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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

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

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Abstract

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

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

Keywords: estrogens, decontamination, wastewaters, hydroxyl radical, sulfate radical, AOPs, photolysis

1. Introduction

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

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

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

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

radiations: UVC lamps are more expensive and can be hazardous to manipulate. The use of UVA or UVB radiations also aims at more sustainable processes. They are less energy-consuming and could even be replaced by solar light for real-scale application. Lamps are nevertheless easier to use and to control for research purposes than solar light.

In this work we investigated the ability of UVA and UVB activation of H_2O_2 and $\text{S}_2\text{O}_8^{2-}$ processes to degrade three commonly found hormones in wastewaters: 17β -estradiol, estrone and 17α -ethinylestradiol. Preliminary degradation studies were carried out on 17β -estradiol in milli-Q water and few parameters such as oxidant dosage were investigated. Subsequent studies were conducted to establish the efficacy of the technique on STP effluent spiked with the three estrogens. Moreover, estrogenic activity assays were performed during degradation process to follow the harmfulness evolvement during irradiation.

2. Materials and methods

2.1. Chemicals and reagents

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

2.2. Irradiation experiments

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

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

2.3. Sample analysis and data processing

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

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

$C_t/C_0 = \exp(-k't)$ where C_0 and C_t are respectively the initial concentration and the concentration at time t and k' is the pseudo-first order rate constant.

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

2.4. Laser flash photolysis

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

All experiments were carried out using the fourth harmonic ($\lambda_{\text{exc}} = 266 \text{ nm}$) of a Quanta Ray GCR 130-01 Nd:YAG laser system instrument and an energy of $\sim 45 \text{ mJ/pulse}$. The experimental setup has been described before (Wu et al., 2015). Briefly, for hydroxyl radical reactivity, a competition kinetic method using thiocyanate anion was used and reactivity was determined following the absorption at 450 nm of $(\text{SCN})_2^{\bullet-}$ transient (Huang et al., 2018). For sulfate radical, the decay (k' , s^{-1}) of $\text{SO}_4^{\bullet-}$ signal at 370 nm was plotted as a function of

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

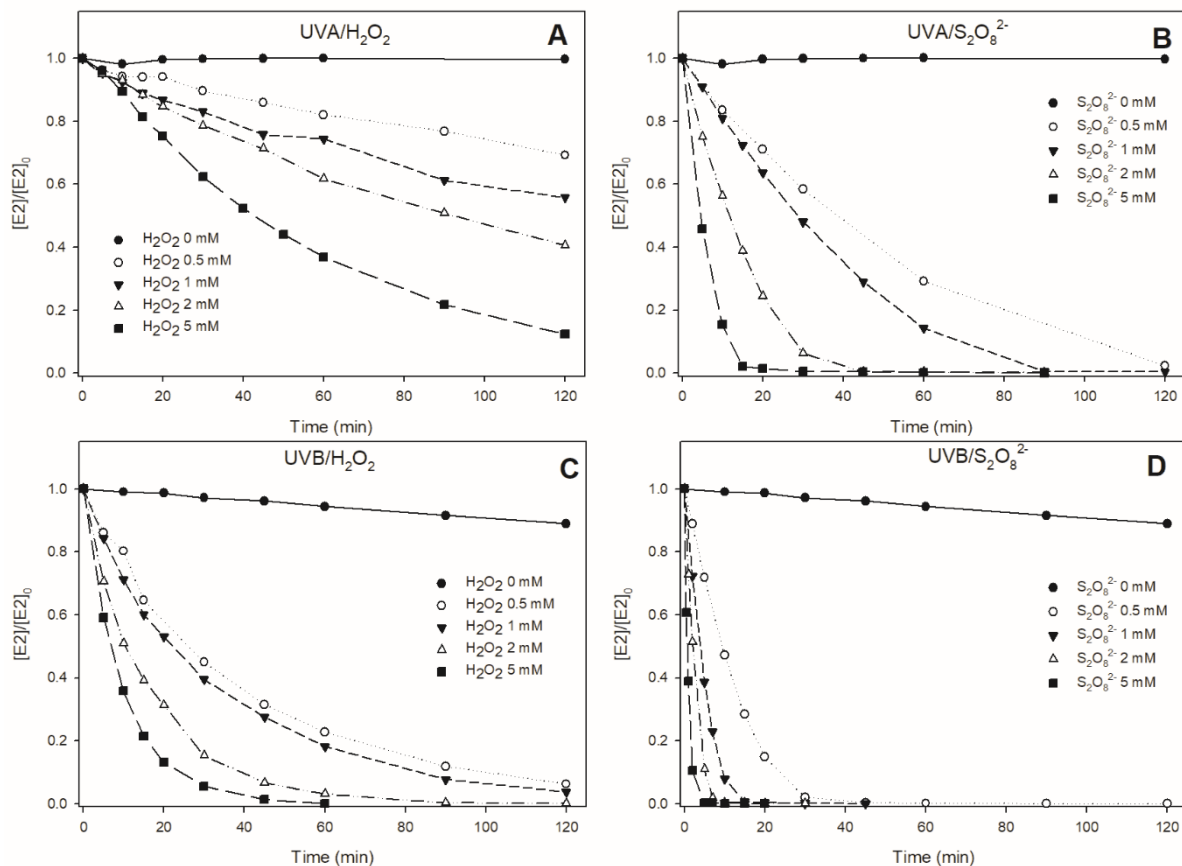
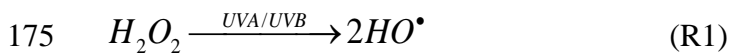
2.5. Estrogenic activity removal

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

3. Results and discussion

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

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



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⁻

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 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 $1.48 \pm 0.07 \times 10^{-6} \text{ s}^{-1}$ under UVA radiation and $6.08 \pm 0.33 \times 10^{-6} \text{ s}^{-1}$ under UVB radiation were measured.

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

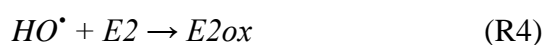
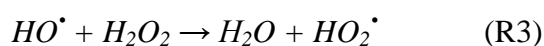


Table 1. Second order rate constant of HO^\bullet and $SO_4^{\bullet-}$ with estrogens or STPW2 carbon, at neutral pH. Data are in $\text{M}^{-1} \text{ s}^{-1}$ for estrogens and in $\text{M}^{-1} \text{ s}^{-1}$ for STPW2. TOC constants were determined after acidification of STPW2 to pH 4 to remove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

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

On the contrary, $S_2O_8^{2-}$ scavenging effect is minor due to the lower reactivity constant 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)

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

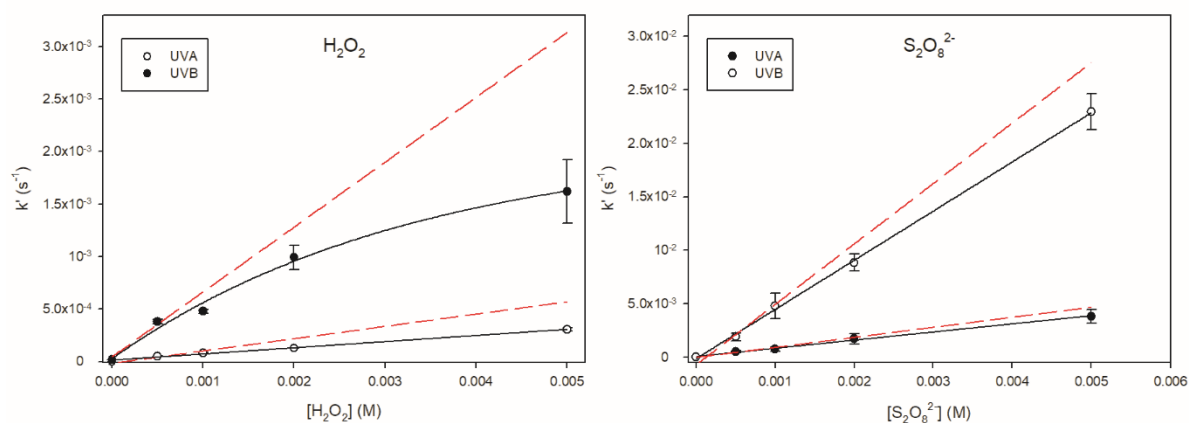


Figure 2. E2 pseudo-first order rate constants (s^{-1}) depending on the oxidant precursor concentrations at pH 6: H_2O_2 (A) and $S_2O_8^{2-}$ (B), under UVA and UVB radiations. Dashed red lines estimate the curves without the oxidant precursors scavenging effects. The error is $\pm 3\sigma$, obtained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

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

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

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

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

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

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 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 |

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

Figure 3 illustrates E1, E2 and EE2 degradations under UVB radiation of a mixture (5 μM each) in milliQ water and in STPW2. For the same reasons as explained about E2 in section 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 to the higher sulfate radical formation rate. The study was carried out with 2 mM of oxidant precursors in order to minimize the oxidant precursors quenching effect (see section 3.1.). It was also seen that all the hormones degradations are inhibited in a wastewater matrix.

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

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

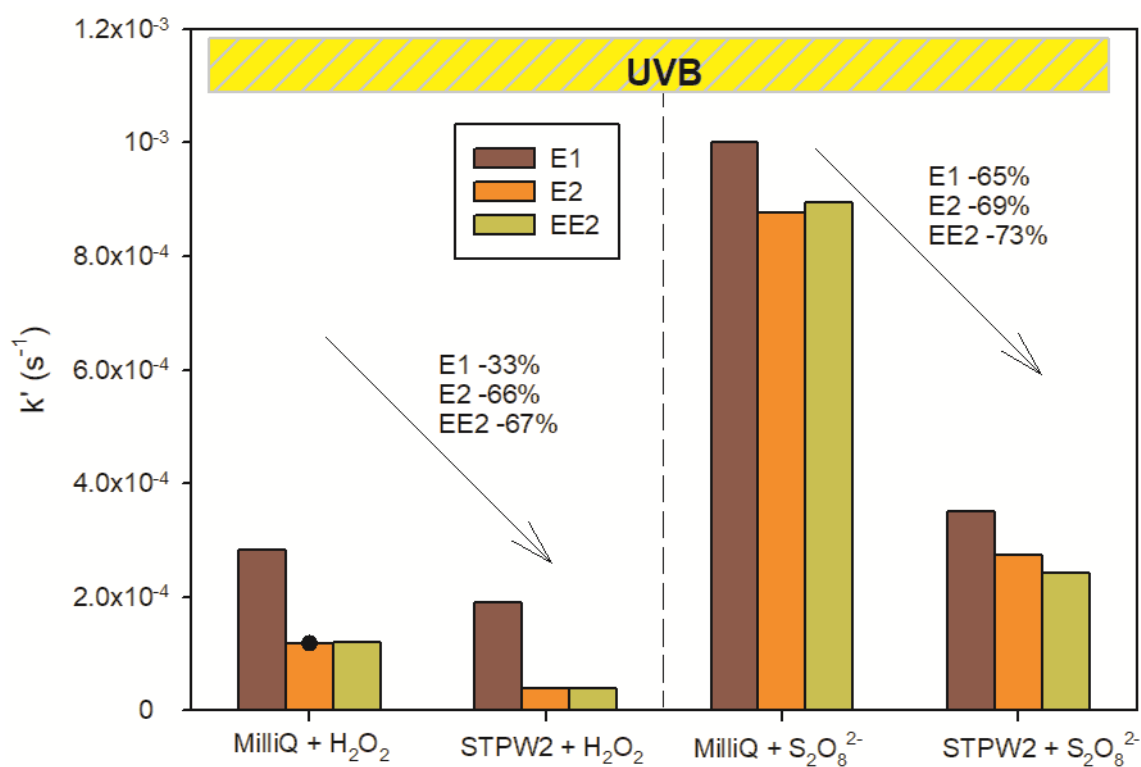


Figure 3. E1, E2 and EE2 pseudo first-order degradation rate constants in a mixture ($5 \mu M$ each) under UVB radiation. Comparison between the use of H_2O_2 and $S_2O_8^{2-}$ (2 mM) as an oxidant precursor and milli-Q water (pH 6) and STP wastewater (pH 8) as a matrix. Inhibition percentages between milli-Q water and STPW2 are mentioned.

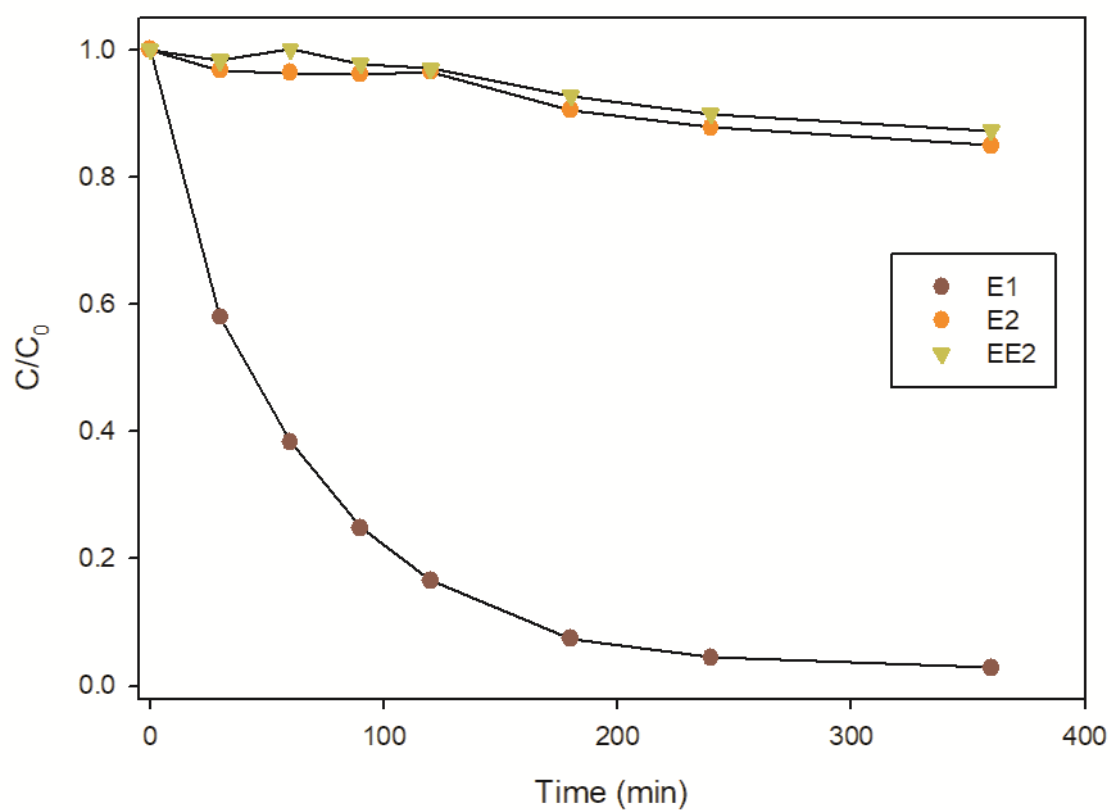


Figure 4. E1, E2 and EE2 photolysis under UVB radiation in milli-Q water (pH 6.5).

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

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

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

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

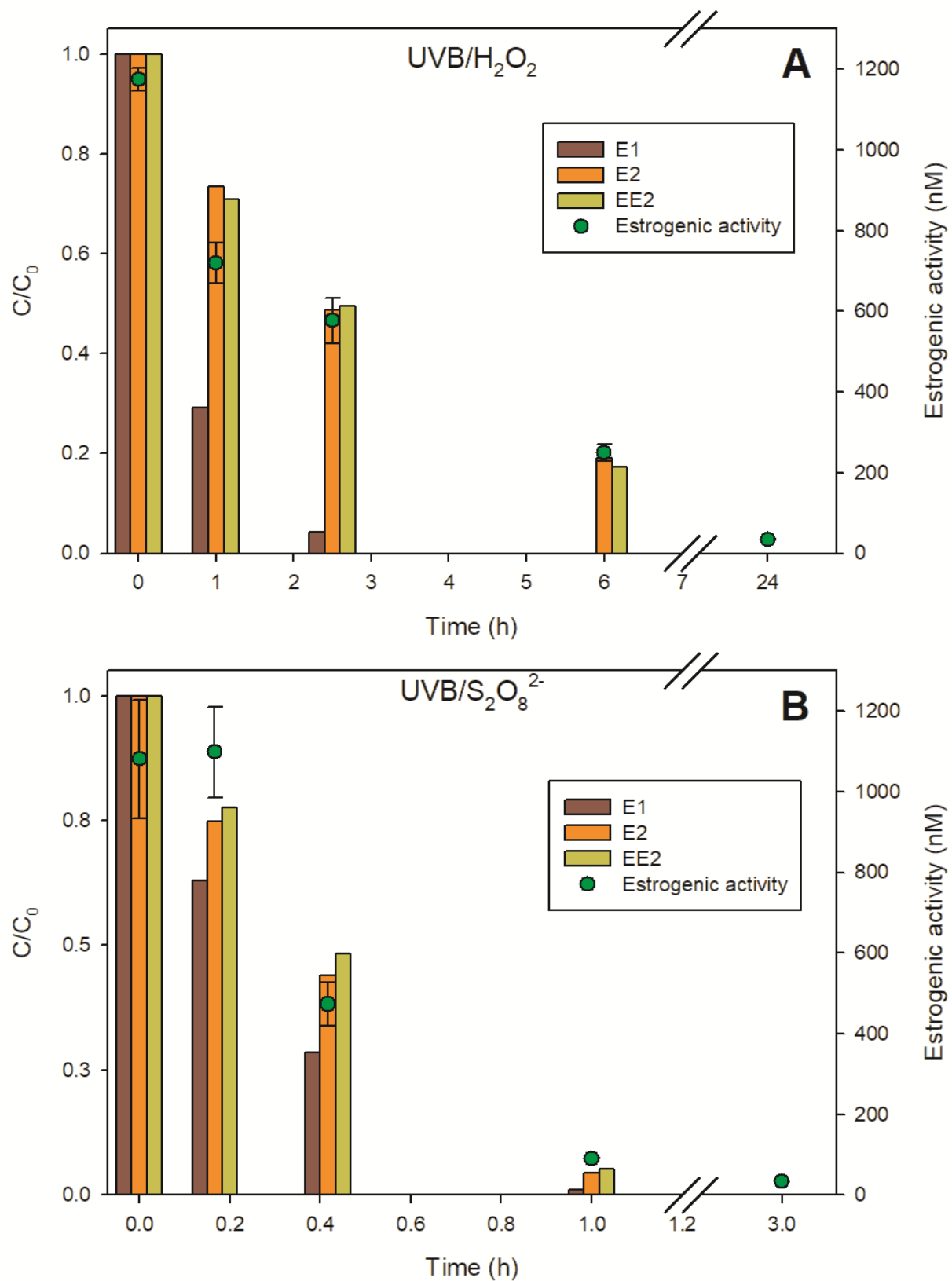


Figure 5. Estrogenic activity assessment of a mixture of E1, E2 and EE2 (0,5 μ M each) depending on UVB irradiation time. H_2O_2 0,1 mM in A, $S_2O_8^{2-}$ 0,1 mM in B, pH 6.

4. Conclusion

In this work, UVA and UVB photoactivation of hydrogen peroxide and persulfate were tested for the degradation of three common estrogens: E2, E1 and EE2. It was seen that UVA and UVB radiations are both efficient to produce hydroxyl and sulfate radicals, although photo-induced degradation is faster under UVB radiation. However, higher efficiency of sulfate radicals formation was observed compared to the hydroxyl radicals under these irradiation wavelengths. Although an increase in the oxidant precursor concentration produced faster degradation, this phenomenon did not follow a linear trend because the radicals are quenched by the oxidant precursors, particularly with H_2O_2 .

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

5. Declaration of Competing Interest

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.

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