



## Solar photocatalysis as a tertiary treatment to remove emerging pollutants from wastewater treatment plant effluents

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### ABSTRACT

Water taken from the outlet of a wastewater treatment plant from the South East of Spain has been treated by means of TiO<sub>2</sub>-based solar photocatalysis. Preliminary analysis showed the presence of significant amounts of nine emerging pollutants (order of magnitude of ng/l): trimethoprim, ofloxacin, enrofloxacin, clarithromycin, acetaminophen, diclofenac, caffeine, thiabendazole and carbamazepine; and trace amounts of another two were detected, namely acetamiprid and erythromycin. Irradiation of the effluent in the presence of TiO<sub>2</sub> resulted in a significant removal of all the emerging pollutants, as most of them were detected only at trace amounts after the treatment. In addition to this, percentages of faecal bacteria elimination were close to 100%. Finally, experiments carried out using caffeine as model compound showed that a mild photo-Fenton process might be employed at neutral media in the presence of humic acids, although the performance was worse than photo-Fenton at acidic pH or TiO<sub>2</sub>.

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### 1. Introduction

Emerging pollutants (EPs) have deserved increasing attention from researchers as well as from public administrations. Although some inorganics can be considered among the EPs (e.g. nanomaterials), in most cases they are organic species such as perfluorinated compounds, pharmaceuticals, hormones, endocrine disruptors, drinking water and swimming pool disinfection byproducts, sunscreens, flame retardants, algal toxins, dioxane or pesticides and their degradation byproducts [1–3]. These pollutants are present at low concentrations at the outlet of wastewater treatment plants, and hence they can reach aquatic ecosystems such as rivers and lakes [4,5]. Although they should not be expected to exhibit an important acute toxicity at low concentrations (typically a few µg/l or even ng/l), they are persistent and phenomena such as bioaccumulation or synergetic toxicity should not be ruled out [5,6]. In addition, the presence of EPs could be considered a major inconvenience for the re-use of treated effluents as drinking water.

Conventional wastewater treatment plants are not so effective in the removal of emerging pollutants [7]. Hence, advanced methods should be applied to deal with this environmental concern, among them absorption by activated carbon, rejection by mem-

branes, biodegradation or chemical advanced oxidation, as recently reviewed [7,8].

Among the chemical advanced oxidation processes, solar photocatalysis deserves major attention. They constitute a group of techniques that involve the “in situ” generation of highly oxidising species under solar irradiation, in the presence of a catalyst; titanium dioxide [9] and the photo-Fenton process (involving iron salts and hydrogen peroxide) [10] are the most widely employed among these methods. In fact, an important number of papers has been written in the last decade reporting on the use of these methods to treat a wide range of pollutants using sunlight as irradiation source [11–15]. Although their use as a pre-treatment to enhance the biocompatibility of toxic or non-biodegradable effluents has deserved much attention in recent years [16–20], using solar photocatalysis as a post-treatment might be an attractive alternative to remove emerging pollutants from the effluents of small wastewater treatment plants, since large surfaces needed for solar reactors might constitute a major limitation for bigger ones. In fact, some reviews have summarized the available information on the applicability of solar photocatalysis to treat EPs [21–23]. In addition, some recent papers have reported on the application of photo-Fenton as a tertiary treatment to remove EPs at relatively low concentrations (ca. 5 µg/l) in simulated effluents from wastewater treatment plants [24,25]. Results were rather satisfactory as important removal of the studied EPs was achieved. However, as far as we know, just a few information is available on the treat-

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ment of real effluents, as they involve important problems such as their intrinsic low reproducibility, and the low EPs concentrations, which are commonly close to their limits of quantification. Nonetheless, the photo-Fenton is not free of disadvantages, in particular, the strong acidic pH required to avoid precipitation of iron; however, some recent papers have studied the possibility of applying (photo)-Fenton processes at circumneutral pH employing complexing agents (e.g. citric acid, humic acids) to increase iron solubility [26–29]. In addition, the small remnant dissolved iron concentration could be used to remove pollutants present in trace amounts. In fact, some elimination of EPs in simulated water by means of a neutral photo-Fenton has been reported [25,30].

With this background, the aim of this paper is to study the elimination of emerging pollutants at the outlet of a wastewater treatment plant from the East of Spain, which contains significant amounts of pharmaceuticals. Titanium dioxide has been tested as a tertiary treatment to remove the EPs previously detected in this effluent. The efficiency of this process has been compared with that of photo-Fenton at neutral conditions using caffeine as model compound.

## 2. Experimental

### 2.1. Reagents

Acetaminophen, diclofenac, caffeine, thiabendazole, acetamidrid, trimethoprim, ofloxacin and carbamazepine (see Scheme 1 for structures) employed as standards and also as pollutants in spiked samples, were purchased from Aldrich. P-25 titanium dioxide, used as photocatalyst, was kindly supplied by Degussa. Hydrogen peroxide (30%, v/v) and ferrous sulphate, used in the photo-Fenton reactions, were purchased from Panreac. Standard solutions were prepared with Milli Q grade water.

Aqueous samples containing the EPs were taken from the effluent of the secondary settling tank of a wastewater treatment plant from the East of Spain. The plant consisted of a physical–chemical primary treatment followed by an aerobic activated sludge biological reactor. The main parameters of this effluent were systematically inside the following ranges: pH, 7.5; conductivity, 2.4–2.8 mS/cm; DOC, 15–50 mg/l; IC 70–90 mg/l; and COD 60–120 mg/l.

### 2.2. Reactions

Experiments using real wastewaters were carried out using two different pilot plants for wastewater detoxification (Solardetox Acadus-2006) based on compound parabolic collectors, CPCs, with a concentration factor ( $R_c$ ) of 1 [15]. One of them, which has been described elsewhere [31] (3.0 m<sup>2</sup> irradiated surface, 24 l irradiated volume), was located at the wastewater treatment plant and it was employed to treat real wastewaters. It was loaded with 50 l of wastewater in each experiment; accumulated and instantaneous UVA radiation (accounting for ca. 7% of the total solar irradiation) was measured by means of a UV radiometer and expressed as  $t_{30W}$ , in order to normalise the changing irradiation conditions typical of solar experiments. Eq. (1) has been used in the  $t_{30W}$  (in seconds) calculations, where  $UV_{ac}$  is the accumulated solar radiation (J/m<sup>2</sup>),  $V_i$  the irradiated volume (l),  $V_t$  the total volume (l) and  $I$  the irradiance, for which an average value of 30 W/m<sup>2</sup> was considered.

$$t_{30W} = \frac{UV_{ac} \cdot V_i}{I \cdot V_t} \quad (1)$$

Experiments with spiked samples (5 extra mg/l of each pollutant, acetaminophen, diclofenac, caffeine, thiabendazole, acetamidrid, and trimethoprim) were carried out in a Solardetox Acadus-

2001 (Ecosystem) plant, with a total surface of 0.26 m<sup>2</sup>, and the irradiated volume was 1.83 l, which was located at the laboratories of Universidad Politécnica de Valencia. For every experiment, a reservoir was charged with 4 l of the solution.

When titanium dioxide was used as photocatalyst, its amount was in the range 0.2–0.5 g/l. In the photo-Fenton process, ferrous sulphate was employed as iron source; the initial concentration of iron was 5 mg/l and it was monitored throughout the experiment in order to add, when required, extra amounts in order to compensate for its precipitation at circumneutral pH. The amount of hydrogen peroxide was kept in the range 5–10 mg/l throughout the experiment in the pilot plant reactions. Blank controls were performed by irradiating the spiked sample in the absence of photocatalyst, and dark controls were also run to determine possible absorption of the pollutants onto the TiO<sub>2</sub> surface.

Finally, laboratory scale reactions were carried out with a model compound, caffeine; this compound was chosen because it reached the highest initial concentrations in the studied samples. In order to minimize experimental errors and to obtain reliable and comparable time resolved data, reactions were irradiated with a solar simulator (Oriel Instruments, Model 81160 equipped with a 300 W xenon lamp) and high initial concentrations of caffeine were used (50 mg/l). Experiments were performed with TiO<sub>2</sub> (0.2 g/l), photo-Fenton at the optimal pH of 2.8, at pH=7 and at pH=7 in the presence of humic acids (2 mg/l); all reactions were run with distilled water and tap water, in order to determine the possible role of carbonates. Irradiations were performed in cylindrical open glass vessels. Magnetic stirring was kept all along the reaction time and water was periodically added in order to compensate for the evaporation loss. 250 mg/l of H<sub>2</sub>O<sub>2</sub> were added in a single addition at the beginning of the reaction in the laboratory scale experiments; this was the stoichiometric amount of H<sub>2</sub>O<sub>2</sub> needed to mineralise completely the caffeine added.

### 2.3. Analysis

Samples were periodically taken from the reactors for identification and quantification of pollutants and immediately filtered (0.45 μm polypropylene, Teknokroma) and concentrated in order to prevent further reaction when H<sub>2</sub>O<sub>2</sub> was present. Solid phase extraction was employed for samples concentration: 200 ml of the aqueous solution at neutral pH were flown through a LiChrolut EN 200 mg (Merck) cartridge; then the organics were recovered with 3 ml of methanol. They were then injected in a GCMS-QP2010S (Shimadzu) gas chromatograph equipped with a quadrupole mass analyser. During the analysis, temperature was increased from 160 °C to 200 °C with a 0.5 °C/min rate and kept at 200 °C for 30 min. A Meta X5 Teknokroma column was used.

Alternatively, HPLC–MS was employed for detection of trace amounts of emerging pollutants. The method is based on the EPA 1694 standardized procedures. Briefly, the sample was divided in two aliquots, the pH adjusted to 2 and 10 respectively and concentrated by solid phase extraction (HLB cartridges). Samples were recovered with methanol and formic acid and injected, at least twice, in a HPLC provided with a triple quadrupole mass detector working in MRM mode.

Dissolved organic carbon (DOC) was determined with a Shimadzu model TOC-V CSH apparatus. It was also provided with a chemoluminescence detector, able to analyse total dissolved nitrogen (TN); samples were at least twice injected. The concentration of iron was determined according to the o-phenantroline standardized procedure [32]; briefly, all the iron was reduced to iron (II) by addition of hydroquinone and the pH was adjusted to 3.5; then o-phenantroline was added and the red complex formed was

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