



Relevance of a photo-Fenton like technology based on peroxymonosulphate for 17 β -estradiol removal from wastewater



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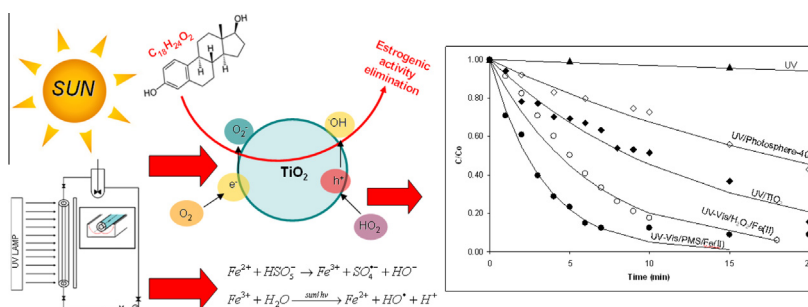
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HIGHLIGHTS

- 1.51 \pm 0.04 mg L⁻¹ E2 initial concentration fully degraded in few minutes in WWTP effluent.
- UV-Vis/PMS/Fe(II) was four times faster than UV/TiO₂ for E2 removal.
- Estrogenic activity of E2 was eliminated at the same rate during UV-Vis/PMS/Fe(II).
- Sulphate and hydroxyl radical attacks hydrogen abstraction at the aliphatic ring.
- Solar irradiation to activate PMS opens new economical feasible remediation strategies.

GRAPHICAL ABSTRACT



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ABSTRACT

The objective of this work was to evaluate the effectiveness of sulphate radical based homogeneous advanced oxidation technologies (SR-AOTs) involving peroxymonosulphate (PMS) as an oxidant and ferrous iron (Fe(II)) as a catalyst, for the removal of 17 β -estradiol (E2) from wastewater effluents collected downstream of a biological WWTP in Perpignan (France). This molecule is used as a surrogate for endocrine disrupting compounds (EDCs) due to its high biological activity at very low concentration levels (ng/L). For this purpose, two different laboratory-scale devices have been employed, one for indoor experiments working with controlled and artificial UV light centered on $\lambda = 365$ nm emission, and the other at a larger scale for outdoor experiments using direct solar irradiation. Comparison of kinetic studies with those obtained with commonly used hydroxyl radical based advanced oxidation technologies (HR-AOTs), i.e., UV-Vis/H₂O₂/Fe(II) and UV/TiO₂ revealed the higher efficiency of the former over the latter ones. Estrogenicity measurement through bioassays confirmed the complete removal of 17 β -estradiol after only a few minutes treatment. Determination of E2 transformation pathways upon sulphate radical reactivity through intermediates identification by mass spectrometry revealed that the oxidation of phenol moiety into quinone might be the main step responsible for the decrease in estrogenicity. UV-Vis/PMS/Fe(II) system appears to be the most suitable method for the treatment of aqueous solutions containing E2.

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1. Introduction

The domestic and industrial use of water generates high quantity of residual wastewater, which direct release into surface water may entail considerable impacts for the environment. As a consequence, removal of recalcitrant and toxic compounds (priority pollutants) from wastewaters is a major problem to be solved to achieve the desired degree of quality before water discharge into the environment and/or water reuse. In recent years, emerging pollutants have received an increasing attention with great focus on endocrine disrupting compounds (EDCs). EDCs can accumulate in surface waters and sewage effluents and influencing the habitat sanctuaries or drinking water district in various countries [1].

Several conventional processes, including adsorption and biological treatment, have been commonly applied for the removal of estrogenic steroid hormones in contaminated water [2–5]. Scientists have been trying in the last few decades to develop much more effective and environmental friendly technologies to remove these EDCs efficiently. For the purpose, advanced oxidation technologies have been investigated. The Fenton reagent is considered one of the traditional environmentally friendly Advance Oxidation Technologies (AOTs) and has been widely applied for water purification since 1960s [6]. Other AOTs which are used for wastewater treatment include photo-Fenton UV-Vis/H₂O₂/Fe(II), UV/H₂O₂ and heterogeneous photocatalyst-assisted processes such as UV/TiO₂. All these advanced oxidation technologies are based on the formation of hydroxyl radicals (OH[•]) which are able to attack and degrade water organic pollutants.

Peroxymonosulphate (PMS) and persulphate (PS) have recently proved to be powerful oxidants that can produce sulphate radicals (SR) upon solar irradiation in presence of iron for the removal of a large array of organic contaminants including pharmaceuticals and pesticides [7]. As a result SR-AOTs have recently received a significant attention [7–12]. Among the various SR-AOTs, UV-Vis/PMS/Fe(II) and UV-Vis/PS/Fe(II) technologies are highly attractive because of their low operational costs and high organic pollutant removal efficiency [13,14]. Compared to H₂O₂, PMS presents the decisive advantage to be stable at room temperature. If provided in the form of potassium peroxymonosulphate (Oxone[®]), PMS is also handled easily due its solid state. However, up till now most of the studies have been evaluated in small volume reactor (<100 mL) and data of the efficiency of such processes at larger scales is lacking in contrast to the well-known HR-AOTs.

Consequently, the major aim of this study was to evaluate the effectiveness of UV-Vis/PMS/Fe(II) system for the degradation of 17 β -estradiol (E2) in two different configurations: one in indoor conditions using controlled UV irradiation and one in outdoor conditions with natural solar irradiation but in both cases with real domestic wastewater. 17 β -estradiol was selected as a probe contaminant representative of the EDCs because: (i) E2 has been found as a relevant surface water contaminant; (ii) E2 is one of the fifteen new molecules to monitor from priority substances list in European Water Framework; (iii) E2 transformation pathway have been investigated upon many oxidative treatment processes including heterogeneous photocatalysis [15,16], photo-Fenton with H₂O₂ [17] which might facilitate intermediates identification and comparison between sulphate and hydroxyl radicals reactivity in water.

The objective of this work is definitively not to provide an in depth kinetic study but is rather an attempt to give a comprehensive view of the different aspects linked to the degradation of E2 with SR-AOTs. In a first step, the performance of UV-Vis/PMS/Fe(II) was investigated with indoor experiments according to basic kinetic criteria, mainly the comparison between apparent first order kinetic rate constants obtained by different SR-AOTs and

HR-AOTs. Then, and in a second step, the treatment efficiency is provided with estrogenic activity measurements. This approach is based on the use of bioluminescent HELN ER α cell line, to detect the presence of estrogenic activity in sample. Bioluminescent cell lines were successfully used to detect EDCs present in environmental or biological samples [18]. In a third step E2 transformation pathways obtained through intermediates identification was suggested in order to better know reasons for estrogenicity decrease against treatment time. Finally, outdoor experiments were performed under natural solar irradiation to assess potential application of SR-AOTs at larger scale.

2. Materials and methods

2.1. Reagents, catalysts and wastewater

For chemical analysis, acetonitrile (ACN) and methanol (MeOH) were HPLC grade from Carlo Erba and water was ultrapure Milli-Q grade (18.2 M Ω cm⁻¹ resistivity at 25 °C). Formic acid (85% purity) was obtained from Riedel de Haën. All chemicals were used as received without further purification.

Analytical standard of 17 β -estradiol (purity \geq 97%), ferrous sulphate heptahydrate (FeSO₄ \times 7H₂O), Oxone[®] monopersulphate compound (PMS) (HKSO₅ \times 0.5 HKSO₄ \times 0.5 K₂SO₄) and sulphuric acid were obtained from Sigma Aldrich. Hydrogen peroxide 30% (H₂O₂) was supplied by Merck (Germany).

The heterogeneous photocatalytic experiments were carried out with slurry suspension of two different forms of TiO₂ i.e., (i) Aeroxide P-25 (Evonik) with primary particle size of 20–30 nm as determined by transmission electronic microscopy, a specific surface area of 54 m² g⁻¹ as estimated by Brunauer Emmett Teller (BET) method; the composition was 78% anatase and 22% rutile as determined by X-ray diffraction; (ii) photospheres-40 from Microsphere Technology Ltd. (Ireland) with spheres diameter of 45 μ m and a catalyst concentration of 12.2 wt.% as determined by the X-ray fluorescence analysis. In the case of heterogeneous photocatalysis, the optimal TiO₂ concentration was defined as a function of the optical pathway. With Degussa P25, according to the reactor design (next section), a TiO₂ catalyst concentration equal to 0.7 g L⁻¹ leads to more than 90% incident light absorption by the catalyst and, as a result, to a degradation rate close to the optimum [19]. Photospheres-40 are hollow silica microsphere coated with TiO₂. Due to their low density (0.22 g cm⁻³), microspheres possess a floating ability [20]; within the objective to make a direct comparison between the two different solid catalysts, the same concentration in terms of catalyst i.e. 4.2 g L⁻¹ of photosphere-40 (taking into account the sphere composition) has been selected. With respect to UV-Vis/PMS/Fe(II) system and in agreement with Mahdi-Ahmed and Chiron [12] findings, the selected composition of reagents was a PMS: Fe(II) ratio of 200:100 μ M. This composition led to the fastest oxidation rate of selected pharmaceutical substances. It corresponds also to the upper limit of iron concentration (approximately 5.5 mg L⁻¹) which is allowed to be directly released in natural water and to the optimum amount of iron to activate PMS [12]. The same composition was also adopted in the case of photo-Fenton using H₂O₂ as an oxidizing agent [21]. In both cases, UV-Vis/H₂O₂/Fe(II) and UV-Vis/PMS/Fe(II), pH was adjusted to 3 with sulphuric acid to avoid iron precipitation.

Real samples of wastewater effluents were collected downstream of a biological WWTP with the following characteristics: [TSS] = <2 mg L⁻¹; [BOD₅] = <3 mg O₂ L⁻¹; [COD] = <30 mg O₂ L⁻¹; [TKN] = 2.4 mg L⁻¹; [Total-P] = 0.88 mg L⁻¹; [Total Nitrogen] = <3.92 mg L⁻¹; [NO₃⁻] = 1.5 mg N L⁻¹; [NO₂⁻] = <0.02 mg N L⁻¹; [NH₄⁺] = <1.2 mg N L⁻¹.

Wastewater samples were spiked with $1.51 \pm 0.04 \text{ mg L}^{-1}$ of E2, an initial concentration level allowing for the identification of by-products during degradation.

2.2. Experimental set-up

The laboratory-scale reactor consisted of a cylindrical borosilicate glass tube with 18 mm of outside radius, wall thickness 1 mm, height 75 cm and operated in a re-circulation batch mode. One liter of effluent to be treated flowed through the reactor and was mixed in the re-circulation tank. Effluent was continuously re-circulated by means of a volumetric pump. The radiation source was an UV lamp at 365 nm (VL-330). The length of the selected lamp made almost uniform radiation intensity possible along the reactor axis. After calibration with a 365 nm UV sensor (UVA 365

of Lutron Electronic Enterprise), the radiation flux at the reactor axis was controlled and fixed to a value equal to 35 W m^{-2} , a value in the range of solar UV irradiation. All the surfaces of the reactor was uniformly irradiated thanks to a CPC collector [22,23] positioned at the back side (Fig. 1a and b).

Outdoor experiments were carried out with 14 L of wastewater spiked with 17β -estradiol in a solar set up. The photoreactor consisted in a module of 3 flat solar “panels” 30 cm by 100 cm and 2 cm of thickness (Fig. 1c). Water samples passed through the reactor from the bottom to the top and the whole reactor was filled with water. In these conditions, the illuminated volume was 6 L. Solutions were continuously re-circulated employing a pump (volumetric pump New-Jet 3000) through the photoreactor and the stirred reservoir tank. Temperature was not controlled. Solar panel was oriented southwards and inclined at an angle of about

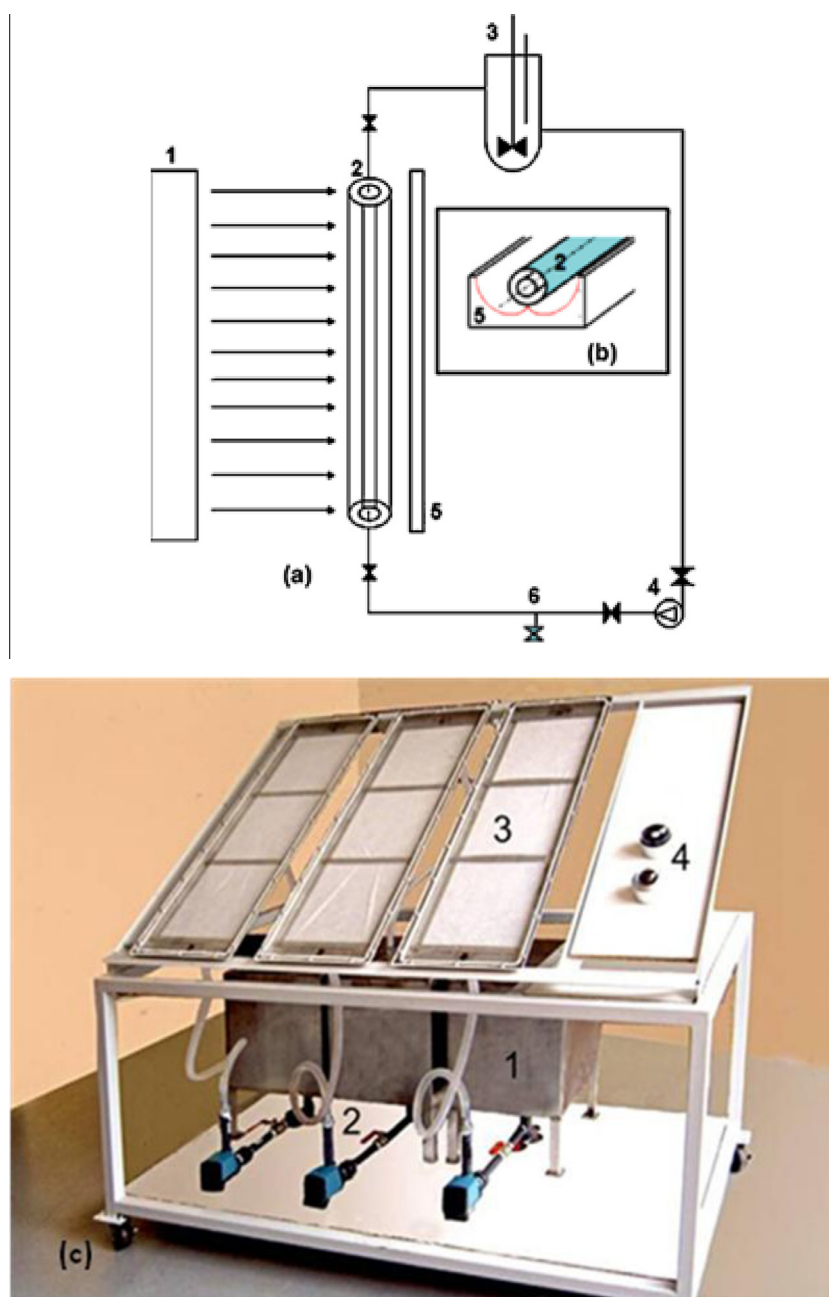


Fig. 1. (a) Experimental set up for the measurements of degradation kinetic: (1) UV lamp 96 mm in height; (2) annular reactor; (3) container of samples stirred during the experiment; (4) volumetric pump; (5) compound parabolic collector (CPC); (6) bleed sample; (b) schematic view of the reactor and the collector; (c) photo solar reactor: (1) tank of samples stirred during the experiment, (2) volumetric pump, (3) flat solar panel, (4) irradiation sensors.

42° (in order to maximize the average solar irradiation throughout the year). Reactors were covered by a special Polymethyl Methacrylate (PMMA) which transmitted 85% of the incident UV radiation [24]. Global solar radiation was measured with a pyranometer (Kipp and Zonen CMP3) effective for wavelengths between 310 and 2800 nm. UV measurements were obtained with a Kipp and Zonen UV-A 3C probe set for wavelengths between 300 and 400 nm.

2.3. Analytical procedure

The E2 concentration evolution for kinetic studies was followed by UHPLC (Dionex Ultimate 3000) equipped with a diode array detector (DAD) and a fluorescence detector (FLD). A guard column was fitted to an Accucore C-18 (Phenomenex, particle size 2.6 μm) 100 × 2.1 mm i.d. column. Analytes were separated with a mixture of acetonitrile: water with 0.01% formic acid (50:50, v/v) at a flow rate of 3 mL min⁻¹ under isocratic elution mode with an injection volume of 2.5 μL and a column temperature of 35 °C. E2 was detected by the fluorescence detector in which the excitation wavelength was λ = 280 nm and the emission wavelength was λ = 305 nm. UV detector wavelength for E2 was set at λ = 200 nm. The UHPLC system was calibrated across a range of 0.05–1.6 mg L⁻¹ E2. The limit of quantification (LOQ) for E2 with the method presented here is 50 μg L⁻¹.

E2 transformation pathways upon sulphate radical have been investigated through the identification of intermediates by high resolution mass spectrometry. Aqueous samples were analyzed on a Waters Acquity UPLC system connected to a Synapt G2S quadrupole time of flight mass spectrometer equipped with an electrospray interface (Waters, Milford, USA) running in the negative mode of ionization. An aliquot of 10 μL sample was injected and TPs were separated using an Acquity UPLC BEH C-18 column (2.1 × 50 mm, 1.7 μm particle size) at a flow rate of 0.8 mL min⁻¹ with a column temperature set at 25 °C. Eluents consisted of water (A) and acetonitrile (B). UPLC method consisted of a linear gradient increasing B from 0% to 50% in 5 min, reaching 100% B at 6 min, maintained at 100% for 1 min and back to initial conditions within 2 min. Ionization source conditions for capillary voltage, source temperature, sampling cone, source offset and desolvation temperature were set at 2.5 kV, 100 °C, 30 V, 80 V and 500 °C, respectively. To ensure mass accuracy, a reference solution (leucine enkephalin) was infused as lock spray and a two points calibration was applied to each spectrum. Centroid data were processed using MassLynx 4.1 software and the intensity of each ion was normalized with respect to the total ion count.

2.4. Estrogenic activity assay

The stably transfected cell line was previously obtained [25]. Briefly, generation of HELN ERα reported cell line was performed in two steps. HeLa cells were first transfected with GAL4RE-ERE-βGlob-Luc-SVNeo plasmids, generating HELN cell line. In a second step, these HELN cells were transfected with estrogen receptor alpha (ERα) plasmid to obtain the HELN ERα cell line. Selection by neomycin (or G418) and puromycin was performed at 1 mg mL⁻¹ and 0.5 μg mL⁻¹, respectively. HELN ERα cell line was cultured in phenol red-free GIBCO® Dulbecco's Modified Eagle Medium: Nutrient Mixture F-12 (DMEM/F-12) supplemented with 5% dextran-coated charcoal fetal calf serum (DCC-FCS) for the strain culture. For experiments, HELN-ERα cells lines were seeded at a density of 4 × 10⁴ cells/well in 96-well white opaque tissue culture plates (Greiner CellStar, D. Dutscher, France) and maintained in 5% DCC-FCS. After 24 h, the cells were exposed to a serial dilution of sample to obtain a dose curve response and incubated for 16 h. At the end of the incubation, luciferase activity was assessed by addition of d-luciferin (0.3 M) and measured on a microtiter plate

luminometer (Top Count, Perkin Elmer). Results are expressed as percentage of luciferase activity obtained in presence of 10 nM E2 (100% of activity). For each sample, estrogenic potency corresponding to the concentration yielding half-maximum luciferase activity (EC₅₀ value) was determined.

3. Results and discussion

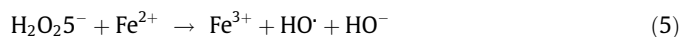
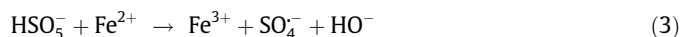
3.1. Kinetic studies under artificial UV

Prior to undertaking the E2 photodegradation studies, and because of its hydrophobicity [26] at pH 6.5, a control experiment was carried out in the dark with an initial concentration of E2 at 1.51 ± 0.04 mg L⁻¹. There was no evidence for E2 degradation and sorption (data not shown) due to the fact the E2 is an acidic compound with a pKa near 10.7 [27] and the point of zero charge of TiO₂ is near 6.8 [28] (Eq. (1)).



Photolysis of spiked wastewater samples using led to a negligible degradation of E2 corresponding to around 1% of the initial concentration as reported in Fig. 2.

In order to compare the efficiency of SR-AOTs i.e., UV-Vis/PMS/Fe(II) with HR-AOTs, a kinetic study of E2 degradation using different systems, such as: UV; UV-Vis/H₂O₂/Fe(II); UV/TiO₂ and UV/Photosphere-40 and represented by the following reactions in Eqs. ((2)–(8)) were carried out.



The reaction represented through Eq. (6) is significative in photo-Fenton and photo-Fenton like experiment due to additional radical oxidizing species produced. Hence, to take advantage of the regeneration of Fe(III) in Fe(II) thanks to UV-Vis radiation, the

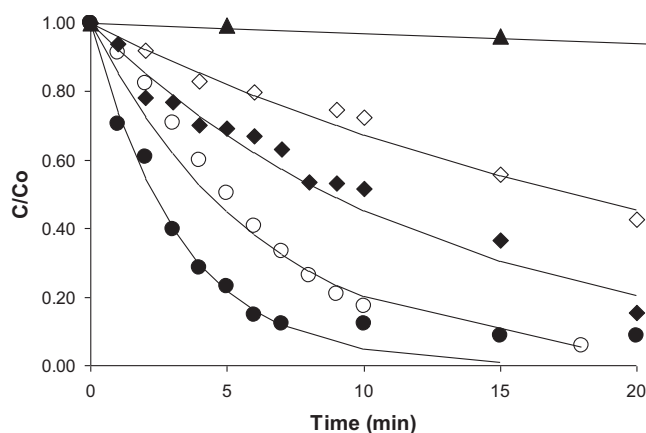


Fig. 2. 17β-Estradiol time concentration profiles in wastewater effluent under artificial UV light (λ = 365 nm): (▲) direct photolysis; (●) PMS/Fe(II); (○) H₂O₂/Fe(II); (◆) TiO₂; (◇) Photosphere 40; (–) solid lines are the calculated concentration profiles with *k*_{app} from Table 1.

Table 1

Apparent first order kinetic rate constants (k_{app}) and half-life time ($t_{1/2}$) for E2 degradation under different oxidation processes in wastewater.

Experiment	k_{app} (min^{-1})	$t_{1/2}$ (min)
UV	0.003	231
*PMS/Fe(II)	0.305	2.27
*H ₂ O ₂ /Fe(II)	0.161	4.31
&TiO ₂	0.079	8.77
&Photospheres	0.039	17.77

Values were obtained by averaging the results of three replicate experiments.

* pH = 3.

& pH = 7.

lamp was turned on as soon as the reagent was added. All processes showed satisfactory performance to degrade E2 in wastewater effluents as reported in Fig. 2. All normalized concentrations of E2 were fitted according to a simple first order kinetic model. The apparent kinetic rate constant (k_{app} (min^{-1})) and the corresponding half-reaction time (Table 1) were determined to find the best fit between the experimental and the calculated concentration of E2 profiles (Fig. 2).

According to these two parameters, degradation by direct photolysis was negligible in comparison to that obtained by advanced oxidation technologies generating HR or SR. As expected [29], oxidation performed with homogeneous system led to faster E2 degradation if compared to heterogeneous photocatalysis. UV-Vis/PMS/Fe(II) led to a degradation kinetic with a ratio almost equal to 4 if compared to E2 degradation performed with UV/TiO₂.

Beyond direct comparison between the different families of AOTs and more basically, the UV radiation activates the oxidants through homolytic cleavage of the peroxide bond which results in the formation of hydroxyl and/or sulphate radicals depending on the chemical nature of the oxidants (Eqs. (2) and (5)), as well as background conditions. The activation of H₂O₂ or PMS with ferrous ions results in the generation of OH \cdot , SO₄ \cdot^- or both OH \cdot and SO₄ \cdot^- , respectively. Since one type of reactive radicals predominates in the above systems, e.g., OH \cdot in UV-Vis/H₂O₂/Fe(II), UV/TiO₂, UV/Photosphere-40 and SO₄ \cdot^- in UV-Vis/PMS/Fe(II), the experimental results achieved tend to indicate that the SO₄ \cdot^- radical is more reactive towards 17 β -estradiol oxidation. The apparent kinetic constant for the UV-Vis/PMS/Fe(II) is almost twice higher than the best k_{app}

obtained for the HR-AOT with UV-Vis/H₂O₂/Fe(II). Taking into account kinetic parameters between the different AOTs studied for the degradation of E2 it can be concluded that UV-Vis/PMS/Fe(II) appears to be the most suitable method for the treatment of aqueous solutions containing E2.

3.2. Evaluation of estrogenic activity

Estrogenic activity was measured with cell line expressing estrogen receptor alpha (ER α). Indeed, *in vitro* assay using reporter gene activation in stably transfected cell lines provide robust, sensitive and specific bioassays to screen endocrine activity, like estrogenic activity, in various samples. Estrogenic activity determination was carried out: (i) E2 without oxidative treatment after 20 h (blank sample); (ii) at the end of a phase (treatment time equal to 15 min) of oxidation in the dark before regeneration of Fe(II) under irradiation; (iii) after 5 and 10 min of irradiation that entailed the total E2 amount removal.

For these different solutions, the activity-concentration relationship (dose-response curve) for E2 and its intermediates was examined (Fig. 3). The 10 nM E2 representative of 100% of luciferase activity is obtained by a dilution applied to the initial sample of WWTP spiked with E2. The same dilution method was systematically applied to the others samples. After 15 min of dark phase oxidation, the estrogenic potency, corresponding to the concentration yielding half-maximum luciferase activity (EC₅₀ value of $1.5 \cdot 10^{-10}$ M), is close to the EC₅₀ value of the sample initial solution (EC₅₀ value of $6 \cdot 10^{-10}$ M). This preliminary phase of oxidation was not efficient to reduce estrogenic activity even though 35% of initial E2 concentration has been already degraded. One or more by-products of the photocatalytic degradation of E2 retained a similar level of estrogenic activity as the parent compound. Phenol is known to be critical for receptor binding and for the appointment of estrogenic activity to all steroid estrogens [30]. As a consequence, this trend tends to demonstrate that the phenol moiety of E2 was preserved, probably because at this step, the lack of Fe(II) in solution might prevent the transformation of hydroquinone-like compounds into quinones (see Section 3.3). In contrast, after few minutes of irradiation, the percentage of luciferase activity was very weak, near the basal of the cell line and the effluent could be considered without estrogenic activity. A better assessment of

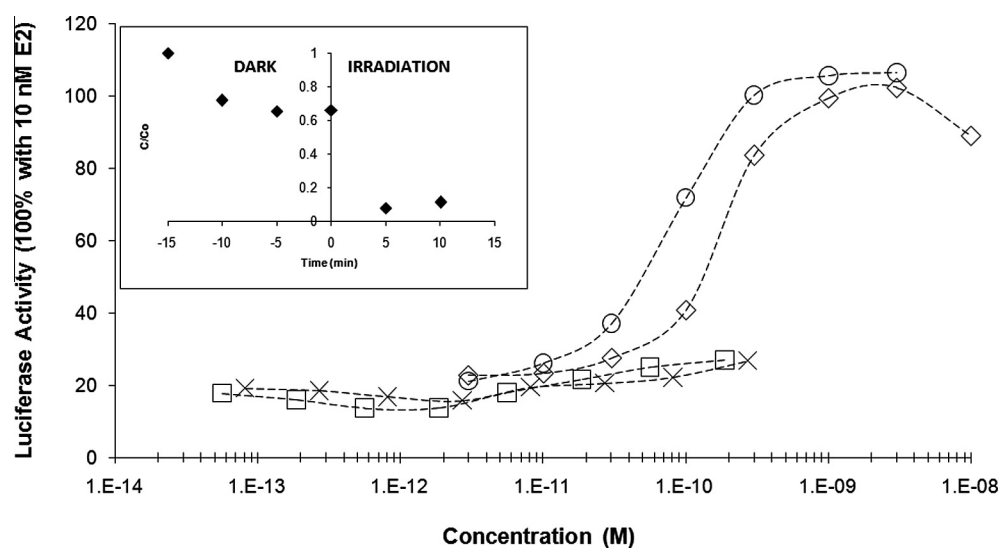


Fig. 3. Estrogenic activity observed with bioluminescent cell line of aqueous solutions containing various amounts of E2 and its TPs: (○) E2 without oxidative treatment after 20 h; (□) PMS/Fe(II) in dark after 15 min and under UV-Vis/PMS/Fe(II); (◇) after 5 min; (×) after 10 min. Insert: E2 concentration evolution during UV-Vis/PMS/Fe(II) treatment.

the toxicity evolution during the treatment needs a better understanding of the mechanisms associated with the different step of degradation. This can be achieved through the knowledge of the by-products.

3.3. E2 transformation pathways in UV-Vis/PMS/Fe(II) system

Even though E2 transformation pathways upon hydroxyl radical reactivity have been already investigated in depth using either TiO₂ photocatalysis [16] or photo-Fenton systems [17], to the best of our knowledge, this is the first time they were determined in case of oxidation by sulphate radical. A view of E2 degradation pathways under UV-Vis/PMS/Fe(II) is provided in Fig. 4a. By-products structure elucidation was carried out at the end of the phase of

oxidation in the dark. Fourteen transformation products (TPs) were detected by LC–HR–MS (see Fig. 4b). However, only six major TPs were definitively identified in part due to the formation of several isomers which precluded from a definite structure assignment of several TPs. Retention times (RT), *m/z* ratios, proposed elemental compositions of identified (P1–P6) and unknown (U1–U8) TPs are reported in Table 2. TPs structures were elucidated on the basis of their accurate mass measurement which allowed for empirical formula to be calculated with an elemental composition calculator tool. The low errors obtained (<2.5 ppm) evidenced for the high grade of confidence in the assignment of the elemental composition. In spite of this partial TPs structural elucidation, different reaction mechanisms upon sulphate radical and hydroxyl radical, which are both simultaneously generated during PMS activation,

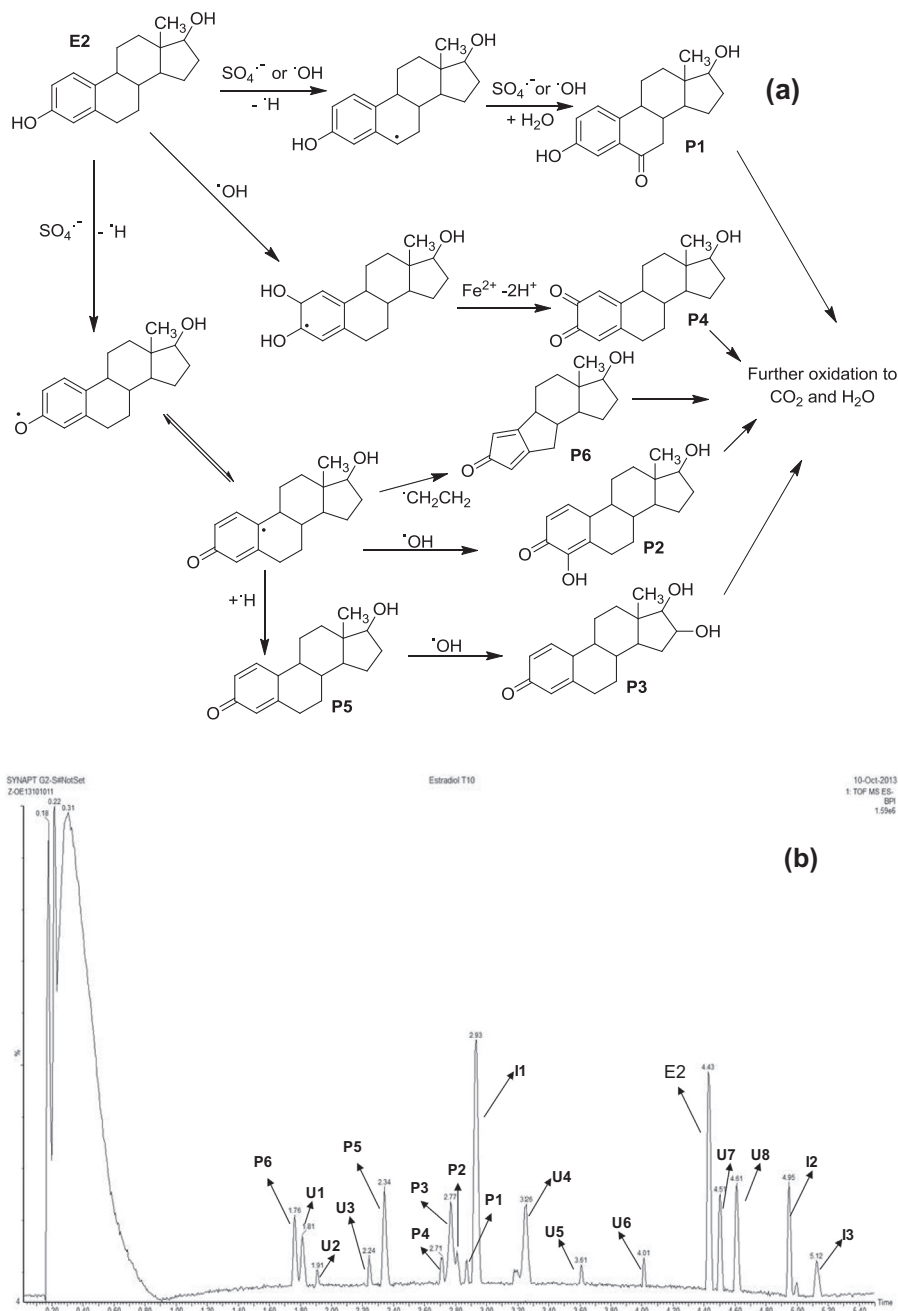


Fig. 4. (a) Proposed E2 transformation pathways upon sulphate and hydroxyl radical generated in UV-Vis/PMS/Fe(II) oxidative system. (b) Total Ion Chromatogram (TIC) obtained after 10 min of treatment.

Table 2

Accurate mass and proposed elemental composition for transformation products identified during E2 oxidation under UV/PMS/Fe(II).

Name	RT (min)	Experimental mass	Calculated mass	Elemental composition	Error (ppm)	DBE
E2	4.43	271.1703	271.1698	C ₁₈ H ₂₃ O ₂	1.82	7.5
P1	2.85	285.1496	285.1490	C ₁₈ H ₂₁ O ₃	1.86	8.5
P2	2.8	285.1487	285.1490	C ₁₈ H ₂₁ O ₃	1.30	8.5
P3	2.77	285.1496	285.1490	C ₁₈ H ₂₁ O ₃	1.86	8.5
P4	2.71	285.1496	285.1490	C ₁₈ H ₂₁ O ₃	1.86	8.5
P5	2.34	271.1689	271.1698	C ₁₈ H ₂₃ O ₂	3.30	7.5
P6	1.76	257.1547	257.1541	C ₁₇ H ₂₁ O ₂	1.09	7.5
U1	1.81	257.1548	257.1541	C ₁₇ H ₂₁ O ₂	1.19	7.5
U2	1.91	257.1547	257.1541	C ₁₇ H ₂₁ O ₂	1.09	7.5
U3	2.24	271.1689	271.1698	C ₁₈ H ₂₃ O ₂	3.30	7.5
U4	3.25	299.0992	299.0973	C ₁₀ H ₁₉ O ₁₀	1.93	1.5
U5	3.51	299.0992	299.0973	C ₁₀ H ₁₉ O ₁₀	1.93	1.5
U6	4.01	327.1412	327.1438	C ₁₆ H ₂₃ O ₇	-2.63	5.5
U7	4.51	236.1105	236.1043	C ₁₃ H ₁₆ O ₄	6.19	6
U8	4.61	305.0912	305.0867	C ₁₂ H ₁₇ O ₉	4.49	4.5

have been emphasized. Briefly, sulphate and hydroxyl radical attacks might proceed through hydrogen abstraction at the aliphatic ring (allylic position) in the E2 structure. In this case, the formation of ketone like product (**P1**) was observed. The specific attack of hydroxyl radical on the phenolic ring through an addition mechanism might lead to the formation hydroquinone like products which was further oxidized into quinone like products (**P4**) probably due to the presence of Fe(II) in the reactive medium or underwent a ring contraction process with CO losses to give **P6**.

All these intermediates were further oxidized by ring opening reactions leading to the formation of short linear carboxylic acid and mineralization. A last pathway which might be specific to sulphate radical, first involved a hydrogen abstraction mechanism from phenol, generating a phenoxyl radical. This latter radical evolved into **P5** through a reduction reaction, into **P3** and **P2** by oxidation followed by hydroxylation steps. This route was also in part identified under TiO₂ photocatalysis through the direct E2 oxidation by the hole (h⁺) resulting from photon absorption. Consequently, E2 transformation in UV-Vis/PMS/Fe(II) system proceeded through at least three different and complementary routes in part accounting for the higher performances of this oxidative system over TiO₂ photocatalysis and photo-Fenton for the E2 elimination from domestic WWTP effluents for which the number of described degradation routes is usually limited to two. E2 estrogenic activity is thought to be related to the phenolic moiety. This latter is quickly oxidized into quinone-like structures during UV-Vis/PMS/Fe(II) probably accounting for the quick decrease in estrogenicity of treated wastewater effluent samples [30].

3.4. Outdoor experiments under solar radiations

Different experiments were carried out with the same solar irradiation using simultaneously three flat solar panels that made up the photoreactor (Section 2.2). After the series of indoor tests, we choose to select for each oxidative process family, homogeneous and heterogeneous, the most efficient in terms of kinetic of degradation, respectively (UV-Vis/PMS/Fe(II) and UV/TiO₂). Taking into consideration the larger volume of the storage tank with

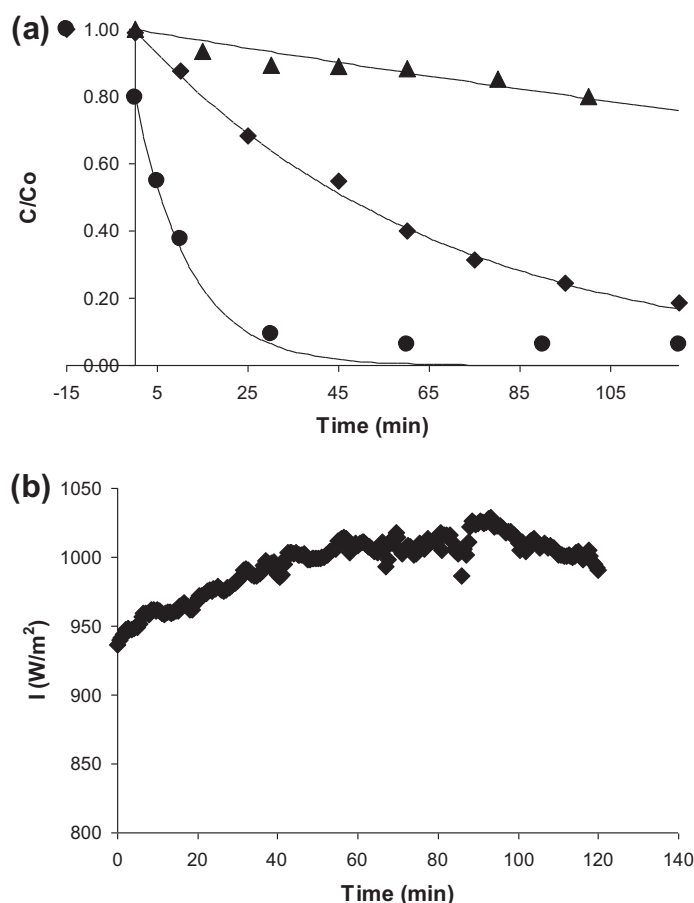


Fig. 5. (a) 17β-Estradiol degradation with the solar set-up under different oxidation processes: (▲) direct photolysis, (●) PMS/Fe(II), (◆) TiO₂; (—) solid lines are the calculated concentration profiles with the apparent kinetic rate constant; (b) irradiation conditions corresponding to the middle of the sunny day.

respect to indoor experiments, a preliminary step consisting of reagents mixing for 15 min (Fig. 5a) was carried out before flowing the effluent in the reactor. Once again in the case of heterogeneous photocatalysis, adsorption of E2 to the surface of TiO₂ was negligible.

Under solar radiation, E2 photolysis was a little bit enhanced as compared to the indoor experiment with UV lamp. This has to be related to the different spectral composition with lower wavelengths available in the case of solar radiations. Nevertheless, photolysis remained negligible when compared to AOTs experiments.

Degradation kinetics were obviously dependent on the irradiation level. The outdoor experiments were performed during favorable conditions corresponding to the middle of a sunny day (Fig. 5b). Taking advantage of an almost constant level (less than 10% of variation) of solar radiation in the range of 1000 W m⁻² for the global radiation, k_{app} were determined according to the first order kinetic model. k_{app} values of 0.0023, 0.015 and 0.084 min⁻¹ were determined for direct photolysis, UV/TiO₂ and UV-Vis/PMS/Fe(II) experiments, respectively. Comparison between experimental and calculated E2 concentrations profiles are provided in Fig. 5a. As claimed before, the objective was not here to determine absolute kinetic constants but only to provide a qualitative basis for comparison between different oxidative processes carried out in a similar set up under similar conditions of irradiations. In outdoor conditions, UV-Vis/PMS/Fe(II) system remained the most efficient process. Moreover, due to Fe(III) recycling into Fe(II) under visible radiation the ratio between apparent kinetic constants of SR-AOTs and HR-AOTs increased in outdoor experiments with respect to indoor experiments. Beside the kinetic improvement, it was also observed that the level of estrogenic activity was no longer detectable after half an hour of treatment.

The obtained results demonstrated the ability of the UV-Vis/PMS/Fe(II) system for the detoxification of domestic effluent polluted with one of the most relevant estrogenic substances. In less than half an hour under solar irradiation, 14 L of a wastewater highly concentrated in E2 was treated with less than a half meter of irradiated surface. Taking into account the exact characteristics of the solar set up for the volume, the irradiated surface and level of solar radiations, the treatment capacity of a wastewater charged with 17 β -estradiol at 1.51 \pm 0.04 mg L⁻¹ can be quantified by a value of 43.2 kJ/L (with an accumulated solar energy calculated with the global irradiations).

4. Conclusion

Result concerning the kinetics degradation, identification by-products and transformation pathways, and the evaluation of residual toxicity delivers a framework which proves the ability of the UV-Vis/PMS/Fe(II) system for the detoxification of a domestic effluent spiked with one of the most relevant estrogenic substances:

- UV-Vis/PMS/Fe(II) demonstrates better kinetic performances when compared to others AOTs such as UV-Vis/H₂O₂/Fe(II) and heterogeneous UV/TiO₂ system. As already mentioned in the literature this is probably the consequence of a higher selectivity in the reactivity of SO₄⁻ with respect to OH⁻ in the case of with a high concentration of organic matter.
- The estrogen screen detects both the parent compounds and any intermediate transformation products that bind to, and activate, the estrogen receptor, regardless of their identity. After few minutes of irradiation, UV-Vis/PMS/Fe(II) process eradicate the major endocrine disruptor effect. The effluent can be considered as environmentally friendly according to the estrogenic activity criterion.

- Three E2 transformation pathways in UV-Vis/PMS/Fe(II) were suggested by identifying E2 transformation products. Hydroxyl radical mainly reacts through an addition mechanism while sulphate radical reacts through an hydrogen abstraction mechanism followed by hydroxylation processes. Nevertheless, both mechanisms lead to the transformation of the phenol function which is thought to be responsible to the binding capacity of E2 to the estrogen receptor.
- In less than half an hour under solar irradiation, 14 L of a wastewater highly concentrated in E2 was treated with less than a half meter of irradiated surface.

Basically, using solar irradiation to activate efficiently PMS into radical species in the UV-Vis/PMS/Fe(II) advanced oxidation system probably opens new economical feasible remediation strategies for WWTPs effluent tertiary treatment. Wastewater reuse in irrigation for instance is one of the relevant applications to be investigated. Future objective will be to apply this kind of investigation to a mix of different pollutants.

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