



Solar photocatalytic degradation of persistent pharmaceuticals at pilot-scale: Kinetics and characterization of major intermediate products

Jelena Radjenović^a, Carla Sirtori^b, Mira Petrović^{a,c}, Damià Barceló^{a,d}, Sixto Malato^{b,*}

^a Department of Environmental Chemistry, IDAEA-CSIC, c/Jordi Girona 18-26, 08034 Barcelona, Spain

^b Plataforma Solar de Almería (CIEMAT), Carretera Senes, Km. 4, 04200 Tabernas (Almería), Spain

^c Institutio Catalana de Reserca i Estudis Avanzats (ICREA), Barcelona, Spain

^d Institut Català de Recerca de l'Aigua (ICRA), Parc Científic i Tecnològic de la Universitat de Girona, Pic de Peguera, 15, 17003 Girona, Spain

ARTICLE INFO

Article history:

Received 17 December 2008

Received in revised form 6 February 2009

Accepted 13 February 2009

Available online 27 February 2009

Keywords:

Acetaminophen

Atenolol

Intermediate products

Solar TiO₂ photocatalysis

Solar photo-Fenton

UPLC-QqToF-MS

ABSTRACT

The technical feasibility and performance of photocatalytic degradation of anti-inflammatory drug acetaminophen (ACTP) and β -blocker atenolol (ATL) have been studied in a well-defined system of a pilot-plant scale Compound Parabolic Collectors (CPCs) under natural illumination. Heterogeneous photocatalysis with titanium dioxide (TiO₂) and homogeneous photocatalysis by photo-Fenton were investigated with two different matrices: distilled water and synthetic municipal wastewater treatment plant effluent (S.E.). The initial concentrations of the pharmaceuticals studied were 10 mg L⁻¹, whereas the concentrations of the catalysts employed were 200 mg L⁻¹ of TiO₂ and 5 mg L⁻¹ of iron. Total disappearance of the parent compounds and discreet mineralization were attained in all experiments. Furthermore, kinetic parameters, release of heteroatoms and formation of carboxylic acids are discussed. The main intermediate products of photocatalytic degradation of atenolol has been structurally elucidated by tandem mass spectrometry (MS²) experiments performed at quadrupole-time of flight (QqToF) mass analyzer coupled to ultra-performance liquid chromatograph (UPLC). Six transformation products were characterized, formed by consecutive attacks of hydroxyl (*OH) radical in concomitance with the disappearance of the primary compound. The proposed TiO₂ and photo-Fenton degradation route of ATL is reported for the first time.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

The presence of pharmaceuticals in the environment is an issue receiving growing attention worldwide. Possible adverse effects that pharmaceuticals might have in the ecosystems are still unknown, whereas many studies have been conducted on their occurrence in the aquatic and terrestrial environmental compartments [1–3].

Acetaminophen (ACTP) is a commonly used analgesic. After being processed in liver ACTP is excreted in urine [4]. Atenolol (ATL) is a β 1 receptor specific antagonist, used primarily to treat cardiovascular diseases. After human consumption, it is excreted also via urine [5], with a small percentage of ATL-glucuronide (0.8–4.4%) and hydroxyATL (1.1–4.4%, hydroxylation of the benzilic position) [6]. The reported removals in sewage treatment plants (STPs) are varying from almost complete for ACTP [7], to no removal or partial removal reported for ATL [7,8]. As far as their photolysis in natural waters is concerned, Liu et al. [9] observed

slow direct photolysis of ATL in water. Andrisano et al. [10] noticed an increase in the photodegradation rate of ATL with the decrease in pH in a UV-irradiated solution. The photodegradation rate of ACTP was found to follow the pseudo-first order kinetic in nitrate solution [11].

In recent years, advanced oxidation processes (AOPs) such as heterogeneous photocatalysis and photo-Fenton treatment have been gaining attention, especially in the treatment of water containing pharmaceuticals [12–15]. Heterogeneous photocatalysis is based on the use of wide band-gap semiconductors. When a semiconductor is illuminated with light energy greater than its band gap energy (BGE), excited high-energy states of electron and hole pairs (e⁻/h⁺) are produced. The photogenerated electrons could reduce the organic substrate [16] and the photogenerated holes can also oxidize either the organic molecule directly, or the OH⁻ ions and the H₂O molecules adsorbed on the catalyst's surface, to *OH radicals. The most commonly used catalyst is titanium dioxide (TiO₂, BGE = 3.2 eV), because of its high reactivity, non-toxicity, low price and chemical stability [17,18]. One of the important advantages of heterogeneous photocatalysis is that solar spectrum can be used to photoexcite the semiconductor catalyst, thus surpassing the cost of UV radiation. In the photo-Fenton method, the reagents used for the

* Corresponding author. Tel.: +34 950387940; fax: +34 950365015.

E-mail address: Sixto.Malato@psa.es (S. Malato).

oxidation of organic compounds are Fe^{2+} salts and hydrogen peroxide (H_2O_2), which is non-toxic and environmentally safe mixture. The UV–vis light enhances the reaction through accelerating the regeneration of the ferrous ions and increasing the formation of $\cdot\text{OH}$ radicals [19].

However, radical-induced reactions occurring in photocatalytic treatments will evolve through complex parallel consecutive pathways of intermediate products. Since hydroxyl-radicals are not selective, various by-products are formed at low concentration levels. The identification of these intermediates and determination of kinetics of their degradation is crucial due to their potential presence in the effluent of the treatment, and apprehension of their degradation pathways in order to determine the key steps of photodecomposition. Moreover, elucidation of mechanisms of photocatalytic reactions can help in gaining information on naturally occurring transformations, such as the case of intermediate photocatalytic products of atrazine that were encountered in soil samples [20], and metabolic products of a doping substance buspirone extracted from the animal liver [21].

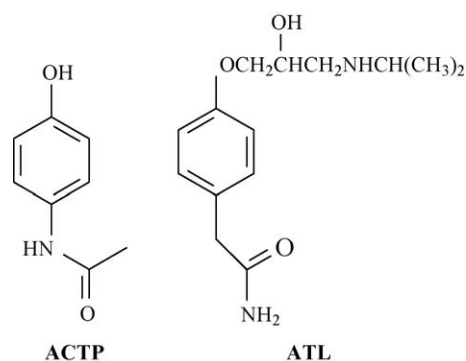
The knowledge on photocatalytic intermediates of pharmaceuticals is still scarce [22–26]. Lambropoulou et al. [24] identified 17 products of photocatalytic degradation of bezafibrate. Pérez-Estrada et al. [23] elucidated the photo-Fenton degradation pathway of diclofenac. Zhang et al. [26] proposed a pathway for photocatalytic degradation of acetaminophen via direct hole oxidation and *ipso*-substitution. Zbaida et al. [25] identified several intermediate products of reaction of cimetidine with Fenton reagent ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$), such as cimetidine sulfoxide, N-desmethylcimetidine, N-desmethylcimetidine sulfoxide, cimetidine guanylurea and 5-hydroxymethylimidazole derivative of cimetidine sulfoxide. As far as ATL is concerned, Liu et al. [9] observed its slow direct photolysis, whereas for propranolol three photodegradation products of aromatic ring oxidation and opening were identified. In the experiments with 5 mL TiO_2 suspensions under simulated solar light, Medana et al. [27] identified several transformation products of ATL, mainly mono-, di- and tri-hydroxylated derivatives.

This study describes the oxidation of ACTP and ATL at pilot-scale Compound Parabolic Collector (CPC) under natural illumination. Two widely used AOP systems, TiO_2 and photo-Fenton solar photocatalysis, were investigated with two types of matrix: distilled water and SE. The specific aim of this study was to investigate the kinetics of the processes and determine the influence that the matrix might have when applying the two abovementioned AOPs for the treatment of wastewater. Since these pharmaceuticals are frequently detected in STP effluents, it is important to evaluate the possible influence of this matrix on the process efficiency. Special attention has been paid to identify the main intermediate products of ATL formed during the treatment. ACTP was not included in the study as its structure is so similar to ATL (and simpler) and due to a previous study already published by Medana et al. [27]. The major transformation products of photo-Fenton and TiO_2 photocatalysis of ATL have been characterized by accurate mass measurements of the tandem mass spectrometry (MS^2) spectra obtained at quadrupole-time of flight (QqToF) instrument, coupled to ultra-performance liquid chromatography (UPLC) system. Possible photocatalytic degradation pathways of the two therapeutic drugs were proposed, whereas the reactions involved either oxidation by the $\cdot\text{OH}$ radical or reduction by conduction band electrons.

2. Experimental

2.1. Chemicals

The test substances and analytical standards for chromatography analysis for ACTP ($\text{C}_8\text{H}_9\text{NO}_2$) and ATL ($\text{C}_{14}\text{H}_{22}\text{N}_2\text{O}_3$) were purchased



Scheme 1. Chemical structures of ACTP and ATL.

from Sigma–Aldrich (Scheme 1). Distilled water used in both pilot plants was obtained from the Plataforma Solar de Almería (PSA) distillation plant (conductivity $< 10 \mu\text{S cm}^{-1}$, $\text{Cl}^- = 0.7\text{--}0.8 \text{ mg L}^{-1}$, $\text{NO}_3^- = 0.5 \text{ mg L}^{-1}$, organic carbon $< 0.5 \text{ mg L}^{-1}$). The heterogeneous photocatalytic degradation tests were carried out using a slurry suspension ($200 \text{ mg L}^{-1} \text{ TiO}_2$) of Degussa (Frankfurt, Germany) P-25 TiO_2 (surface area $51\text{--}55 \text{ m}^2 \text{ g}^{-1}$, size of the primary particles: $30\text{--}50 \text{ nm}$, 80% anatase, 20% rutile). Photo-Fenton experiments were performed using iron sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), reagent-grade hydrogen peroxide (30% w/v) and sulfuric acid for pH adjustment. The chemical composition of the synthetic municipal wastewater treatment plant effluent (S.E.) was adapted of OECD Guidelines for Testing of Chemicals [28]: Peptone (32 mg L^{-1}), meat extract (22 mg L^{-1}), urea (6 mg L^{-1}), K_2HPO_4 (28 mg L^{-1}), $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (4 mg L^{-1}), NaCl (7 mg L^{-1}) and $\text{Mg}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ (2 mg L^{-1}), $\text{TOC} = 20 \text{ mg L}^{-1}$.

2.2. Experiment set-up

All experiments were carried out under sunlight in a pilot plant at the PSA (latitude 37°N , longitude 2.4°W). A compound parabolic collector field (CPC) has been used for the photocatalytic degradation assays. The pilot plant operates in batch mode and it has been described in detail in previous works [29]. It basically consists of 2 modules connected in series containing each 8 parallel reflectors (3.2 m^2 , polished aluminium) with UV transparent tubular receivers (i.d. 48 mm). The contaminated water flows directly from one to the other and finally to a reservoir tank. A centrifugal pump then returns the water to the collectors in a closed circuit. The overall capacity of the reactor (V_T) is 150 L . It consists of 36 L of total irradiated volume (V_i) and the dead reactor volume (tank + high density polyethylene tubes, 114 L). The experiments were performed during May 2008, between 9 a.m. and 4 p.m.

Solar UV radiation was measured by a global UV radiometer (KIPP&ZONEN, model CUV 4), mounted on a platform tilted 37° (the same as the CPCs), which provides data in terms of incident $W_{\text{UV}} \text{ m}^{-2}$. In this way, the energy reaching any surface in the same position with regard to the sun is measured. With Eq. (1), combination of the data from several days' experiments and their comparison with other photocatalytic experiments is possible.

$$t_{30\text{W},n} = t_{30\text{W},n-1} + \Delta t_n \frac{\text{UV } V_i}{30 V_T}; \quad \Delta t_n = t_n - t_{n-1} \quad (1)$$

where t_n is the experimental time for each sample, UV is the average solar ultraviolet radiation measured during Δt_n , and $t_{30\text{W}}$ is a "normalized illumination time". In this case, time refers to a constant solar UV power of 30 W m^{-2} (typical solar UV power on a perfectly sunny day around noon).

Download English Version:

<https://daneshyari.com/en/article/47858>

Download Persian Version:

<https://daneshyari.com/article/47858>

[Daneshyari.com](https://daneshyari.com)