

1 **Removal of emerging contaminants from municipal WWTP secondary effluents**  
2 **by solar photocatalytic ozonation. A pilot-scale study.**

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9 **ABSTRACT**

10 Ozonation, solar photocatalytic oxidation and a combination of both systems (i.e., solar  
11 photocatalytic ozonation) have been studied to treat a secondary effluent from a municipal  
12 wastewater treatment plant containing a selection of six emerging contaminants  
13 (acetaminophen, antipyrine, bisphenol A, caffeine, metoprolol and testosterone). Fe(III),  
14 Fenton reagent and TiO<sub>2</sub> were used in photocatalytic experiments, which were conducted in  
15 a pilot-scale compound parabolic collector photo-reactor using solar radiation as energy  
16 source. Emerging contaminants (0.2 mg·L<sup>-1</sup> each), at pH 3, were completely removed by  
17 photo-Fenton and single ozonation in 90 and 25 min, respectively. Moreover, solar  
18 photocatalytic ozonation treatments (Fe(III)/O<sub>3</sub>/light and Fe(III)/H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub>/light systems) were  
19 able to completely remove the ECs in about 20 min with UV doses of 2-6 kJ·L<sup>-1</sup>. However,  
20 the organic matter mineralization level achieved was limited (< 35% TOC removal) even after  
21 the application of solar photocatalytic ozonation, for which an enhanced generation of  
22 hydroxyl radicals was measured in experiments carried out in the presence of the hydroxyl  
23 radical probe p-chlorobenzoic acid. *Daphnia magna* bioassays were used to test toxicity of  
24 samples before and after their treatment, showing that samples subjected to solar  
25 photocatalytic ozonation were less toxic (% inhibition < 15%) than the mixture of emerging  
26 contaminants in the secondary effluent (% inhibition about 25%). Finally, a simplified  
27 estimation of operating costs shows some solar photocatalytic ozonation processes  
28 advantageous over the solar photo-Fenton system.

29  
30 **Keywords:** Domestic wastewater, emerging contaminant, solar photocatalytic ozonation, toxicity.

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## 1 **1. Introduction**

2 The development of advanced analytical techniques has allowed the detection of emerging  
3 contaminants (ECs) in aquatic environments revealing a worldwide issue [1]. Many of these  
4 compounds, which are incorporated into the sewage system through domestic and industrial  
5 drains, have been found to be recalcitrant to the biological and physicochemical processes  
6 typically applied in wastewater treatment plants (WWTP). As a result, they remain in treated  
7 wastewaters being discharged into natural waters bodies (rivers, lakes, seas and streams)  
8 [1,2].

9 The EC group includes a wide variety of compounds such as pharmaceuticals, personal care  
10 products, hormones, industrial additives and household chemicals. Usually, their metabolites  
11 and degradation products are also included in this category of pollutants [2]. Most of the ECs  
12 are bio-accumulative, have endocrine disrupting effects and can cause health and mutagenic  
13 effects on living beings that benefit from aquatic systems [3,4].

14 This situation is leading to stringent regulations on wastewater management [3,5], though  
15 most of the ECs are not yet regulated [6]. Advanced oxidation processes (AOPs) can be  
16 considered as potential effective alternatives for the treatment of ECs in water. This is so  
17 because AOPs, characterized by the generation of short-life reactive species such as the  
18 hydroxyl radical ( $\cdot\text{OH}$ ), can completely degrade a wide range of water contaminants,  
19 transforming them into less harmful species. Since the application of AOPs to treat  
20 wastewaters leads to better quality effluents, wastewater recycling can be considered a  
21 management option [7].

22 Currently, ozonation processes are applied in wastewater treatment as disinfectant, oxidant  
23 of organic pollutants and pre or post-treatment of other unit operations (as coagulation,  
24 flocculation, biological oxidation, etc) [8]. However, the use of ozone usually implies high  
25 operating costs due to its production. Moreover, although ozone itself can remove most of

1 the organic compounds present in domestic wastewaters, due to its selective nature, it is not  
2 usually able to mineralize them, remaining ozonation by-products in the effluents. If  
3 combined with other agents, such as UV light and/or catalysts, significant improvements in  
4 the level of organic matter mineralization and the efficiency on the use of ozone can be  
5 achieved. Such enhancements were observed in a previous work where a first approach to  
6 the application, at pilot-scale, of solar photocatalytic ozonation assisted by Fe(III),  
7 Fe(III)/H<sub>2</sub>O<sub>2</sub> and TiO<sub>2</sub> to remove selected ECs from water was carried out [9]. As part of our  
8 continuing work on solar photocatalytic ozonation, here the treatment method has been  
9 applied to degrade ECs in a secondary effluent from a municipal WWTP. The use of solar  
10 radiation instead of UV lamps may drastically reduce the operating cost associated with the  
11 treatment system [10].

## 12 **2. Materials and methods**

### 13 *2.1. Secondary effluent samples*

14 First, secondary effluent samples from a municipal WWTP (Badajoz, Spain) were collected  
15 and their pH was lowered to 3 by adding concentrated hydrochloric acid solution while  
16 bubbling air to remove their carbonate and bicarbonate content, which have been found to be  
17 detrimental for the efficiency of AOPs since these species can scavenge hydroxyl radicals  
18 [11]. The main characteristics of the secondary effluent samples after this pretreatment are  
19 summarized in Table 1.

20 Acetaminophen (ACE), antipyrine (ANT), bisphenol A (BIS), caffeine (CAF), metoprolol  
21 (MET) and testosterone (TST), purchased from Sigma–Aldrich and used as received, were  
22 the ECs selected as target compounds for this work. Secondary effluent samples were  
23 spiked to 200 µg·L<sup>-1</sup> of each compound. Additionally, p-chlorobenzoic acid (pCBA, Merck)  
24 was used as hydroxyl radical probe compound in some experiments. The chemical  
25 structures of all these compounds are shown in Fig.1.

## 1 2.2. Experimental set up and procedure

2 Experiments were conducted at ambient temperature in a pilot-scale solar plant located in  
3 Badajoz, Spain (38°52'43" N, 6°58'15" W). The solar plant consists mainly of an air  
4 compressor (Pintuc Extreme 3), an ozone generator (OZVa 1200E, ProMinent) and a  
5 compound parabolic collector (CPC, Ecosystem-Environmental Services S.A.) operated in  
6 semi-batch mode. Additionally, the plant was equipped with measurement devices (e.g.,  
7 ozone analyzers) and controllers as shown in Fig.2. Thus, the CPC inlet gas stream was  
8 regulated by a precision gas flow controller (MC-10SLPM-D, Alicat Scientific) while two  
9 ozone analyzers (GM-6000-RTI and GM-6000-PRO, Anseros) were used to monitor the  
10 ozone concentration in the inlet and outlet gas streams, respectively.

11 The CPC used as photo-reactor consisted of four borosilicate-glass tubes (32 mm external  
12 diameter, 1.4 mm thickness, 750 mm length, ~90% transmittance) connected in series (total  
13 irradiated volume of 1.8 L) reflected by involute-type mirrors (320 G electropolished  
14 aluminum, 0.25 m<sup>2</sup> reflection surface ), which were mounted on a fixed platform tilted 45°.  
15 The reactor also had two ports for inlet and outlet of gas, a reservoir tank of 7 L total  
16 capacity, a recirculation centrifugal pump (15-24 L·min<sup>-1</sup>), and connecting tubing and valves.  
17 The pH of the aqueous solution in the tank was automatically controlled at set-point values  
18 (i.e., 3 or 7) by an in-line pH control system provided with WP1000-P1/8S4-J4-C Welco  
19 pumps to feed hydrochloric acid or sodium hydroxide solutions to the system. The photo-  
20 reactor was also equipped with a Pt-100 probe and a broadband UV radiometer (Acadus 85-  
21 PLS) to record continuously the temperature and the incident UV radiation ( $\lambda < 400$  nm),  
22 respectively. Radiation data were acquired as instantaneous and accumulated UV energy  
23 (Proasis DCS-Win 3.55 software, Design Instruments S.A.). In a typical experiment, the  
24 photo-reactor reservoir tank was first loaded with 5 L of the secondary effluent containing a  
25 mixture of ECs and the required amount of catalyst (Fe(III) or TiO<sub>2</sub>) was added afterwards.  
26 Initial concentrations of catalysts were as follows: 2.8 mg·L<sup>-1</sup> of Fe(III) as iron(III) perchlorate

1 hydrate (Sigma–Aldrich) or 200 mg·L<sup>-1</sup> of TiO<sub>2</sub> Aeroxide ® P25 (Evonik Industries). After  
2 adding the catalyst, the solution was recirculated through the CPC by a centrifugal pump at a  
3 flow rate of 8.7 L·min<sup>-1</sup> so that the flux pattern inside the tubes was turbulent (Re > 7500).  
4 The CPC tubes were kept covered to avoid sunlight illumination for the first 30 min of each  
5 experiment (dark stage). This time was used for homogenization purposes and it was  
6 enough to reach the adsorption equilibria of ECs onto TiO<sub>2</sub> (if used). After that, the CPC was  
7 uncovered and a continuous gas flow (0.67 L·min<sup>-1</sup> flow rate) was supplied to the reactor.  
8 Also, if needed, hydrogen peroxide (Panreac) was added at this point to the CPC system.  
9 The gas stream entering the CPC tube was either air or an ozone-air mixture (c.a. 13 mg·L<sup>-1</sup>  
10 ozone). Experiments lasted 5 hours plus the 30 min of the dark stage. During the whole  
11 course of the experiment liquid samples were withdrawn from the reactor at intervals through  
12 a sampling port to determine the EC concentration, total organic carbon (TOC), and the  
13 concentrations of hydrogen peroxide, ozone and iron. Also, the concentration of phenolic  
14 compounds was analyzed in some liquid samples. In addition, biodegradability (i.e. the ratio  
15 between the 5-day biochemical oxygen demand and the chemical oxygen demand,  
16 BOD<sub>5</sub>/COD ratio) and ecotoxicity (*Daphnia magna* assay) was measured in selected  
17 samples.

### 18 2.3. Analytical methods

19 Samples taken during the course of experiments using ozone were immediately bubbled with  
20 helium to remove residual ozone. Likewise, excess hydrogen peroxide in samples was  
21 quenched by adding an aliquot of concentrated sodium thiosulfate solution. These  
22 procedures, which did not alter the organic content of the samples, avoided further ozone  
23 and/or hydrogen peroxide reactions while samples were kept before ECs and other organic  
24 content analyses. Prior to analysis, the samples were filtered through a 0.45 µm PET filtering  
25 membrane (Chromafil Xtra). Samples used in ecotoxicity tests were withdrawn from the  
26 photo-reactor, bubbled with helium if ozone was used, mixed with catalase solution (0.1 g·L<sup>-1</sup>

1 bovine liver, 3390 units·mg<sup>-1</sup> solid, Sigma–Aldrich) to eliminate the residual H<sub>2</sub>O<sub>2</sub>, neutralized  
2 and filtered through a 0.45 µm cellulose nitrate filtering membrane (Sartorius Stedim) before  
3 analysis. Samples used to analyze the dissolved ozone concentration were withdrawn from  
4 the reactor and, without any further pretreatment, analyzed immediately by the indigo method  
5 [12].

6 An Agilent 1100 Series HPLC (Hewlett Packard) equipped with a Kromasil C18 column (5  
7 µm particle size, 150 mm length, 4 mm diameter, Teknokroma) as stationary phase was  
8 used to measure compounds concentration. A binary mixture of acetonitrile and 0.1% v/v  
9 phosphoric acid aqueous solution was used as mobile phase. ANT, CAF and MET were  
10 analyzed at 240, 275 and 225 nm detection wavelength, respectively, using a 15%  
11 acetonitrile mobile phase eluted at 0.65 mL·min<sup>-1</sup>. BIS, TST and pCBA were analyzed at  
12 220, 250 and 250 nm, respectively, with a 50% acetonitrile mobile phase at 1 mL min<sup>-1</sup>. ACE  
13 was analyzed with a 15% acetonitrile mobile phase at 1 mL min<sup>-1</sup> and 244 nm as detection  
14 wavelength. A Shimadzu TOC-V<sub>SCH</sub> analyzer equipped with an infrared detector was used to  
15 measure the total, inorganic and organic carbon content. An ion chromatography apparatus  
16 (881 compact IC pro, Metrohm) equipped with a Metrosep A Supp 7 column (150 mm length,  
17 4 mm diameter) was used to measure phosphate, sulfate, nitrate, chloride and ammonium in  
18 the secondary effluent samples. Hydrogen peroxide was measured by the Eisenberg method  
19 [13]. Total phenolic content in solution was determined by the method proposed by Singleton  
20 and Rossi [14] and expressed as mg BIS·L<sup>-1</sup>. Dissolved Fe(II) was measured as indicated by  
21 Zuo [15]. COD was measured by the dichromate method using the Lange cuvette test while  
22 BOD<sub>5</sub> was determined measuring the oxygen consumed during a 5-day incubation period  
23 [16] using ST-OxiTop ® devices. Acute toxicity tests were conducted with Daphtoxkit F™  
24 magna toxicity test kits (MicroBioTests) using water flea *Daphnia magna* according to OECD  
25 Guidelines [17]). pH, conductivity and turbidity of samples were measured using a GLP 21+

1 pHmeter (Crison), a 524 conductivity meter (Crison) and a HI 93414 turbidity meter (Hanna  
2 Instruments), respectively.

### 3 **3. Results and discussion**

#### 4 *3.1 ECs depletion and TOC removal*

5 Samples of the MWWTP secondary effluent containing a mixture of the six above-mentioned  
6 ECs were subjected to the following treatments at pH 3: single photolysis (exposure to  
7 sunlight without reagents and/or catalyst), single ozonation in the dark ( $O_3$ ), photolytic  
8 ozonation ( $O_3$ /light), Fe(III)-based photocatalytic oxidation (Fe(III)/ $O_2$ /light), Fe(III)-based  
9 photocatalytic ozonation (Fe(III)/ $O_3$ /light), photo-Fenton (Fe(III)/ $H_2O_2$ / $O_2$ /light) and photo-  
10 Fenton-based photocatalytic ozonation (Fe(III)/ $H_2O_2$ / $O_3$ /light). For comparison purposes, also  
11  $TiO_2$ -based photocatalytic oxidation ( $TiO_2$ / $O_2$ /light),  $TiO_2$  photocatalytic ozonation  
12 ( $TiO_2$ / $O_3$ /light) and ozonation ( $O_3$ ) processes were applied at pH 7.

13 Single photolysis was not able to degrade the ECs. Thus, only TST was removed to some  
14 extent by single photolysis (34% removal after 5h irradiation, which meant  $33 \text{ kJ}\cdot\text{L}^{-1}$  UV  
15 radiation supplied). Fe(III) photocatalytic oxidation experiments only led to EC removal  
16 percentages between 26% (ANT) and 43% (TST) after 5 h treatment ( $39 \text{ kJ}\cdot\text{L}^{-1}$  UV radiation  
17 dose). However, complete removal of ECs was achieved in photo-Fenton experiments in less  
18 than 90 min reaction time ( $8 \text{ kJ}\cdot\text{L}^{-1}$  UV radiation dose) and in single ozonation experiments at  
19 pH 3 and 7 in about 25 min (c.a.  $28 \text{ mg } O_3\cdot\text{L}^{-1}$ ) and 45 min (c.a.  $100 \text{ mg } O_3\cdot\text{L}^{-1}$ ), respectively.  
20 Moreover, systems involving ozone and solar radiation (i.e.  $O_3$ /light, Fe(III)/ $O_3$ /light and  
21 Fe(III)/ $H_2O_2$ / $O_3$ /light) were able to eliminate, at pH 3, the ECs faster (20-30 min) and with  
22 UV doses lower than  $6 \text{ kJ}\cdot\text{L}^{-1}$ . Among them, the Fe(III)/ $H_2O_2$ / $O_3$ /light system was observed to  
23 be the most efficient, leading to complete removal of ECs with UV radiation and ozone doses  
24 of about  $2 \text{ kJ}\cdot\text{L}^{-1}$  and  $19 \text{ mg } L^{-1}$ , respectively.  $TiO_2$  photocatalytic experiments, carried out at  
25 pH 7, also led to the complete disappearance of the ECs but they required higher UV

1 radiation doses than photo-Fenton and photocatalytic ozonation experiments performed at  
 2 pH 3. Thus, TiO<sub>2</sub> photocatalytic oxidation experiments (TiO<sub>2</sub>/O<sub>2</sub>/light) absorbed about 15  
 3 kJ·L<sup>-1</sup> of UV radiation (c.a. 2 h of irradiation) to eliminate the parent ECs while in TiO<sub>2</sub>/O<sub>3</sub>/light  
 4 experiments the consumptions of UV light and ozone were about 12 kJ·L<sup>-1</sup> and 37 mg L<sup>-1</sup>,  
 5 respectively (c.a. 40 min of simultaneous irradiation and ozonation).

6 Fig.3 shows a comparison of the efficiency of some of the solar treatment systems applied in  
 7 this work in terms of the use of radiation to remove the selected ECs. The delivered UV  
 8 radiation per volume unit, Q<sub>UV,n</sub>, as represented in Fig.3, has been computed using the Eq.(1)  
 9 [18]:

$$10 \quad Q_{UV,n} = Q_{UV,n-1} + (t_n - t_{n-1}) \overline{UV}_{G,n} \frac{A}{V} \quad (1)$$

11 where t<sub>n</sub> is the elapsed irradiation time until sample n,  $\overline{UV}_{G,n}$  is the average incident UV  
 12 radiation in the period t<sub>n-1</sub> – t<sub>n</sub>, V is the total reaction volume and A is the illuminated reactor  
 13 surface. As it can be seen in Fig.3, the treatment systems involving ozone were the most  
 14 efficient in removing the selected ECs while the Fe(III)/O<sub>2</sub>/light system was the one that  
 15 required the highest UV radiation dose to remove the ECs. Also, it is apparent from Fig.3  
 16 that, in all cases, the ECs depletion profiles followed a pseudo first-order kinetics with  
 17 respect to the UV radiation dose. Accordingly, Eq.(2) was satisfactory fulfilled:

$$18 \quad \ln \left( \frac{\sum C_{EC,0}}{\sum C_{EC}} \right) = k_{UV} Q_{UV} \quad (2)$$

19 The value of the pseudo first-order rate constant, k<sub>UV</sub>, was used to estimate the time required  
 20 to remove 99% of the initial concentration of ECs (t<sub>99</sub>) at a given average incident UV  
 21 irradiation ( $\overline{UV}_G$ ). Thus, Eq.(3) was applied:



1 
$$t_{99} = \frac{\ln(100)}{k_{UV}} \frac{V}{UV_G A} \quad (3)$$

2 where A and V are the reactor irradiation area and the reaction volume, respectively.  
 3 Experimental data from single ozonation experiments, carried out in absence of radiation,  
 4 were satisfactorily fitted to Eq.(4):

5 
$$\ln\left(\frac{\Sigma C_{EC,0}}{\Sigma C_{EC}}\right) = k t \quad (4)$$

6 where k is the apparent pseudo first-order rate constant for total EC depletion and t is the  
 7 irradiation time. In accordance with this,  $t_{99}$  was estimated by the expression (5):

8 
$$t_{99} = \frac{\ln(100)}{k} \quad (5)$$

9 Table 2 shows the values of the pseudo first-order rate constants for the various treatment  
 10 systems derived from experimental data (for conditions see the legend of Fig.3) and  $t_{99}$   
 11 values computed either by Eq.(3) considering an average incident UV irradiation of  $30 \text{ W}\cdot\text{m}^{-2}$ ,  
 12 which is the typical average UV flux in a sunny day [18] or by Eq.(5).

13 As far as TOC removal is concerned, Fig.4 shows, for selected experiments, the evolution of  
 14 TOC conversion as a function of the UV radiation supplied. It should be mentioned here that  
 15 the overall TOC in the wastewater samples subjected to treatment was composed of TOC  
 16 from occurring compounds in the secondary effluent (average TOC =  $20 \text{ mg}\cdot\text{L}^{-1}$ ) and TOC  
 17 from added ECs (TOC =  $0.8 \text{ mg}\cdot\text{L}^{-1}$ ). Accordingly, about 96% of TOC in the samples to be  
 18 treated was due to the organics present in the MWWTP secondary effluent. As it can be  
 19 observed in Fig.4, TOC removal was far from being complete (<35% TOC removal) in any of  
 20 the experiments carried out despite the high average incident radiation, which was ranged  
 21 between  $35$  and  $46 \text{ W}\cdot\text{m}^{-2}$  (i.e., cumulative UV radiation dose in 5-h experiments was higher

1 than 30 kJ·L<sup>-1</sup>). Nevertheless, it should be mentioned that COD removals (up to 70%) were  
2 greater than TOC removals in all cases. Thus, the COD/TOC ratio decreased from the initial  
3 value of about 3 to final values of 1.5-2, suggesting that the oxidation progressed to yield  
4 organic products which were recalcitrant and, therefore, difficult to degrade. Under the  
5 experimental conditions applied in this work, low TOC removal (< 5%) was observed after the  
6 application of ozonation in the dark (O<sub>3</sub>), both at pH 3 and 7, and the Fe(III)/O<sub>2</sub>/light (pH 3)  
7 system (results not shown). Photocatalytic ozonation systems (i.e., Fe(III)/O<sub>3</sub>/light and  
8 Fe(III)/H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub>/light) at pH 3, however, were much more effective leading to 20-35% TOC  
9 conversion (see Fig.4). In TiO<sub>2</sub> photocatalytic experiments (pH 7), it was observed an initial  
10 period where the TOC removal negligible followed by a period of higher TOC conversion up  
11 to reach 8% (TiO<sub>2</sub>/O<sub>2</sub>/light) and 20% (TiO<sub>2</sub>/O<sub>3</sub>/light) removals after the 5-h treatment. The  
12 induction period in TiO<sub>2</sub> catalytic systems could be ascribed to the formation of agglomerates  
13 of catalyst crystallites or to the adsorption of some inorganic ions on the catalyst surface [19].

14 For comparative purposes, TOC experimental data were fitted to a first-order kinetic  
15 equation. Fig.5 shows the apparent first-order rate constant,  $k_{\text{TOC,app}}$ , computed for some of  
16 the systems applied as well as the average incident radiation measured during each  
17 experiment. As it can be deduced from Fig.5, the mineralization (i.e., TOC removal) rate  
18 constants followed the order: Fe(III)/H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub>/light (pH 3) > Fe(III)/O<sub>3</sub>/light (pH 3) >  
19 Fe(III)/H<sub>2</sub>O<sub>2</sub>/O<sub>2</sub>/light (pH 3) > TiO<sub>2</sub>/O<sub>3</sub>/light (pH 7) > TiO<sub>2</sub>/O<sub>2</sub>/light (pH 7). Single ozonation (pH  
20 3 and 7), single photolysis (pH 3) and Fe(III)/O<sub>2</sub>/light (pH 3) experiments led to very low  
21 values of  $k_{\text{TOC,app}}$  (< 5×10<sup>-4</sup> min<sup>-1</sup>) as limited TOC removal (< 5%) was observed after the 5-h  
22 experiments. The Fe(III)/H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub>/light system, which showed the highest mineralization rate  
23 constant, was also the most efficient system in terms of use of energy (7.5 kJ per mg of TOC  
24 removed). Fe(III)/O<sub>3</sub>/light (pH 3) and TiO<sub>2</sub>/O<sub>3</sub>/light (pH 7) experiments showed similar energy  
25 efficiencies, ranging between 14.5 and 16.8 kJ per mg of TOC removed. Accordingly, these  
26 systems led to similar mineralization degrees (19-23% TOC removal). Photocatalytic

1 oxidation systems such as Fe(III)/H<sub>2</sub>O<sub>2</sub>/O<sub>2</sub>/light (pH 3) and TiO<sub>2</sub>/O<sub>2</sub>/light (pH 7) required more  
2 UV energy to remove each mg of TOC (90 and 35 kJ·mg<sup>-1</sup>, respectively) and led to lower  
3 mineralization levels (6-9% TOC removal) than the photocatalytic ozonation systems tested.

### 4 3.2 Hydroxyl radical exposure

5 In the applied AOPs, the depletion of the pollutants might take place mainly by three  
6 pathways: photolysis, direct reaction with molecular ozone and oxidation by hydroxyl  
7 radicals. Taking into account those contributions, the degradation of each compound can be  
8 expressed by Eq.(6):

$$9 \quad \frac{dC_{EC}}{dt} = -(k_{\text{phot.}} + k_{\text{OH}}C_{\text{OH}} + k_{\text{O}_3}C_{\text{O}_3})C_{\text{EC}} \quad (6)$$

10 In Eq(6),  $k_{\text{phot.}}$  is the first order rate constant for compound photolysis,  $k_{\text{OH-EC}}$  and  $k_{\text{O}_3\text{-EC}}$  are  
11 the rate constants for the reaction of each EC with the hydroxyl radical and dissolved ozone,  
12 respectively;  $C_{\text{EC}}$ ,  $C_{\text{OH}}$  and  $C_{\text{O}_3}$  are the concentration of EC, hydroxyl radical and ozone,  
13 respectively. After integration and variable separation, the following expression is obtained:

$$14 \quad \ln\left(\frac{C_{\text{EC},0}}{C_{\text{EC}}}\right) = k_{\text{phot.}} \int_0^t dt + k_{\text{OH}} \int_0^t C_{\text{OH}} dt + k_{\text{O}_3} \int_0^t C_{\text{O}_3} dt \quad (7)$$

15 where  $\int C_{\text{OH}} dt$  and  $\int C_{\text{O}_3} dt$  are the corresponding hydroxyl radicals and ozone exposures.

16 Hydroxyl radical exposure is thought to have a high impact on the mineralization of organic  
17 compounds in the secondary effluent (both added ECs and naturally occurring compounds)  
18 through the AOPs studied because direct photolysis and single ozonation at pH 3, where low  
19 concentration of  $\cdot\text{OH}$  is expected, did not lead to significant TOC removals (< 2%).

20 The hydroxyl radical exposure can be calculated using pCBA as a probe compound [20]  
21 because of its high reactivity with  $\cdot\text{OH}$  ( $k_{\text{OH}} = 5 \times 10^9 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$  [21]) and negligible reactivity

1 with ozone ( $k_{O_3} < 0.15 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$  [22]). In addition, aqueous pCBA does not absorb radiation  
2 beyond 290 nm wavelength and, therefore, pCBA does not undergo direct photolysis under  
3 solar irradiation (i.e.,  $k_{\text{phot}} \sim 0$ ). Accordingly, the  $\cdot\text{OH}$  exposure can be calculated by Eq.(8):

$$4 \quad \int_0^t C_{\text{OH}} dt = \frac{\ln\left(\frac{C_{\text{pCBA},0}}{C_{\text{pCBA}}}\right)}{k_{\text{OH}}} \quad (8)$$

5 Table 3 summarizes the  $\cdot\text{OH}$  exposure during the first minutes of experiments of degradation  
6 of ECs in the secondary effluent in the presence of pCBA. It can be seen that the  $\cdot\text{OH}$   
7 exposure increased with the UV radiation dose for any of the system tested. For a given  
8 radiation dose, the ozone/light systems (pH 3) led to higher  $\cdot\text{OH}$  production than those  
9 systems carried out in the absence of ozone. The Fe(III)/H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub>/light (pH 3) system can be  
10 highlighted as that leading to the highest  $\cdot\text{OH}$  exposure and, as a result, the highest TOC  
11 removal after 5-h treatment (35%).

### 12 3.3 Phenolic intermediates

13 Given the molecular structures of the selected ECs (see Fig.1) as well as those of other  
14 organic compounds typically present in MWWTP secondary effluents, some of the primary  
15 intermediates expected to be formed during their oxidation are phenolic compounds. Fig. 6  
16 shows the evolution of the concentration of phenolic compounds during the course of  
17 selected experiments. As can be seen, during the first minutes of reaction, an increase in the  
18 phenolic compounds concentration was observed in Fe(III)/O<sub>2</sub>/light (pH 3) and TiO<sub>2</sub>/O<sub>2</sub>/light  
19 (pH 7) experiments, which clearly indicates that rates of formation of these species are  
20 higher than rates of consumption. As shown in Table 3, these systems are, among the  
21 studied, those that led to the lowest hydroxyl radical exposures and, as a consequence,  
22 showed the lowest organic matter degradation rates. Thus, accumulation of phenolic  
23 intermediates was more pronounced during the course of these experiments. On the other

1 hand, photolytic ozonation and photocatalytic ozonation systems, which led to the formation  
2 of hydroxyl radicals to a significant extent (see Table 3), were more effective in removing the  
3 phenolic content of samples. Thus, no accumulation of phenolic substances was observed  
4 throughout the course of these experiments and percentages of removal after the 5-h  
5 experiments were around 60-75% as it is apparent from Fig. 6. The Fe(III)/H<sub>2</sub>O<sub>2</sub>/O<sub>2</sub>/light (pH  
6 3) system was also able to remove phenolic compounds to some extent, though no more  
7 than 30% removal was achieved after 5 hours of experiment. Finally, single ozonation  
8 systems (pH 3 and 7, not shown in Fig. 6) led to 45-50% removal of the initial phenolic  
9 content after 5 h of treatment.

#### 10 3.4 Biodegradability measurements

11 The BOD<sub>5</sub>/COD ratio in samples before and after the experiments was measured to assess  
12 changes in biodegradability. It was found that samples taken after the 5-h experiments had  
13 BOD<sub>5</sub>/COD ratios ranged from 0.15 to 0.47. Since the initial BOD<sub>5</sub>/COD value was 0.17 (see  
14 Table 1), it can be concluded that, in general, the AOPs tested enhanced the biodegradability  
15 of samples. Particularly, the Fe(III)/H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub>/light (pH 3) system led to a 2.5-fold increase of  
16 the BOD<sub>5</sub>/COD ratio.

#### 17 3.5 Toxicity tests

18 One important aspect about the application of AOPs is the possible formation of toxic  
19 intermediates or by-products, which could be even more toxic than the compounds initially  
20 present in the samples. Toxicity bioassays of some selected reaction samples were carried  
21 out using acute *Daphnia magna*. For this purpose, samples were taken from the reactor at a  
22 time when complete ECs removal was almost achieved (i.e, t<sub>99</sub> as defined in equations (3) or  
23 (5)) and after the 5-h experiments. Table 4 shows the results of immobilization of *Daphnia*  
24 *magna* after 48 hours exposure. It should be mentioned here that no data for t<sub>99</sub> were  
25 obtained for the Fe(III)/O<sub>2</sub>/light (pH 3) system since no complete removal of ECs could be

1 achieved after 5 hours of application of this treatment (see Table 2). The results of toxicity  
2 bioassays showed an increase of toxicity after the addition of ECs to the secondary effluent.  
3 Thus, the percentage of inhibition increased from 5% (without added ECs) to about 25%  
4 (second column (t=0) in Table 4). Also, changes in sample toxicity were observed during the  
5 course of the photocatalytic experiments. As a rule, toxicity of samples increased at the  
6 beginning of the photocatalytic treatment, likely as a consequence of the accumulation of  
7 phenolic and other toxic intermediates and then decreased. This result is in agreement with  
8 that reported for the removal of other ECs by ozonation and solar photocatalytic oxidation  
9 with TiO<sub>2</sub> [23,24]. Toxicity removal below the baseline level (c.a., 25% inhibition) was only  
10 observed when a large degree of TOC removal (i.e., mineralization) was achieved. This  
11 applies especially for the Fe(III)/O<sub>3</sub>/light (pH 3) and Fe(III)/H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub>/light (pH 3) photocatalytic  
12 ozonation systems.

### 13 3.6 Influence of the H<sub>2</sub>O<sub>2</sub>/Fe(III) ratio

14 The Fe(III)/H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub>/light treatment at pH 3 has been proved so far as a good choice for the  
15 treatment of the secondary effluent contaminated with the ECs, as complete removal of ECs,  
16 high mineralization of organic matter (i.e., 35 % TOC removal) and great removal of phenolic  
17 compounds (i.e., 71% removal) were achieved after 5 h of treatment (i.e., 38.7 kJ·L<sup>-1</sup>  
18 radiation dose). In addition, the effluent from the treatment did not show toxicity towards  
19 *Daphnia magna* (i.e., < 5% inhibition) and presented a favourable BOD<sub>5</sub>/COD ratio. A key  
20 parameter of the process performance and the process efficiency for this AOP is the  
21 H<sub>2</sub>O<sub>2</sub>/Fe(III) ratio. To study the effect of this variable a series of experiments were carried out  
22 at varying mass ratios in the range 6.1-18.3. Following results of Table 5, where some  
23 process performance parameters are presented, the best H<sub>2</sub>O<sub>2</sub>/Fe(III) mass ratio, in the  
24 range considered here, was 12.2. Although, the greater H<sub>2</sub>O<sub>2</sub>/Fe(III) ratio the faster EC  
25 removal observed (i.e., lower t<sub>99</sub>), the TOC removal rate was the highest when applying a  
26 12.2 H<sub>2</sub>O<sub>2</sub>/Fe(III) mass ratio. The lower TOC removal rate obtained at the highest

1 H<sub>2</sub>O<sub>2</sub>/Fe(III) mass ratio compared to the optimum is likely to be a consequence of the  
2 hydroxyl radical scavenger character of hydrogen peroxide.

### 3 *3.7 Simplified comparison of operating costs*

4 Operating an efficient and cost-effective treatment process is the goal of every successful  
5 MWWTP. Therefore, before process development and scale-up economic analysis must be  
6 considered. In this work a simplified economic comparison of operating costs associated with  
7 the investigated treatment process is presented. The economic analysis accounts for the  
8 costs of the main reagents and/or catalysts used (i.e., iron (III), hydrogen peroxide and  
9 titanium dioxide) according to vendors (Proquiman and Quimidroga, Spain) as well as that of  
10 the electricity (Red Eléctrica de España, Spain) to power the air compressor, the ozone  
11 generator and the CPC reactor of the pilot-plant used in this work. Pre-treatment costs (e.g.,  
12 pH adjustment) have not been accounted for. As basis for the evaluation, experimental  
13 conditions used throughout this investigation have been considered. Also, two criteria have  
14 been used: (1) operating costs to reach complete removal of ECs; (2) operating costs to  
15 remove 20% of the TOC of the secondary effluent. Results are shown, as relative cost, in  
16 Table 6. Relative cost of the solar photo-Fenton process has been set as 1 as this system is,  
17 so far, the best known solar photo-catalytic treatment process. Recently, Durán and co-  
18 workers [25] estimated an operating cost of 1.56 €·m<sup>-3</sup> for the treatment of a secondary  
19 effluent from a MWWTP contaminated with antipyrine by a solar photo-Fenton method at  
20 semi-industrial scale. In the present work, the operating cost of the solar photo-Fenton  
21 process was found to be 0.80 or 1.68 €·m<sup>-3</sup> depending on whether the treatment objective  
22 was the complete removal of ECs or the reduction of TOC by a 20%. From the results of  
23 Table 6, it is apparent that the systems which involve the use of ozone, except the  
24 TiO<sub>2</sub>/O<sub>3</sub>/light (pH 7) system, are the most economic choices when the goal is just the 99%  
25 removal of the ECs, with relative costs ranging from 0.32 to 0.38. On the other hand, the  
26 operating cost of the Fe(III)/O<sub>2</sub>/light (pH 3) system is the highest due to the long treatment

1 time needed to remove the ECs (see Table 2). If the treatment goal is also the removal of  
2 TOC to some extent (i.e., 20% TOC removal) the solar photocatalytic ozonation systems  
3 using iron or iron and H<sub>2</sub>O<sub>2</sub> have the lowest operating costs while the use of TiO<sub>2</sub> as catalyst  
4 increases significantly the cost due to the expensiveness of this material.

#### 5 **4. Conclusions**

6 From the results of this study, it can be concluded that iron-mediated solar photocatalytic  
7 ozonation can be a suitable method to degrade ECs in secondary effluents from MWWTPs.  
8 The ECs used in this investigation (acetaminophen, antipyrine, bisphenol A, caffeine,  
9 metoprolol and testosterone) were easily removed by ozone but the organic matter in the  
10 effluent was difficult to mineralize at the experimental conditions applied. Thus, TOC  
11 conversion was found lower than 35% after 5 h of treatment. In any case, solar photocatalytic  
12 ozonation processes were shown to be more efficient than single ozonation and single  
13 photocatalytic oxidation systems in terms of TOC removal due to an enhanced generation of  
14 hydroxyl radicals. Treated effluents after the application of solar photocatalytic ozonation  
15 showed low toxicity towards *Daphnia magna* (inhibition percentage < 15%, while the non-  
16 treated secondary effluent showed about 25% inhibition) and higher biodegradability  
17 (BOD<sub>5</sub>/COD ratio = 0.15-0.47) than the non-treated secondary effluent. Finally, a simplified  
18 estimation of operating costs revealed that some solar photocatalytic ozonation processes  
19 (e.g., Fe(III)/O<sub>3</sub>/light and Fe(III)/H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub>/light) can be cheaper than the solar photo-Fenton  
20 system.

#### 21 **Acknowledgements**

22 This study was supported by Spanish Ministerio de Economía y Competitividad (MINECO)  
23 and European Regional Development Funds through the projects CTQ2009/13459-C05-05  
24 and CTQ2012-35789-C02-01. D. H. Quiñones is grateful to MINECO for the concession of a  
25 predoctoral FPI grant.



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**List of tables:**

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Table 1. Main characteristics of the secondary effluent samples used in this work (after pH adjustment treatment)

Parameter	Value
Inorganic carbon ( $\text{mg L}^{-1}$ )	$0.3 \pm 0.2$
Total organic carbon ( $\text{mg L}^{-1}$ )	$20.0 \pm 2.1$
pH	$3.0 \pm 0.1$
BOD <sub>5</sub> ( $\text{mg L}^{-1}$ )	$10 \pm 3$
COD ( $\text{mg L}^{-1}$ )	$58.6 \pm 3.5$
Turbidity (NTU)	$7.8 \pm 1.1$
Conductivity ( $\mu\text{S cm}^{-1}$ )	$1330 \pm 9$
PO <sub>4</sub> <sup>3-</sup> ( $\text{mg L}^{-1}$ )	$10.4 \pm 1.0$
SO <sub>4</sub> <sup>2-</sup> ( $\text{mg L}^{-1}$ )	$63.6 \pm 0.5$
Cl <sup>-</sup> ( $\text{mg L}^{-1}$ )	$295.7 \pm 4.6$
NH <sub>4</sub> <sup>+</sup> ( $\text{mg L}^{-1}$ )	$2.5 \pm 0.6$
NO <sub>3</sub> <sup>-</sup> ( $\text{mg L}^{-1}$ )	$5.7 \pm 0.8$

Table 2. Pseudo first-order rate constants and estimated depletion time for 99% total EC concentration removal for the AOPs studied in this work.

AOP	$k_{UV}$ (L·kJ <sup>-1</sup> ) <sup>a</sup> or $k$ (min <sup>-1</sup> ) <sup>b</sup>	$t_{99}$ (min)
O <sub>3</sub> /light/pH 3	1.438 <sup>a</sup>	36 <sup>c</sup>
Fe(III)/O <sub>2</sub> /light/pH 3	0.021 <sup>a</sup>	2344 <sup>c</sup>
Fe(III)/O <sub>3</sub> /light/pH 3	1.476 <sup>a</sup>	35 <sup>c</sup>
Fe(III)/H <sub>2</sub> O <sub>2</sub> /O <sub>2</sub> /light/pH 3	0.325 <sup>a</sup>	158 <sup>c</sup>
Fe(III)/H <sub>2</sub> O <sub>2</sub> /O <sub>3</sub> /light/pH 3	1.501 <sup>a</sup>	34 <sup>c</sup>
TiO <sub>2</sub> /O <sub>2</sub> /light/pH 7	0.258 <sup>a</sup>	198 <sup>c</sup>
TiO <sub>2</sub> /O <sub>3</sub> /light/pH 7	0.975 <sup>a</sup>	60 <sup>c</sup>
O <sub>3</sub> /pH 3	0.110 <sup>b</sup>	42 <sup>d</sup>
O <sub>3</sub> /pH 7	0.069 <sup>b</sup>	67 <sup>d</sup>

<sup>a</sup> Calculated by equation (2); <sup>b</sup> Calculated by equation (4); <sup>c</sup> Calculated by equation (3), assuming  $UV_G=30$  W m<sup>-2</sup>,  $V = 5$  L and  $A = 0.25$  m<sup>2</sup>; <sup>d</sup> Calculated by equation (5)

Table 3. Hydroxyl radical exposures ( $\int C_{HO\cdot} dt$ , M·s) observed in experiments of degradation of ECs in the secondary effluent by different AOPs <sup>(a)</sup>

UV radiation dose applied (kJ·L <sup>-1</sup> )	1.0	2.5	5.0
AOP	$\int C_{HO\cdot} dt \times 10^{10}$	$\int C_{HO\cdot} dt \times 10^{10}$	$\int C_{HO\cdot} dt \times 10^{10}$
Fe(III)/O <sub>2</sub> /light/pH 3	0.16	0.35	0.40
TiO <sub>2</sub> /O <sub>2</sub> /light/pH 7	0.11	0.58	1.34
Fe(III)/H <sub>2</sub> O <sub>2</sub> /O <sub>2</sub> /light/pH 3	0.62	1.12	1.63
TiO <sub>2</sub> /O <sub>3</sub> /light/pH 7	0.50	2.05	2.27
O <sub>3</sub> /light/pH 3	0.37	1.32	3.97
Fe(III)/O <sub>3</sub> /light/pH 3	0.41	1.24	4.36
Fe(III)/H <sub>2</sub> O <sub>2</sub> /O <sub>3</sub> /light/pH 3	0.85	2.68	5.47

<sup>(a)</sup> For experimental AOP conditions see Fig. 3.

Table 4. Toxicity towards *Daphnia magna* of reaction samples from experiments of degradation of ECs in the secondary effluent by different AOPs <sup>(a)</sup>

Reaction time	0	t <sub>99</sub>	5 h
AOP	Percentage inhibition (%)		
Fe(III)/O <sub>2</sub> /light/pH 3	25	NM	30
TiO <sub>2</sub> /O <sub>2</sub> /light/pH 7	21	31	26
Fe(III)/H <sub>2</sub> O <sub>2</sub> /O <sub>2</sub> /light/pH 3	24	18	9
TiO <sub>2</sub> /O <sub>3</sub> /light/pH 7	27	32	14
O <sub>3</sub> /light/pH 3	24	44	33
Fe(III)/O <sub>3</sub> /light/pH 3	28	33	5
Fe(III)/H <sub>2</sub> O <sub>2</sub> /O <sub>3</sub> /light/pH 3	25	38	2

t<sub>99</sub>= time needed to reach 99% removal of ECs; NM= not measured as t<sub>99</sub> was greater than 5 h.

<sup>(a)</sup> For experimental AOP conditions see Fig. 3.



Table 5. Effect of the H<sub>2</sub>O<sub>2</sub>/Fe(III) ratio on the performance of the Fe(III)/H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub>/light treatment at pH 3

H <sub>2</sub> O <sub>2</sub> /Fe(III) mass ratio	6.1	12.2	18.3
k <sub>TOC</sub> × 10 <sup>3</sup> (min <sup>-1</sup> )	3.01	3.32	2.58
% TOC removal	35	42.6	39.6
% Phenolic compounds removal	70.8	75.4	73.1
UV radiation dose (kJ·L <sup>-1</sup> )	38.7	24.3	28.6
t <sub>99</sub> (min)	34	22	18

Experimental conditions: EC concentration= 200 µg L<sup>-1</sup>, each; Applied ozone = 520 mg h<sup>-1</sup>; C<sub>Fe(III),0</sub> = 2.8 mg L<sup>-1</sup>; Overall radiation dose ~30 kJ L<sup>-1</sup>; Treatment time = 5 h.

Table 6. Estimated relative operating costs of the AOPs studied at pilot-plant scale.

Treatment system	Relative cost	
	Objective: Complete EC removal	Objective: 20% TOC removal
O <sub>3</sub> /light/pH 3	0.32	0.62
Fe(III)/O <sub>3</sub> /light/pH 3	0.32	0.46
Fe(III)/H <sub>2</sub> O <sub>2</sub> /light/pH 3	1.00	1.00
Fe(III)/O <sub>2</sub> /light/pH 3	14.28	*
O <sub>3</sub> /pH 3	0.38	*
Fe(III)/H <sub>2</sub> O <sub>2</sub> /O <sub>3</sub> /light/pH 3	0.35	0.44
TiO <sub>2</sub> /light/pH 7	2.57	1.92
TiO <sub>2</sub> /O <sub>3</sub> /light/pH 7	1.88	1.25

Notes: Fe(III)/H<sub>2</sub>O<sub>2</sub>/O<sub>2</sub>/light has been chosen as reference system (relative cost = 1); Experimental conditions as indicated in Fig.3.

(\*) Not calculated, as very low mineralization (< 2.5%) was achieved in 5 hours by the treatment method at the conditions applied.

**Figure captions:**

**Fig. 1.** Chemical structures of the chemical compounds used in this work

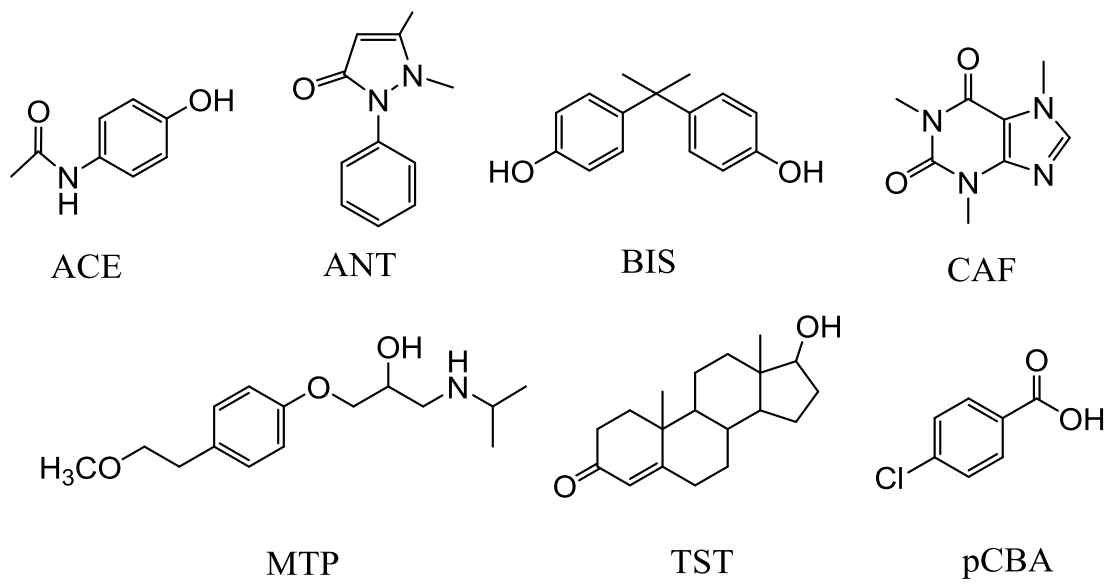
**Fig. 2.** Simplified scheme of the solar pilot plant used in this work

**Fig.3.** Plot of  $\Sigma C_{ECs,0}/\Sigma C_{ECs}$  against the UV radiation dose ( $Q_{UV}$ ) for some experiments. Experimental conditions: EC concentration= 200  $\mu\text{g L}^{-1}$ , each; Applied ozone = 520  $\text{mg h}^{-1}$ ;  $C_{Fe(III),0} = 2.8 \text{ mg L}^{-1}$ ; Initial  $\text{H}_2\text{O}_2/\text{Fe(III)}$  mass ratio = 6.1;  $C_{TiO_2,0} = 200 \text{ mg L}^{-1}$ . Symbols: (⊙)  $\text{O}_3/\text{light}/\text{pH } 3$ , (○)  $\text{Fe(III)}/\text{O}_2/\text{light}/\text{pH } 3$ , (◇)  $\text{Fe(III)}/\text{O}_3/\text{light}/\text{pH } 3$ , (▣)  $\text{Fe(III)}/\text{H}_2\text{O}_2/\text{O}_2/\text{light}/\text{pH } 3$ , (▲)  $\text{Fe(III)}/\text{H}_2\text{O}_2/\text{O}_3/\text{light}/\text{pH } 3$ , (△)  $\text{TiO}_2/\text{O}_2/\text{light}/\text{pH } 7$ , (●)  $\text{TiO}_2/\text{O}_3/\text{light}/\text{pH } 7$ . Lines: linear regression ( $R^2 > 0.96$ )

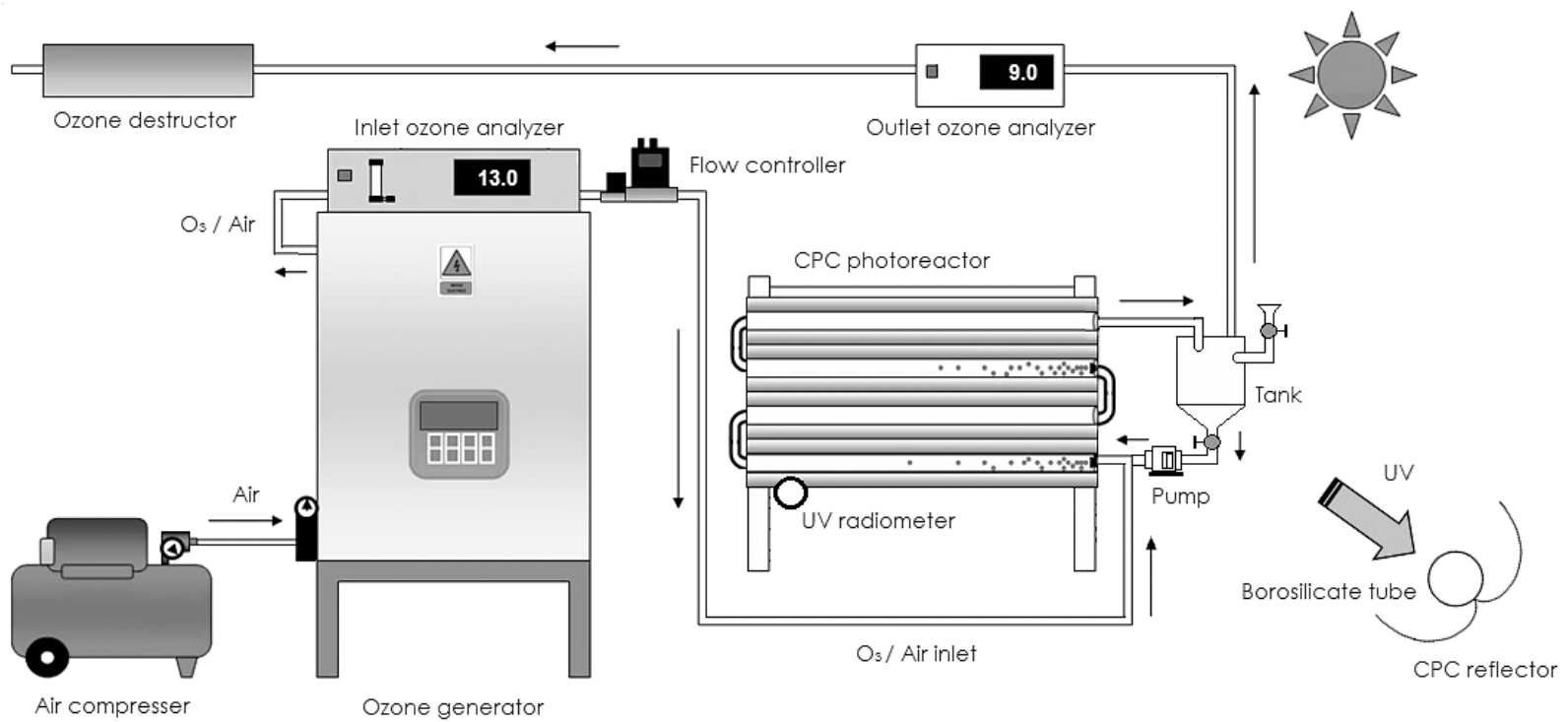
**Fig. 4.** TOC removal vs UV energy dose for some experiments. Experimental conditions: EC concentration= 200  $\mu\text{g L}^{-1}$ , each; Applied ozone = 520  $\text{mg h}^{-1}$ ;  $C_{Fe(III),0} = 2.8 \text{ mg L}^{-1}$ ; Initial  $\text{H}_2\text{O}_2/\text{Fe(III)}$  mass ratio = 6.1;  $C_{TiO_2,0} = 200 \text{ mg L}^{-1}$ .

**Fig.5.** Apparent mineralization rate constant and average incident radiation for some experiments. Experimental conditions: EC concentration= 200  $\mu\text{g L}^{-1}$ , each; Applied ozone = 520  $\text{mg h}^{-1}$ ;  $C_{Fe(III),0} = 2.8 \text{ mg L}^{-1}$ ; Initial  $\text{H}_2\text{O}_2/\text{Fe(III)}$  mass ratio = 6.1;  $C_{TiO_2,0} = 200 \text{ mg L}^{-1}$ .

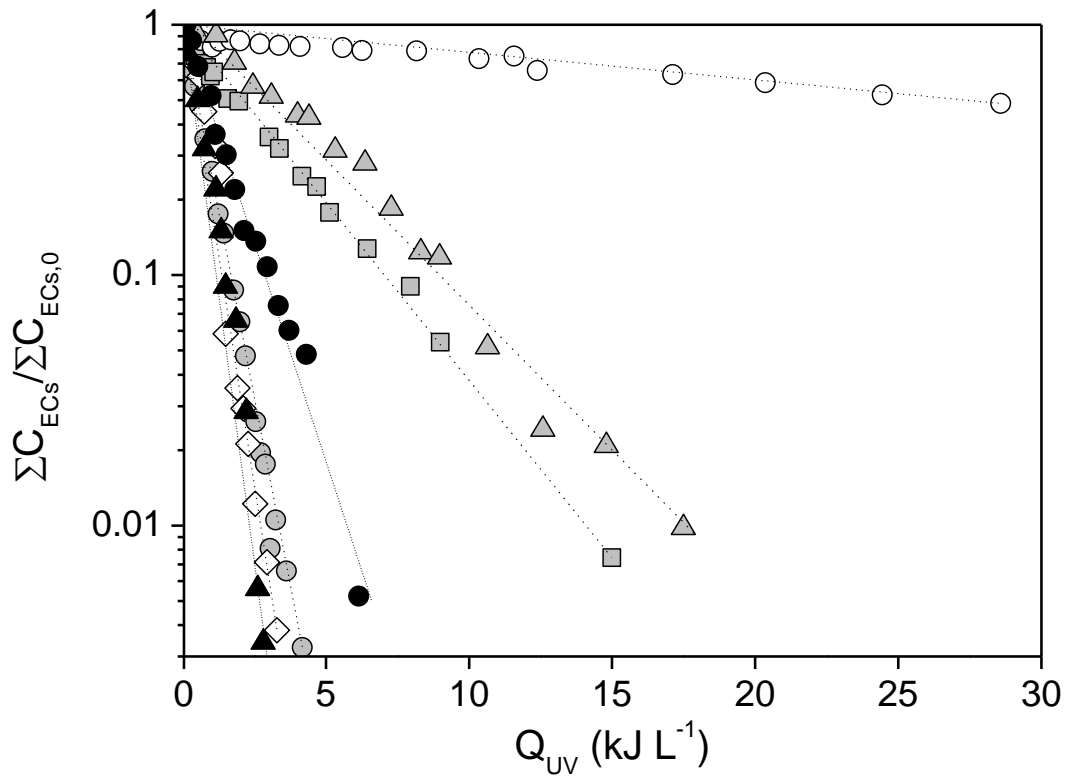
**Fig.6.** Evolution of the phenolic concentration with the dose of UV radiation during the course of some photocatalytic experiments. Experimental conditions: EC concentration= 200  $\mu\text{g L}^{-1}$ , each; Applied ozone = 520  $\text{mg h}^{-1}$ ;  $C_{Fe(III),0} = 2.8 \text{ mg L}^{-1}$ ; Initial  $\text{H}_2\text{O}_2/\text{Fe(III)}$  mass ratio = 6.1;  $C_{TiO_2,0} = 200 \text{ mg L}^{-1}$ . Symbols: (⊙)  $\text{O}_3/\text{light}/\text{pH } 3$ , (○)  $\text{Fe(III)}/\text{O}_2/\text{light}/\text{pH } 3$ , (◇)  $\text{Fe(III)}/\text{O}_3/\text{light}/\text{pH } 3$ , (▣)  $\text{Fe(III)}/\text{H}_2\text{O}_2/\text{O}_2/\text{light}/\text{pH } 3$ , (▲)  $\text{Fe(III)}/\text{H}_2\text{O}_2/\text{O}_3/\text{light}/\text{pH } 3$ , (△)  $\text{TiO}_2/\text{O}_2/\text{light}/\text{pH } 7$ , (●)  $\text{TiO}_2/\text{O}_3/\text{light}/\text{pH } 7$



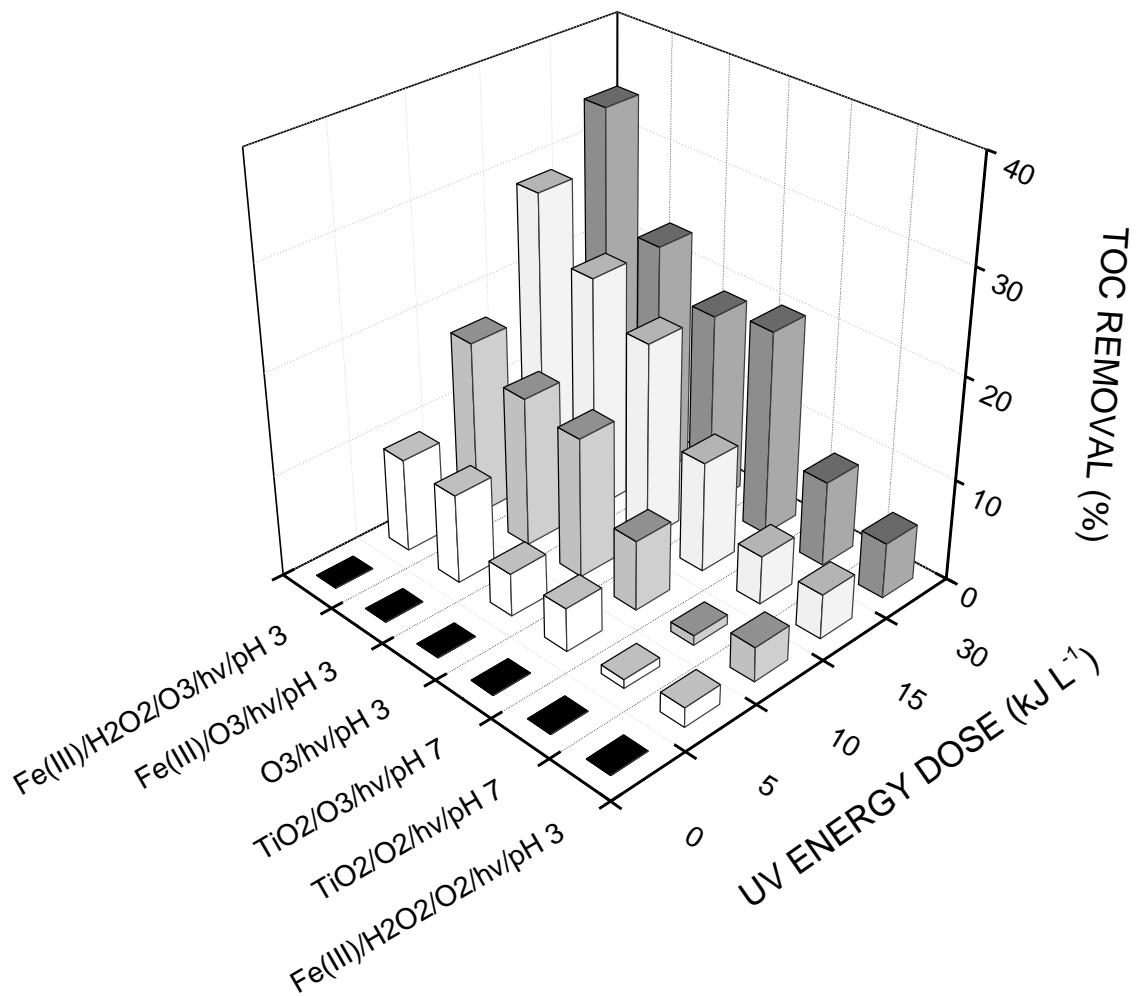
**Fig.1.** Chemical structures of the chemical compounds used in this work



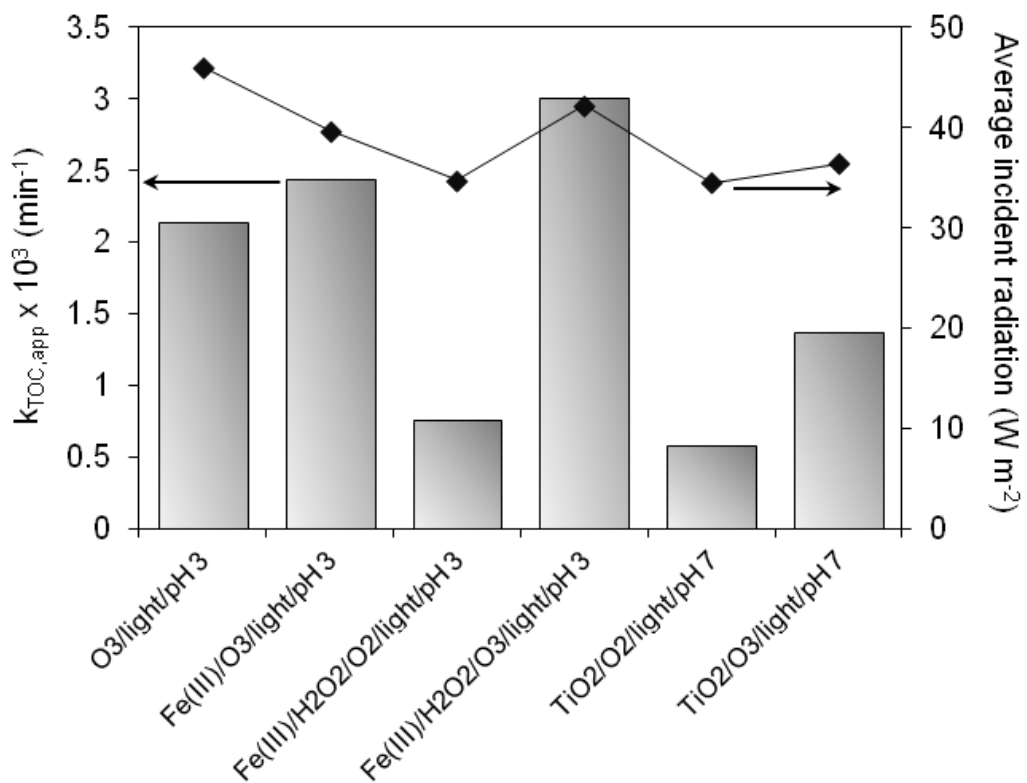
**Fig. 2.** Scheme of the solar pilot plant used in this work



**Fig.3.** Plot of  $\Sigma C_{ECs,0} / \Sigma C_{ECs}$  against the UV radiation dose ( $Q_{UV}$ ) for some experiments. Experimental conditions: EC concentration =  $200 \mu\text{g L}^{-1}$ , each; Applied ozone =  $520 \text{ mg h}^{-1}$ ;  $C_{Fe(III),0} = 2.8 \text{ mg L}^{-1}$ ; Initial  $\text{H}_2\text{O}_2/\text{Fe(III)}$  mass ratio = 6.1;  $C_{TiO_2,0} = 200 \text{ mg L}^{-1}$ . Symbols: (○)  $\text{O}_3/\text{light}/\text{pH } 3$ , (○)  $\text{Fe(III)}/\text{O}_2/\text{light}/\text{pH } 3$ , (◇)  $\text{Fe(III)}/\text{O}_3/\text{light}/\text{pH } 3$ , (□)  $\text{Fe(III)}/\text{H}_2\text{O}_2/\text{O}_2/\text{light}/\text{pH } 3$ , (▲)  $\text{Fe(III)}/\text{H}_2\text{O}_2/\text{O}_3/\text{light}/\text{pH } 3$ , (Δ)  $\text{TiO}_2/\text{O}_2/\text{light}/\text{pH } 7$ , (●)  $\text{TiO}_2/\text{O}_3/\text{light}/\text{pH } 7$ . Lines: linear regression ( $R^2 > 0.96$ )

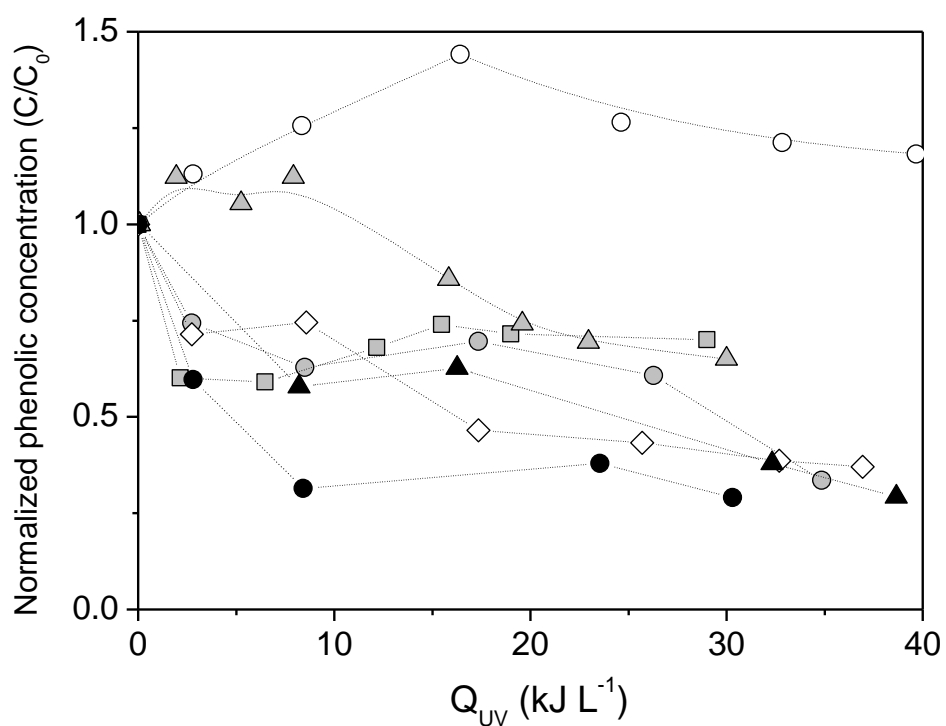


**Fig.4.** TOC removal vs UV energy dose for some experiments. Experimental conditions: EC concentration= 200  $\mu\text{g L}^{-1}$ , each; Applied ozone = 520  $\text{mg h}^{-1}$ ;  $C_{\text{Fe(III),0}} = 2.8 \text{ mg L}^{-1}$ ; Initial  $\text{H}_2\text{O}_2/\text{Fe(III)}$  mass ratio = 6.1;  $C_{\text{TiO}_2,0} = 200 \text{ mg L}^{-1}$ .



**Fig.5.** Apparent mineralization rate constant and average incident radiation for some experiments. Experimental conditions: EC concentration=  $200 \mu\text{g L}^{-1}$ , each; Applied ozone =  $520 \text{ mg h}^{-1}$ ;  $C_{\text{Fe(III),0}} = 2.8 \text{ mg L}^{-1}$ ; Initial  $\text{H}_2\text{O}_2/\text{Fe(III)}$  mass ratio = 6.1;  $C_{\text{TiO}_2,0} = 200 \text{ mg L}^{-1}$ .





**Fig.6.** Evolution of the phenolic concentration with the dose of UV radiation during the course of some photocatalytic experiments. Experimental conditions: EC concentration=  $200 \mu\text{g L}^{-1}$ , each; Applied ozone =  $520 \text{ mg h}^{-1}$ ;  $C_{\text{Fe(III),0}} = 2.8 \text{ mg L}^{-1}$ ; Initial  $\text{H}_2\text{O}_2/\text{Fe}/(\text{III})$  mass ratio = 6.1;  $C_{\text{TiO}_2,0} = 200 \text{ mg L}^{-1}$ . Symbols: (○)  $\text{O}_3/\text{light}/\text{pH } 3$ , (○)  $\text{Fe(III)}/\text{O}_2/\text{light}/\text{pH } 3$ , (◇)  $\text{Fe(III)}/\text{O}_3/\text{light}/\text{pH } 3$ , (□)  $\text{Fe(III)}/\text{H}_2\text{O}_2/\text{O}_2/\text{light}/\text{pH } 3$ , (▲)  $\text{Fe(III)}/\text{H}_2\text{O}_2/\text{O}_3/\text{light}/\text{pH } 3$ , (△)  $\text{TiO}_2/\text{O}_2/\text{light}/\text{pH } 7$ , (●)  $\text{TiO}_2/\text{O}_3/\text{light}/\text{pH } 7$