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Drugs degrading photocatalytically: Kinetics and mechanisms of ofloxacin and atenolol removal on titania suspensions

E. Hapeshi [a], A. Achilleos [a], M.I. Vasquez [a], C. Michael [a], N.P. Xekoukoulotakis [b], D. Mantzavinos [b], D. Kassinos [a,*]

[a] Department of Civil and Environmental Engineering, University of Cyprus, 75 Kallipoleos St., 1678 Nicosia, Cyprus
[b] Department of Environmental Engineering, Technical University of Crete, Polytechneioupolis, GR-73100 Chania, Greece

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ABSTRACT

The conversion of the antibiotic ofloxacin and the β-blocker atenolol by means of TiO_2 photocatalysis was investigated. Irradiation was provided by a UVA lamp at 3.37×10^{-6} einstein/s photon flux, while emphasis was given on the effect of catalyst type and loading (50–1500 mg/L), initial substrate concentration (5–20 mg/L), initial pH (3–10) and the effect of H_2O_2 (0.07–1.4 mM) as an additional oxidant on substrate conversion and mineralization in various matrices (i.e. pure water, groundwater and treated municipal effluent). Conversion was assessed measuring sample absorbance at 288 and 224 nm for ofloxacin and atenolol, respectively, while mineralization measuring the dissolved organic carbon. Degussa P25 TiO_2 was found to be more active than other TiO_2 samples for either substrate degradation, with ofloxacin being more reactive than atenolol. Conversion generally increased with increasing catalyst loading, decreasing initial substrate concentration and adding H_2O_2, while the effect of solution pH was substrate-specific. Reaction rates, following a Langmuir–Hinshelwood kinetic expression, were maximized at a catalyst to substrate concentration ratio (w/w) of 50 and 15 for ofloxacin and atenolol, respectively, while higher ratios led to reduced efficiency. Likewise, high concentrations of H_2O_2 had an adverse effect on reaction, presumably due to excessive oxidant scavenging radicals and other reactive species. The ecotoxicity of ofloxacin and atenolol to freshwater species *Daphnia magna* was found to increase with increasing substrate concentration (1–10 mg/L) and exposure time (24–48 h), with atenolol being more toxic than ofloxacin. Photocatalytic treatment eliminated nearly completely toxicity and this was more pronounced for atenolol.

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1. Introduction

During the past fifteen years, pharmaceuticals and personal care products (PPCPs) have been recognized as an important class of organic pollutants due to their potential hazardous effects on humans and the aquatic ecosystem (Calza et al., 2008). Many studies have reported the presence of PPCPs at concentrations ranging between μg/L and ng/L levels in aquatic environments worldwide (Fatta et al., 2007). Pharmaceuticals are designed to have physiological effect on humans and animals at trace concentrations. These compounds are persistent against biological degradation and natural attenuation and, therefore, may remain in the environment for a long time (Klavarioti et al., 2009).

* *Corresponding author*. Tel.: +357 22892275; fax: +357 22892295.
E-mail address: dfatta@ucy.ac.cy (D. Kassinos).
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Antibiotics have been used for several decades in both human and veterinary medicine. They are often partially metabolized in the organism and are excreted in the form of the parent substance or as metabolites in urine into wastewater. These substances were shown to be quite resistant to biodegradation (Kümmerer, 2009). Ofloxacin is one of the most frequently used fluorinated quinolone-type antibiotics with a broad spectrum of activity against both Gram-positive and Gram-negative bacteria (Zivanovic et al., 2006).

Another important class of pharmaceuticals is β-blockers, which are also released in the environment through urban wastewater treatment plants' discharges (Gros et al., 2006). Atenolol is one of the most frequently used β-blockers against cardiovascular diseases, because of its anti-hypertensic and anti-arrhytmic properties (Arvand et al., 2008).

Significant concentrations of these pharmaceuticals have been detected in municipal sewage. According to Radjenović et al. (2009) a range of 0.09–31.7 μg/L was found for ofloxacin in the raw effluents of a Spanish wastewater treatment plant while the corresponding values for atenolol were 0.84–2.8 μg/L. The study also determined the daily aqueous mass output loads for the compounds though the treated wastewater which are 2.1–267.2 g/d for ofloxacin and 2.2–50.8 g/d for atenolol.

Conventional sewage treatment plants are not able to degrade residues of these chemicals, and as a result they are introduced into the aquatic environment (Nikolaou et al., 2007). During the past years many investigations on chemical and biological technologies have been reported for the decomposition of organic pollutants in aqueous matrices. In this context, various advanced oxidation processes (AOPs) have been successfully employed for the degradation of a wide range of organic pollutants in water and wastewater (Parsons, 2004). Among the various AOPs, heterogeneous semiconductor photocatalysis using TiO_2 as the photocatalyst has been found capable of achieving complete oxidation of the organic pollutants via hydroxyl radicals HO• and/or valence band holes h^+ generated when the semiconductor is exposed to UV irradiation (Fujishima et al., 2008). TiO_2 is cheap, commercially available in various crystalline forms and particle characteristics, non-toxic and photochemically stable. Moreover, TiO_2 photocatalysis works at ambient conditions and may be induced by solar irradiation (Malato et al., 2009).

The present work focuses on the degradation of ofloxacin and atenolol via TiO_2 photocatalysis and provides information on the influence of different parameters, including TiO_2 loading, initial substrate concentration, addition of hydrogen peroxide, pH of the aqueous solution and the water matrix, on the drug conversion and dissolved organic carbon reduction. Moreover, the acute and chronic toxicity of ofloxacin and atenolol to *D. magna* prior to and after photocatalytic treatment is assessed. The original aspects of the present work include the elucidation of the kinetics and mechanisms of the ofloxacin and atenolol removal on titania suspensions and also the investigation of the toxicity potential of the solutions during TiO_2 photocatalysis. In addition, to the authors' knowledge, this is the first study that includes a systematic examination of the various parameters that affect the oxidation process of the two pharmaceutical compounds including the type and loading of the catalyst, initial substrate concentration, addition of hydrogen peroxide, pH and water matrix.

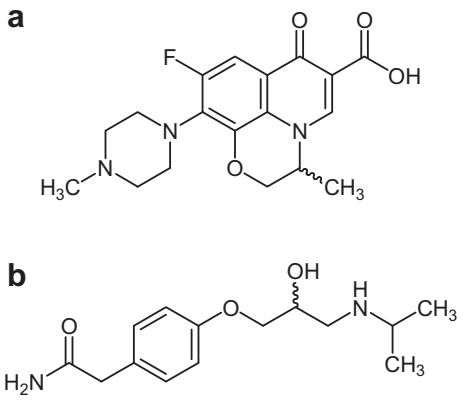
2. Materials and methods

2.1. Chemicals

Ofloxacin and atenolol (their chemical structures are shown in Scheme 1 and major properties are summarized in Table 1) were purchased from Sigma–Aldrich and used as received. Solutions containing each compound under investigation at concentrations up to 20 mg/L were prepared by adding the appropriate mass of the pharmaceutical to ultrapure water (UPW) and stirred for several hours to ensure complete dissolution. Such concentrations, although considerably greater than those typically found in waters, were chosen to allow (i) the assessment of process efficiency within a measurable time scale, and (ii) the accurate determination of residual concentrations with the analytical techniques employed in this work. Groundwater (GW) taken from a pumping well and the effluent from the central municipal wastewater treatment plant (WWTPEf) of Limassol, Cyprus, were also spiked with either substrate to assess the effect of water matrix on conversion. The quality characteristics of the GW and WWTPEf are presented in Tables 2 and 3, respectively. Hydrogen peroxide (35% w/w solution) was supplied by Merck. Six commercially available TiO_2 samples were employed, namely (a) Degussa P25 supplied by Degussa AG (anatase:rutile 75:25, 21 nm particle size, 50 m^2/g BET area); (b) Hombikat UV 100 supplied by Sachtleben Chemie GmbH (anatase, 5 nm particle size, >250 m^2/g BET area); (c) Tronox A-K-1 (anatase, 20 nm particle size, 90 m^2/g BET area); (d) Tronox TR (rutile, 300 nm particle size, 5.5 m^2/g BET area); (e) Tronox TR-HP-2 (rutile, 7 m^2/g BET area) supplied by Kerr-McGee Chemicals LLC; (f) Aldrich (A) supplied by Aldrich (anatase, 15 nm particle size, 190–290 m^2/g BET area).

2.2. Photocatalytic experiments

Photocatalytic experiments with artificial irradiation were performed in a photochemical reactor (ACE Glass Inc., USA)



Scheme 1 – Chemical structures of (a) ofloxacin and (b) atenolol.

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