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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**

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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 $\beta$ -estradiol (E2), which are naturally excreted by humans and animals, as  
38 well as 17 $\alpha$ -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  $\mu\text{g}$  of E1, 7.70  $\mu\text{g}$  of E2 and 0.41  $\mu\text{g}$  of EE2 per day. As a consequence, these  
43 hormones tend to reach concentrations up to tens of  $\text{ng L}^{-1}$  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  $\text{ng L}^{-1}$  (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<sup>-1</sup> 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<sup>-1</sup> 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/H<sub>2</sub>O<sub>2</sub> process to remove the  
70 estrogenic activity of estrogen spiked water samples. Numerous recent studies have also  
71 shown the ability of sulfate radicals (SO<sub>4</sub><sup>•-</sup>), 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  $\text{H}_2\text{O}_2$  and  $\text{S}_2\text{O}_8^{2-}$   
81 processes to degrade three commonly found hormones in wastewaters:  $17\beta$ -estradiol, estrone  
82 and  $17\alpha$ -ethinylestradiol. Preliminary degradation studies were carried out on  $17\beta$ -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  $17\beta$ -estradiol (E2), estrone (E1) and  $17\alpha$ -ethinylestradiol (EE2) were purchased from Sigma-  
91 Aldrich, as well as hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) (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 ( $\lambda_{\max} = 352$  nm) and UVB ( $\lambda_{\max} = 308$  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<sub>2</sub>O<sub>2</sub> 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<sub>2</sub>O<sub>2</sub>  
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<sup>-1</sup> 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  $3\sigma$ , 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)<sub>2</sub><sup>-</sup> transient (Huang et al., 2018). For  
149 sulfate radical, the decay ( $k'$ , s<sup>-1</sup>) of SO<sub>4</sub><sup>-</sup> 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<sup>-1</sup>, along with two blanks. The samples were diluted to  
162 fit in the studied range and analysed in triplicates.

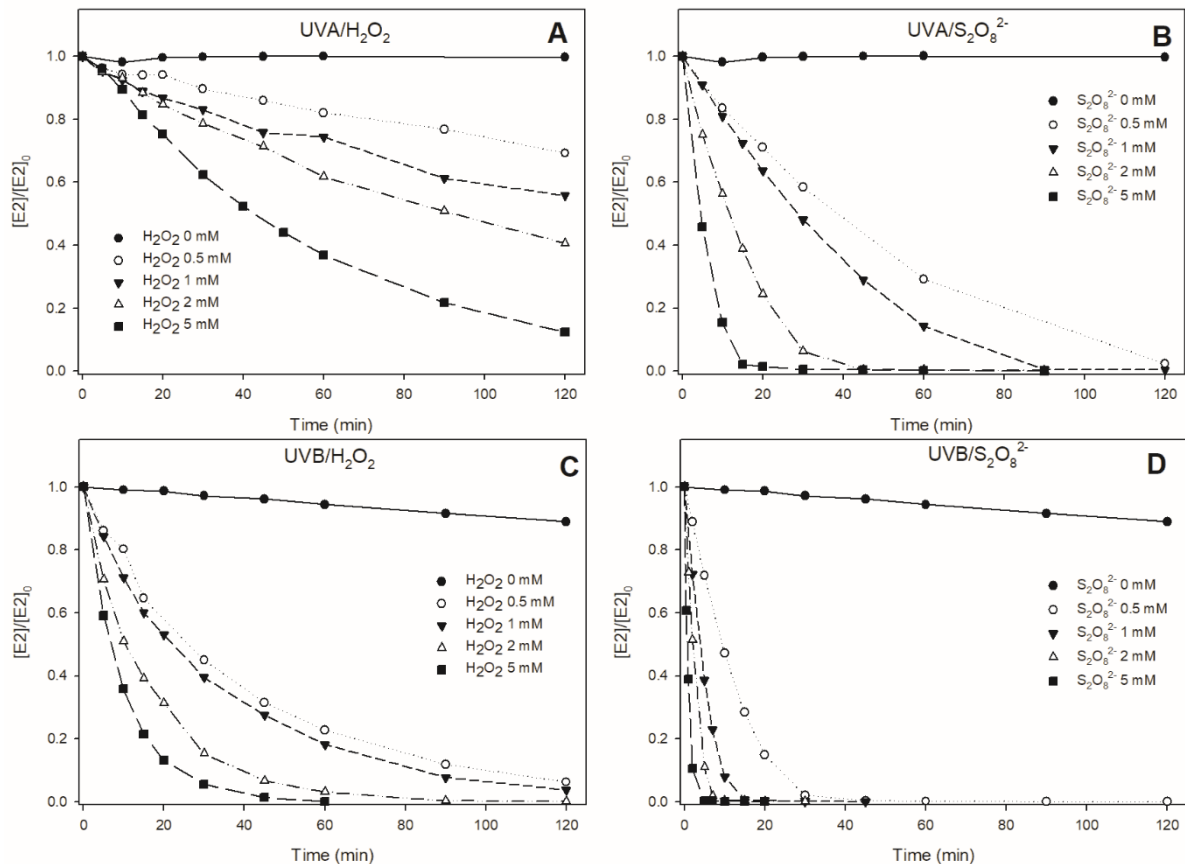
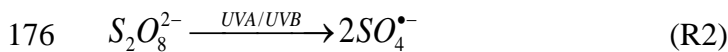
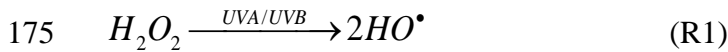
163

## 164 3. Results and discussion

### 165 3.1. Effects of H<sub>2</sub>O<sub>2</sub> and S<sub>2</sub>O<sub>8</sub><sup>2-</sup> 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 H<sub>2</sub>O<sub>2</sub> or S<sub>2</sub>O<sub>8</sub><sup>2-</sup> 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 H<sub>2</sub>O<sub>2</sub> and S<sub>2</sub>O<sub>8</sub><sup>2-</sup>. 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<sup>•</sup>) and sulfate (SO<sub>4</sub><sup>•-</sup>)  
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).



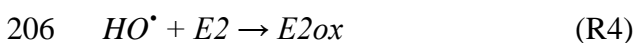
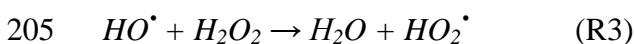


177  
 178 *Figure 1. Effect of the oxidant precursor concentration (from 0 to 5 mM) on E2 (5 μM) degradation in milli-Q water at pH 6*  
 179 *under various conditions: UVA/H<sub>2</sub>O<sub>2</sub> (A), UVA/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> (B), UVB/H<sub>2</sub>O<sub>2</sub> (C) and UVB/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> (D).*

180 As clearly depicted on Figure 1, S<sub>2</sub>O<sub>8</sub><sup>2-</sup> allows for faster degradation than H<sub>2</sub>O<sub>2</sub> under both  
 181 UVA and UVB radiations. Degradation of E2 up to 99% was achieved after 45 min under  
 182 UVB + 5 mM H<sub>2</sub>O<sub>2</sub> and after 5 min under UVB + 5 mM S<sub>2</sub>O<sub>8</sub><sup>2-</sup>. In fact, E2 degradation can  
 183 be attributed to the higher photolysis yield of radicals in the S<sub>2</sub>O<sub>8</sub><sup>2-</sup> system compared to H<sub>2</sub>O<sub>2</sub>.  
 184 Oxidant precursors photolysis yield under the polychromatic UVA and UVB lights were  
 185 determined following their degradations in solutions containing respectively H<sub>2</sub>O<sub>2</sub> and S<sub>2</sub>O<sub>8</sub><sup>2-</sup>  
 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. S<sub>2</sub>O<sub>8</sub><sup>2-</sup>

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).

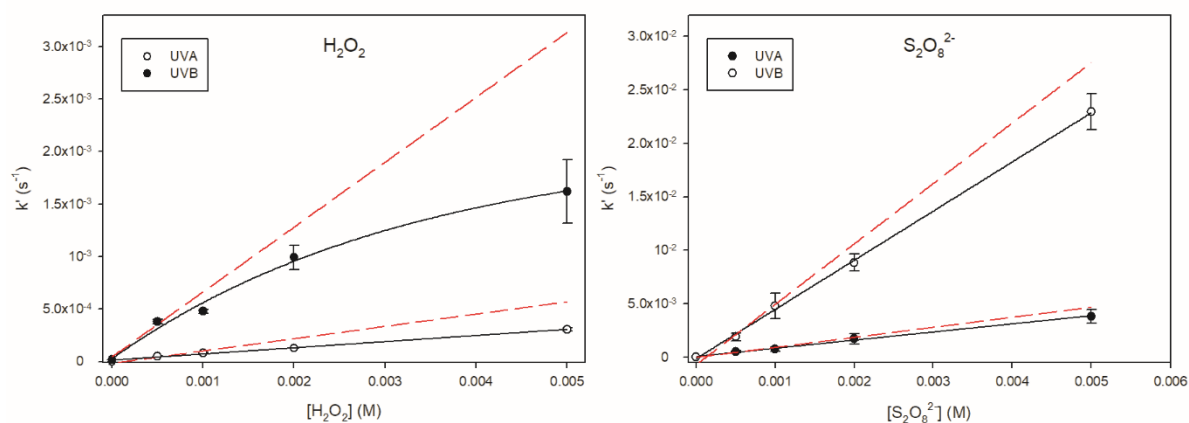


207 *Table 1. Second order rate constant of  $HO^\bullet$  and  $SO_4^{\bullet-}$  with estrogens or STPW2 carbon, at neutral pH. Data are in  $M^{-1} s^{-1}$  for*  
 208 *estrogens and in  $M_C^{-1} s^{-1}$  for STPW2. TOC constants were determined after acidification of STPW2 to pH 4 to remove the*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

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

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<sup>-1</sup>) depending on the oxidant precursor concentrations at pH 6: H<sub>2</sub>O<sub>2</sub> (A) and*  
 218 *S<sub>2</sub>O<sub>8</sub><sup>2-</sup> (B), under UVA and UVB radiations. Dashed red lines estimate the curves without the oxidant precursors scavenging*  
 219 *effects. The error is ± 3σ, 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% (± 3%) in STPW using 2 mM of H<sub>2</sub>O<sub>2</sub> or S<sub>2</sub>O<sub>8</sub><sup>2-</sup> 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<sup>-</sup>), bicarbonates (HCO<sub>3</sub><sup>-</sup>)  
 229 and occasionally nitrate (NO<sub>3</sub><sup>-</sup>) 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  $\text{HO}^{\cdot}$  and  $\text{SO}_4^{\cdot-}$  are scavenged by organic matter of  
 244 STPW2 in the  $\text{H}_2\text{O}_2$  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  $\text{HO}^{\cdot}$  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  $\text{H}_2\text{O}_2$  or  $\text{S}_2\text{O}_8^{2-}$  (2*  
 253 *mM) under UVA/UVB radiations at neutral pH.*

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

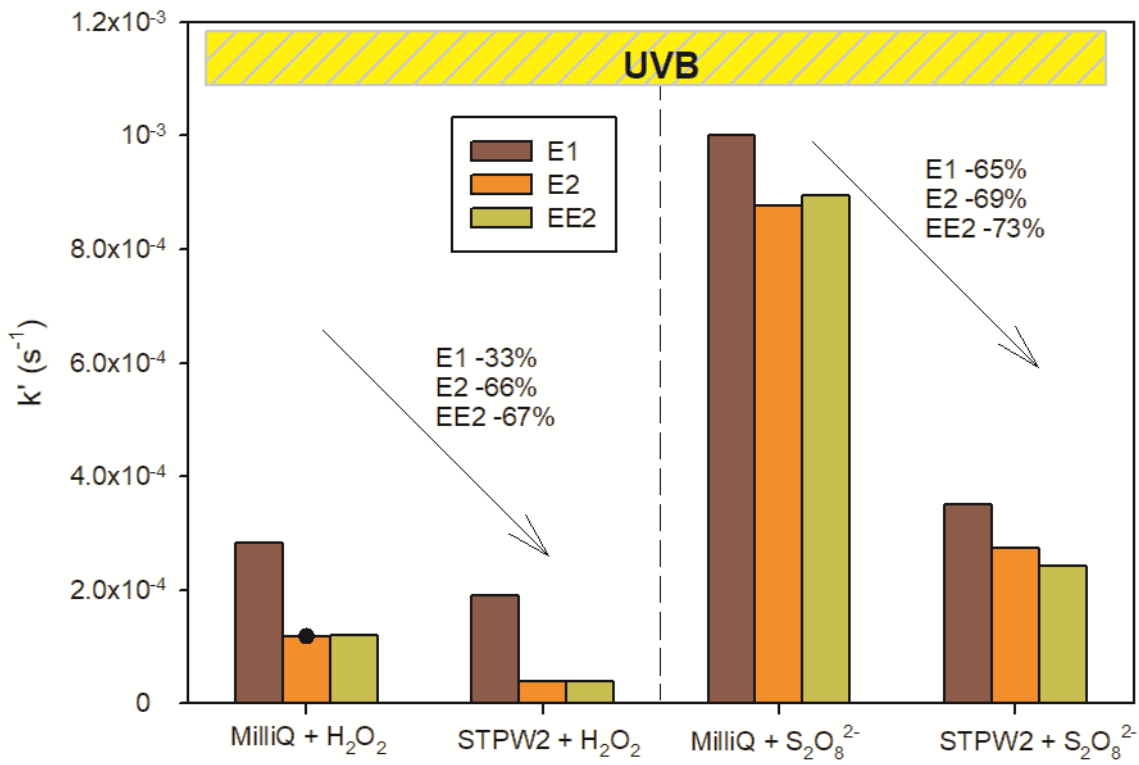
254

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  $\mu\text{M}$   
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  $\text{H}_2\text{O}_2$  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  $\text{H}_2\text{O}_2$ . As seen in Table 1, second order reaction rate constants between each  
265 hormone and  $\text{HO}^\bullet$  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  $\text{H}_2\text{O}_2$  (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.



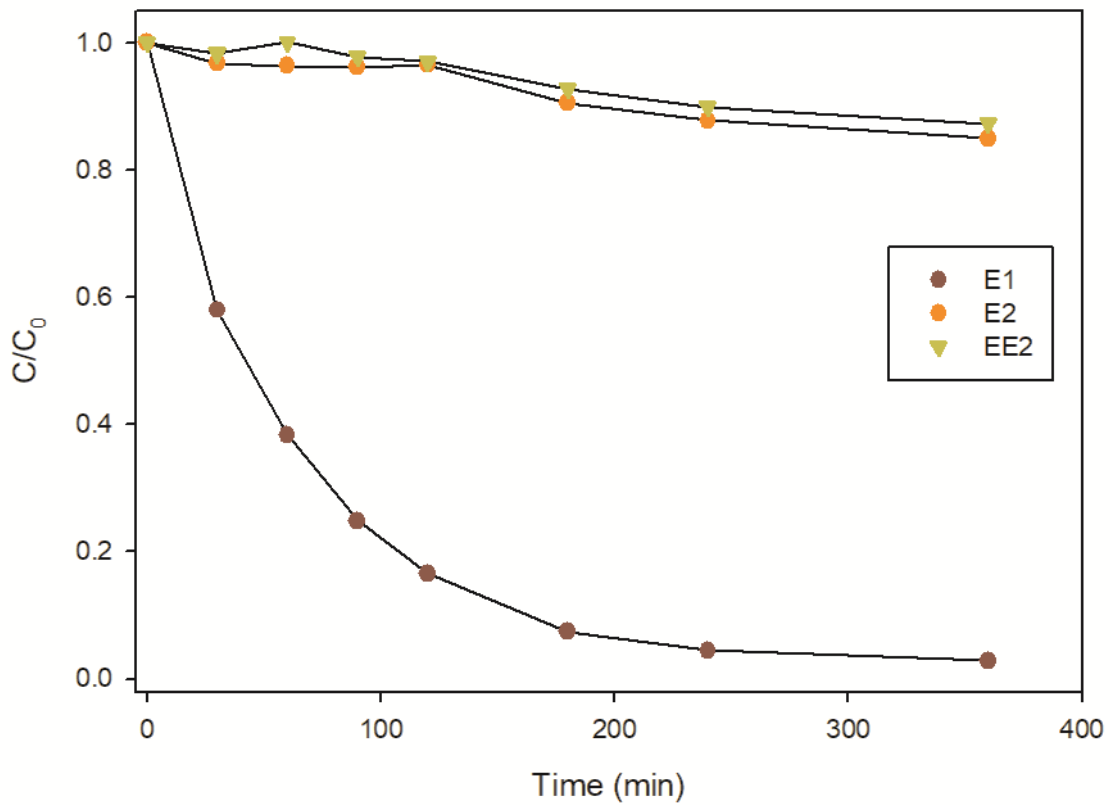
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Figure 3. E1, E2 and EE2 pseudo first-order degradation rate constants in a mixture (5 μM each) under UVB radiation. Comparison between the use of H<sub>2</sub>O<sub>2</sub> and S<sub>2</sub>O<sub>8</sub><sup>2-</sup> (2 mM) as an oxidant precursor 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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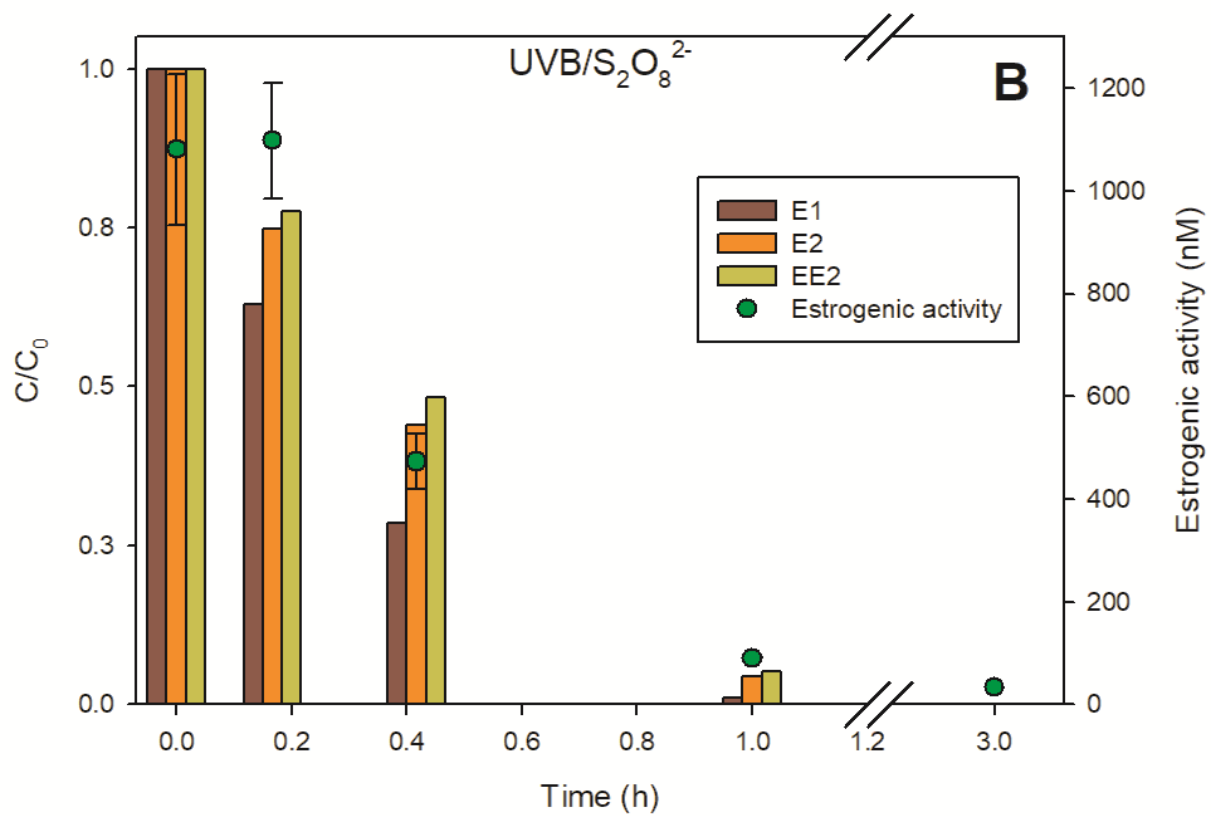
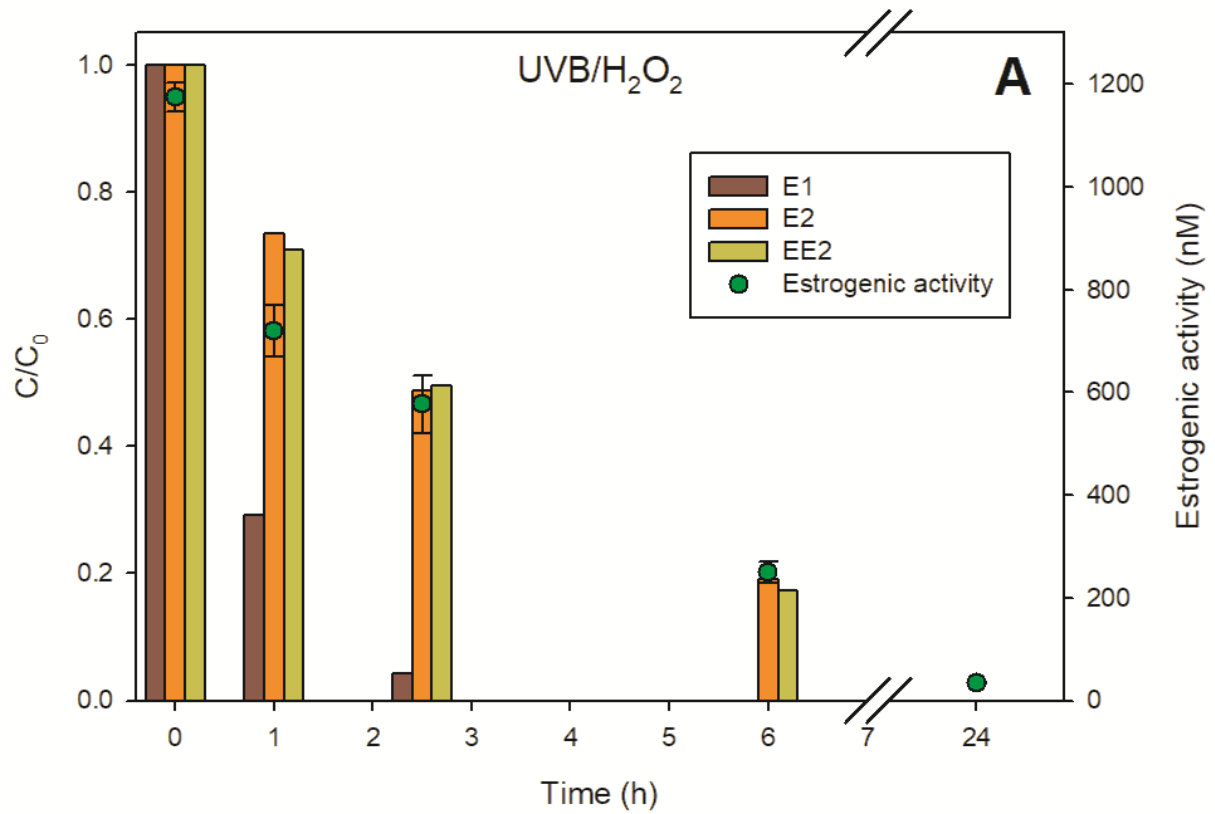
Figure 4. E1, E2 and EE2 photolysis under UVB radiation in milli-Q water (pH 6.5).

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  $\mu\text{M}$  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  $\text{H}_2\text{O}_2$  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 *H<sub>2</sub>O<sub>2</sub> 0,1 mM in A, S<sub>2</sub>O<sub>8</sub><sup>2-</sup> 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 H<sub>2</sub>O<sub>2</sub>.

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.

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344

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