



## Application of solar photocatalytic ozonation for the degradation of emerging contaminants in water in a pilot plant



Diego H. Quiñones<sup>a</sup>, Pedro M. Álvarez<sup>a</sup>, Ana Rey<sup>a</sup>, Sandra Contreras<sup>b</sup>, Fernando J. Beltrán<sup>a,\*</sup>

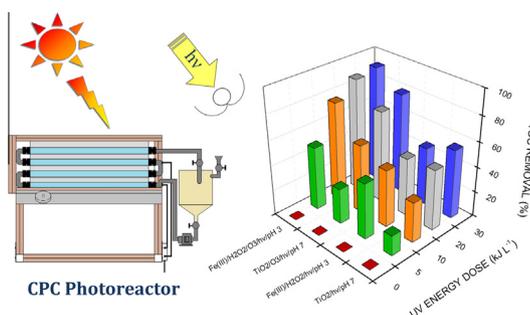
<sup>a</sup> Departamento de Ingeniería Química y Química Física, Facultad de Ciencias, Universidad de Extremadura, Av. de Elvas s/n, 06071 Badajoz, Spain

<sup>b</sup> Departament d'Enginyeria Química, Universitat Rovira i Virgili, Campus Sescelades, Av. Països Catalans 26, 43007 Tarragona, Spain

### HIGHLIGHTS

- Emerging pollutants were successfully degraded by solar AOPs in a CPC photo reactor.
- Ozonation and photolytic ozonation can completely remove the emerging compounds.
- Combination of photocatalysis and ozone enhances considerably the system efficiency.
- TOC conversion kinetics can be fitted to pseudo-first order reaction models.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Aqueous mixtures of six commonly detected emerging contaminants (acetaminophen, antipyrine, bisphenol A, caffeine, metoprolol and testosterone), selected as model compounds, were treated by different solar-driven photochemical processes including photolysis, photocatalytic oxidation with Fe(III) or TiO<sub>2</sub>, photo-Fenton and single, photolytic and photocatalytic ozonations. Experiments were carried out in a compound parabolic collector photoreactor. It was found that photolysis and photocatalytic oxidation using Fe(III) are not effective for the complete removal of the selected contaminants, while TiO<sub>2</sub> photocatalysis, photo-Fenton, single, photolytic and photocatalytic ozonations can rapidly remove them and decrease total organic carbon to some extent. The combination of photocatalytic oxidation and ozonation considerably enhances the system efficiency by reducing the ozone demand and energy requirements to completely remove the contaminants. Results also demonstrate that, at the operational conditions applied in this work, the contaminant removal and mineralization by ozone processes takes place in the slow kinetic regime, therefore the application of the ozone combined processes studied instead of single ozonation is recommended. Kinetic considerations on the application of solar photocatalytic processes for mineralization have been also assessed.

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### 1. Introduction

Nowadays a great number of pharmaceuticals and personal care products, commonly known as emerging contaminants (ECs), are being detected in aqueous systems such as rivers, lakes, streams,

aquifers and wastewater treatment plant influents and effluents. These compounds are considered potentially hazardous as some are ubiquitous, persistent to conventional wastewater treatments and biologically active, many of them with recognized endocrine disruption functions [1,2].

Advanced Oxidation Processes (AOPs) constitute an alternative for the degradation of ECs. AOPs are physicochemical processes based on the generation of hydroxyl radicals ( $\cdot\text{OH}$ ) under mild

\* Corresponding author. Tel.: +34 924289300; fax: +34 924289385.

E-mail address: [fbeltran@unex.es](mailto:fbeltran@unex.es) (F.J. Beltrán).

experimental conditions. The hydroxyl radical has a non-selective, high oxidizing power ( $E^\circ = 2.8 \text{ V vs. SHE}$ ), which makes it able to mineralize almost any organic molecule, yielding  $\text{CO}_2$  and inorganic ions [3].

Heterogeneous photocatalytic oxidation, being one of the most applied AOPs, involves the absorption in a semiconductor particle of photons of energy ( $h\nu$ ) equal to or exceeding the band gap energy ( $E_g$ ) of the semiconductor, resulting in the excitation of an electron ( $e_{CB}^-$ ) from the valence band to the conduction band and, therefore, in the generation of a positive hole ( $h_{VB}^+$ ) in the valence band. Electron/hole pairs might further trigger a process leading to the generation of  $\cdot\text{OH}$  and, as a result, to the degradation of pollutants. Titanium dioxide is, so far, the most extensively used photocatalyst due to its high chemical stability, its non-toxicity, its relatively low cost and its highly oxidizing power in solar-driven processes as it is capable to absorb UV radiation from the solar spectrum [3].

Likewise, homogeneous photocatalytic systems using iron-based catalysts have been widely applied. Thus, Fe(III) photocatalytic oxidation can generate iron (III) aqua complexes, primarily  $\text{Fe}(\text{OH})^{2+}$ , which undergoes photolysis under radiation of  $\lambda > 300 \text{ nm}$  to yield  $\cdot\text{OH}$  radicals. Moreover, if hydrogen peroxide is added, the resulting system, known as photo-Fenton, enhances the generation of hydroxyl radicals through the decomposition of  $\text{H}_2\text{O}_2$ . Iron-based catalysts are not toxic, easily available and can be efficiently used at acidic conditions [4,5].

Ozonation has also been extensively used in water treatment. Ozone is a selective oxidant ( $E^\circ = 2.07 \text{ V vs. SHE}$  in acidic medium and  $1.27 \text{ V vs. SHE}$  in alkaline medium), which can react directly

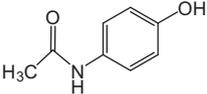
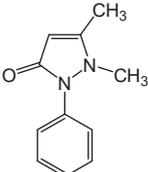
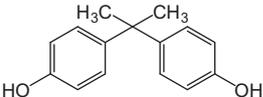
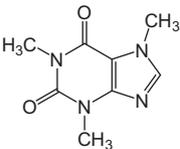
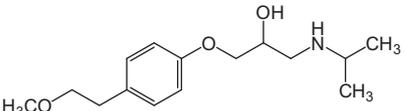
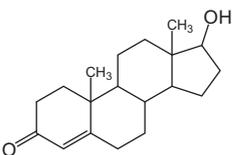
with many organic compounds. In addition, it can also decompose, especially at alkaline conditions, into hydroxyl radicals [6].

It is well known that the combination of various AOPs may lead to an enhanced production of  $\cdot\text{OH}$  radicals and other oxidizing species and, as consequence, to faster degradation of pollutants. In this sense, photocatalytic ozonation, which involves the combination of photocatalytic oxidation and ozonation, can be a promising treatment method [7]. Some previous studies have already shown that synergistic effect might occur when photocatalysis and ozonation are carried out simultaneously [8,9].

In this work, various AOPs, such as ozonation, photolytic ozonation, Fe(III) photocatalytic oxidation, photo-Fenton,  $\text{TiO}_2$  photocatalytic oxidation and the combination of some of them have been applied to degrade aqueous mixtures of six ECs under solar illumination and process performance has been compared. The ECs used have been acetaminophen (ACE), antipyrine (ANT), bisphenol A (BIS), caffeine (CAF), metoprolol (MTP) and testosterone (TST). Their chemical structures, common uses and some reported data on their detection in water bodies are summarized in Table 1.

Previous works have addressed the abatement of ECs in water using solar-driven photocatalysis [10–12] and ozonation [13–15]. However, to the best of our knowledge, only three works have been published so far dealing with solar photocatalytic ozonation at pilot scale [16–18]. The present work is focused on a study on the kinetic aspects concerning these AOPs, such as oxidation pathways, ozone reaction regimes of absorption and apparent reaction rate constants, as well as on the synergistic effect of some solar-driven combined processes.

**Table 1**  
Chemical structures, common uses and occurrence in water bodies of the ECs used in this work.

Compound	Chemical structure	Common uses	Detected in
ACE		Analgesic, antiinflammatory	WWTP influents and effluents (up to $1534 \text{ ng L}^{-1}$ ) [1], groundwater (up to $1890 \text{ ng L}^{-1}$ ) [19], surface waters (up to $10,000 \text{ ng L}^{-1}$ ) [20,21]
ANT		Antipyretic, analgesic	WWTP influents (up to $72 \text{ ng L}^{-1}$ ) and effluents (up to $58 \text{ ng L}^{-1}$ ) [15], and surface waters (up to $752 \text{ ng L}^{-1}$ ) [21]
BIS		Plasticizer	WWTP effluents (up to $3642 \text{ ng L}^{-1}$ ) [22], surface waters (up to $12,000 \text{ ng L}^{-1}$ ) [20], and paper industry effluents (up to $370,000 \text{ ng L}^{-1}$ ) [23]
CAF		Stimulant	WWTP influents (up to $230,000 \text{ ng L}^{-1}$ ) [24] and effluents (up to $1589 \text{ ng L}^{-1}$ ) [15], and surface waters (up to $6000 \text{ ng L}^{-1}$ ) [20]
MTP		Beta-blocker	WWTP effluents and surface waters (both up to $2200 \text{ ng L}^{-1}$ ) [25]
TST		Steroid hormone	WWTP effluents (up to $4.9 \text{ ng L}^{-1}$ ) [22] and surface waters (up to $214 \text{ ng L}^{-1}$ ) [20]

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