixture of E1, E2 and EE2 (0,5 μM each) depending on UVB irradiation time.*
311 *H₂O₂ 0,1 mM in A, S₂O₈²⁻ 0,1 mM in B, pH 6.*

312

313 **4. Conclusion**

314 In this work, UVA and UVB photoactivation of hydrogen peroxide and persulfate were tested
315 for the degradation of three common estrogens: E2, E1 and EE2. It was seen that UVA and
316 UVB radiations are both efficient to produce hydroxyl and sulfate radicals, although photo-
317 induced degradation is faster under UVB radiation. However, higher efficiency of sulfate
318 radicals formation was observed compared to the hydroxyl radicals under these irradiation
319 wavelengths. Although an increase in the oxidant precursor concentration produced faster
320 degradation, this phenomenon did not follow a linear trend because the radicals are quenched
321 by the oxidant precursors, particularly with H₂O₂.

322 In a mixture, E2, E1 and EE2 are competing to react with the generated radicals because the
323 different reaction constants are similar. E1 was seen to degrade faster because it undergoes
324 higher photolysis than E2 and EE2 under UVB radiation. E2 degradation speed was slowed
325 down by approximately 90% in a STP effluent. Experiments have shown that the dissolved
326 carbon and particularly the organic carbon present in the matrix was the main quencher of the
327 hydroxyl and sulfate radicals. The YES assay was seen to give very enriching data confirming
328 that the studied processes allow to remove efficiently the estrogenic activity responsible for
329 the estrogens harmfulness in the environment. These experiments were carried out on a lab-
330 scale. However, further experiments on a pilot or real scale are required to fully assess the
331 different processes efficiency on real wastewaters.

332

333 **5. Declaration of Competing Interest**

334 All authors declare no conflict of interest.

335 **Acknowledgements**

336 The authors wish to acknowledge the financial support of the “Région Auvergne-Rhône-
337 Alpes” for their financial support through the “Pack Ambition Recherche”. This work was
338 performed within the framework of the EUR H2O’Lyon (ANR-17-EURE-0018) of Université
339 de Lyon (UdL), within the program "Investissements d'Avenir” operated by the French
340 National Research Agency (ANR). This work was also supported by the “Federation des
341 Recherches en Environnement” through the CPER “Environnement” founded by the “Région
342 Auvergne,” the French government and FEDER from European community. The authors
343 thank Muriel Joly for her involvement and her help in conducting the A-YES assays.

344

345 **References**

- 346 Al Hakim, S., Jaber, S., Zein Eddine, N., Baalbaki, A., & Ghauch, A. (2020). Degradation of
347 theophylline in a UV254/PS system : Matrix effect and application to a factory
348 effluent. *Chemical Engineering Journal*, 380, 122478.
349 <https://doi.org/10.1016/j.cej.2019.122478>
- 350 Amin, M. M., Bina, B., Ebrahimi, A., Yavari, Z., Mohammadi, F., & Rahimi, S. (2018). The
351 occurrence, fate, and distribution of natural and synthetic hormones in different types
352 of wastewater treatment plants in Iran. *Chinese Journal of Chemical Engineering*,
353 26(5), 1132- 1139. <https://doi.org/10.1016/j.cjche.2017.09.005>
- 354 Anderson, P. D., Johnson, A. C., Pfeiffer, D., Caldwell, D. J., Hannah, R., Mastrocco, F.,
355 Sumpter, J. P., & Williams, R. J. (2012). Endocrine disruption due to estrogens
356 derived from humans predicted to be low in the majority of U.S. surface waters.
357 *Environmental Toxicology and Chemistry*, 31(6), 1407- 1415.
358 <https://doi.org/10.1002/etc.1824>
- 359 Angkaew, A., Sakulthaew, C., Satapanajaru, T., Poapolathep, A., & Chokejaroenrat, C.
360 (2019). UV-activated persulfate oxidation of 17 β -estradiol : Implications for discharge
361 water remediation. *Journal of Environmental Chemical Engineering*, 7(2), 102858.
362 <https://doi.org/10.1016/j.jece.2018.102858>
- 363 Armstrong, D. A., Huie, R. E., Koppenol, W. H., Lyman, S. V., Merényi, G., Neta, P., Ruscic,
364 B., Stanbury, D. M., Steenken, S., & Wardman, P. (2015). Standard electrode potentials
365 involving radicals in aqueous solution: inorganic radicals (IUPAC Technical Report). *Pure*
366 *and Applied Chemistry*, 87, 1139-1150. <https://doi.org/10.1515/pac-2014-0502>
- 367 Bui, X. T., Vo, T. P. T., Ngo, H. H., Guo, W. S., & Nguyen, T. T. (2016). Multicriteria
368 assessment of advanced treatment technologies for micropollutants removal at large-

369 scale applications. *Science of The Total Environment*, 563- 564, 1050- 1067.
370 <https://doi.org/10.1016/j.scitotenv.2016.04.191>

371 Buxton, G. V., Greenstock, C. L., Helman, W. P., & Ross, A. B. (1988). Critical Review of
372 rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl
373 radicals ($\cdot\text{OH}/\cdot\text{O}^-$ in Aqueous Solution. *Journal of Physical and Chemical Reference*
374 *Data*, 17(2), 513- 886. <https://doi.org/10.1063/1.555805>

375 Desbrow, C., Routledge, E. J., Brighty, G. C., Sumpter, J. P., & Waldock, M. (1998).
376 Identification of estrogenic chemicals in STW effluent. 1. Chemical fractionation and in
377 vitro biological screening. *American Chemical Society*, 32(11), 1549-1558.
378 <https://doi.org/10.1021/es9707973>

379 Cédât, B., de Brauer, C., Métivier, H., Dumont, N., & Tutundjan, R. (2016). Are UV
380 photolysis and UV/H₂O₂ process efficient to treat estrogens in waters? Chemical and
381 biological assessment at pilot scale. *Water Research*, 100, 357- 366.
382 <https://doi.org/10.1016/j.watres.2016.05.040>

383 Ghauch, A., Baalbaki, A., Amasha, M., El Asmar, R., & Tantawi, O. (2017). Contribution of
384 persulfate in UV-254 nm activated systems for complete degradation of
385 chloramphenicol antibiotic in water. *Chemical Engineering Journal*, 317, 1012- 1025.
386 <https://doi.org/10.1016/j.cej.2017.02.133>

387 Hettwer, K., Jähne, M., Frost, K., Giersberg, M., Kunze, G., Trimborn, M., Reif, M., Türk, J.,
388 Gehrmann, L., Dardenne, F., De Croock, F., Abraham, M., Schoop, A., Waniek, J. J.,
389 Bucher, T., Simon, E., Vermeirssen, E., Werner, A., Hellauer, K., Wallentis, U., Drewes,
390 J., Dietzmann, D., Routledge, E., Beresford, N., Zietek, T., Siebler, M., Simon, A., Bielak,
391 H., Hollert, H., Müller, Y., Harff, M., Schiwy, S., Simon, K., & Uhlig, S. (2018).
392 Validation of Arxula Yeast Estrogen Screen assay for detection of estrogenic activity in

393 water samples : Results of an international interlaboratory study. *Science of The Total*
394 *Environment*, 621, 612- 625. <https://doi.org/10.1016/j.scitotenv.2017.11.211>

395 Huang, B., Li, X., Sun, W., Ren, D., Li, X., Li, X., Liu, Y., Li, Q., & Pan, X. (2014).
396 Occurrence, removal, and fate of progestogens, androgens, estrogens, and phenols in
397 six sewage treatment plants around Dianchi Lake in China. *Environmental Science*
398 *and Pollution Research*, 21(22), 12898- 12908. [https://doi.org/10.1007/s11356-014-](https://doi.org/10.1007/s11356-014-3236-6)
399 3236-6

400 Huang, W., Bianco, A., Brigante, M., & Mailhot, G. (2018). UVA-UVB activation of
401 hydrogen peroxide and persulfate for advanced oxidation processes : Efficiency,
402 mechanism and effect of various water constituents. *Journal of Hazardous Materials*,
403 347, 279- 287. <https://doi.org/10.1016/j.jhazmat.2018.01.006>

404 Imai, A., Fukushima, T., Matsushige, K., Kim, Y.-H., & Choi, K. (2002). Characterization of
405 dissolved organic matter in effluents from wastewater treatment plants. *Water*
406 *Research*, 36(4), 859- 870. [https://doi.org/10.1016/S0043-1354\(01\)00283-4](https://doi.org/10.1016/S0043-1354(01)00283-4)

407 McElroy, W. J., & Waygood, S. J. (1990). Kinetics of the reactions of the $\text{SO}_4^{\cdot-}$ radical with
408 SO_4^- , $\text{S}_2\text{O}_8^{2-}$, H_2O and Fe^{2+} . *Journal of the Chemical Society, Faraday Transactions*,
409 86(14), 2557- 2564. <https://doi.org/10.1039/FT9908602557>

410 Kidd, K. A., Blanchfield, P. J., Mills, K. H., Palace, V. P., Evans, R. E., Lazorchak, J. M., &
411 Flick, R. W. (2007). Collapse of a fish population after exposure to a synthetic estrogen.
412 *Proceedings of the National Academy of Sciences*, 104(21), 8897- 8901.
413 <https://doi.org/10.1073/pnas.0609568104>

414 Laurenson, J. P., Bloom, R. A., Page, S., & Sadrieh, N. (2014). Ethinyl estradiol and other
415 human pharmaceutical estrogens in the aquatic environment : A review of recent risk
416 assessment data. *The American Association of Pharmaceutical Scientists Journal*, 16(2),
417 299- 310. <https://doi.org/10.1208/s12248-014-9561-3>

418 Li, W., Jain, T., Ishida, K., & Liu, H. (2017). A mechanistic understanding of the degradation
419 of trace organic contaminants by UV/hydrogen peroxide, UV/persulfate and UV/free
420 chlorine for water reuse. *Environmental Science: Water Research & Technology*, 3(1),
421 128- 138. <https://doi.org/10.1039/C6EW00242K>

422 Ma, H., Allen, H. E., & Yin, Y. (2001). Characterization of isolated fractions of dissolved
423 organic matter from natural waters and a wastewater effluent. *Water Research*, 35(4),
424 985- 996. [https://doi.org/10.1016/S0043-1354\(00\)00350-X](https://doi.org/10.1016/S0043-1354(00)00350-X)

425 Ma, J., Yang, Y., Jiang, X., Xie, Z., Li, X., Chen, C., & Chen, H. (2018). Impacts of inorganic
426 anions and natural organic matter on thermally activated persulfate oxidation of BTEX in
427 water. *Chemosphere*, 190, 296-306. <https://doi.org/10.1016/j.chemosphere.2017.09.148>

428 Miller, W. L., & Kester, D. R. (1988). Hydrogen peroxide measurement in seawater by (p-
429 hydroxyphenyl)acetic acid dimerization. *Analytical Chemistry*, 60(24), 2711- 2715.
430 <https://doi.org/10.1021/ac00175a014>

431 Murk, A. J., Legler, J., Lipzig, M. M. H. van, Meerman, J. H. N., Belfroid, A. C., Spenkeliink,
432 A., Burg, B. van der, Rijs, G. B. J., & Vethaak, D. (2002). Detection of estrogenic
433 potency in wastewater and surface water with three in vitro bioassays. *Environmental*
434 *Toxicology and Chemistry*, 21(1), 16- 23. <https://doi.org/10.1002/etc.5620210103>

435 Olmez-Hanci, T., Dursun, D., Aydin, E., Arslan-Alaton, I., Girit, B., Mita, L., Diano, N.,
436 Mita, D. G., & Guida, M. (2015). $S_2O_8^{2-}$ /UV-C and H_2O_2 /UV-C treatment of Bisphenol A:
437 Assessment of toxicity, estrogenic activity, degradation products and results in real water.
438 *Chemosphere*, 119, S115- S123. <https://doi.org/10.1016/j.chemosphere.2014.06.020>

439 Pal, A., Gin, K. Y.-H., Lin, A. Y.-C., & Reinhard, M. (2010). Impacts of emerging organic
440 contaminants on freshwater resources : Review of recent occurrences, sources, fate
441 and effects. *Science of The Total Environment*, 408(24), 6062- 6069.
442 <https://doi.org/10.1016/j.scitotenv.2010.09.026>

443 Palharim, P. H., Graça, C. A. L., & Teixeira, A. C. S. C. (2020). Comparison between UVA-
444 and zero-valent iron-activated persulfate processes for degrading propylparaben.
445 *Environmental Science and Pollution Research*, 27(18), 22214- 22224.
446 <https://doi.org/10.1007/s11356-020-08141-4>

447 Praveena, S. M., Lui, T. S., Hamin, N., Razak, S. Q. N. A., & Aris, A. Z. (2016). Occurrence
448 of selected estrogenic compounds and estrogenic activity in surface water and
449 sediment of Langat River (Malaysia). *Environmental Monitoring and Assessment*,
450 188(7), 442. <https://doi.org/10.1007/s10661-016-5438-5>

451 Purdom, C. E., Hardiman, P. A., Bye, V. V. J., Eno, N. C., Tyler, C. R., & Sumpter, J. P.
452 (1994). Estrogenic effects of effluents from sewage treatment works. *Chemistry and*
453 *Ecology*, 8(4), 275- 285. <https://doi.org/10.1080/02757549408038554>

454 Jobling, S., Nolan, M., Tyler, C., Brighty, G., & Sumpter, J. P. (1998). *Widespread Sexual*
455 *Disruption in Wild Fish*, 32(17), 2498-2506. American Chemical Society.
456 <https://doi.org/10.1021/es9710870>

457 Tao, Y., Monfort, O., Brigante, M., Zhang, H., & Mailhot, G. (2020). Phenanthrene
458 decomposition in soil washing effluents using UVB activation of hydrogen peroxide
459 and peroxydisulfate. *Chemosphere*, 127996.
460 <https://doi.org/10.1016/j.chemosphere.2020.127996>

461 Valdés, M. E., Marino, D. J., Wunderlin, D. A., Somoza, G. M., Ronco, A. E., &
462 Carriquiriborde, P. (2015). Screening Concentration of E1, E2 and EE2 in Sewage
463 Effluents and Surface Waters of the “Pampas” Region and the “Río de la Plata”
464 Estuary (Argentina). *Bulletin of Environmental Contamination and Toxicology*, 94(1),
465 29- 33. <https://doi.org/10.1007/s00128-014-1417-0>

466 Wu, Y., Bianco, A., Brigante, M., Dong, W., de Sainte-Claire, P., Hanna, K., & Mailhot, G.
467 (2015). Sulfate Radical Photogeneration Using Fe-EDDS : Influence of Critical

468 Parameters and Naturally Occurring Scavengers. *Environmental Science &*
469 *Technology*, 49(24), 14343- 14349. <https://doi.org/10.1021/acs.est.5b03316>

470 Yu, J., Lv, L., Lan, P., Zhang, S., Pan, B., & Zhang, W. (2012). Effect of effluent organic
471 matter on the adsorption of perfluorinated compounds onto activated carbon. *Journal*
472 *of Hazardous Materials*, 225- 226, 99- 106.
473 <https://doi.org/10.1016/j.jhazmat.2012.04.073>

474 Zhang, H., Qu, J., Liu, H., & Zhao, X. (2009). Characterization of isolated fractions of
475 dissolved organic matter from sewage treatment plant and the related disinfection by-
476 products formation potential. *Journal of Hazardous Materials*, 164(2), 1433- 1438.
477 <https://doi.org/10.1016/j.jhazmat.2008.09.057>

478 Zhang, W., Zhou, S., Sun, J., Meng, X., Luo, J., Zhou, D., & Crittenden, J. (2018). Impact of
479 Chloride Ions on UV/H₂O₂ and UV/Persulfate Advanced Oxidation Processes.
480 *Environmental Science & Technology*, 52(13), 7380- 7389.
481 <https://doi.org/10.1021/acs.est.8b01662>

482 Zuo, Y., Zhang, K., & Zhou, S. (2013). Determination of estrogenic steroids and microbial
483 and photochemical degradation of 17 α -ethinylestradiol (EE2) in lake surface water, a
484 case study. *Environmental Science: Processes & Impacts*, 15(8), 1529- 1535.
485 <https://doi.org/10.1039/C3EM00239J>

486