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Solar photo-Fenton process on the abatement of antibiotics at a pilot scale: Degradation kinetics, ecotoxicity and phytotoxicity assessment and removal of antibiotic resistant enterococci

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ABSTRACT

This work investigated the application of a solar driven advanced oxidation process (solar photo-Fenton), for the degradation of antibiotics at low concentration level (μg L^{-1}) in secondary treated domestic effluents at a pilot-scale. The examined antibiotics were ofloxacin (OFX) and trimethoprim (TMP). A compound parabolic collector (CPC) pilot plant was used for the photocatalytic experiments. The process was mainly evaluated by a fast and reliable analytical method based on a UPLC-MS/MS system. Solar photo-Fenton process using low iron and hydrogen peroxide doses ($[Fe^{2+}]_0$ = 5 mg L^{-1}; $[H_2O_2]_0$ = 75 mg L^{-1}) was proved to be an efficient method for the elimination of these compounds with relatively high degradation rates. The photocatalytic degradation of OFX and TMP with the solar photo-Fenton process followed apparent first-order kinetics. A modification of the first-order kinetic expression was proposed and has been successfully used to explain the degradation kinetics of the compounds during the solar photo-Fenton treatment. The results demonstrated the capacity of the applied advanced process to reduce the initial wastewater toxicity against the examined plant species (*Sorghum saccharatum*, *Lepidium sativum*, *Sinapis alba*) and the water flea *Daphnia magna*. The phytotoxicity of the treated samples, expressed as root growth inhibition, was higher compared to that observed on the inhibition of seed germination. Enterococci, including those resistant to OFX and TMP, were completely eliminated at the end of the treatment. The total cost of the full scale unit for the treatment of 150 m^3 day^{-1} of secondary wastewater effluent was found to be 0.85 € m^{-3}.

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1. Introduction

Antibiotics are among the most frequently prescribed medications since they are commonly used in human and veterinary medicine for the purpose of treating bacterial infections (Kümmerer, 2009). Antibiotics may escape conventional biological treatment and thus enter receiving environmental media either in their parent form or as transformation products. It appears from the literature that the greatest risk related to their presence in the environment is their potential to cause antibiotic resistance among bacteria (Akiyama and Savin, 2010; Novo and Manaia, 2010). Although antibiotics are found in the environment at sub-inhibitory levels, relatively low concentrations of antimicrobial agents can still promote bacterial resistance (Castiglioni et al., 2008).

Reusable treated wastewater (especially for irrigation purposes in countries with dry weather conditions) should be free of antibiotic compounds; therefore the application of new and improved wastewater treatment technologies are a necessary task. Advanced Oxidation Processes (AOPs) are considered promising methods for the remediation of contaminated wastewaters containing non-biodegradable organic pollutants (Oller et al., 2011; Rizzo, 2011). These processes involve the generation of powerful transitory species, principally the hydroxyl radical ($HO^{\bullet}$) (Andreozzi et al., 1999). Among the various AOPs, Fenton process has been extensively used with success for the oxidation of many classes of organic compounds due to its high efficiency to generate $HO^{\bullet}$ by the catalytic decomposition of hydrogen peroxide in reaction with ferrous (or ferric) ions in acidic medium (Perez-Estrada et al., 2005). In the photo-Fenton process, additional reactions occur in the presence of light (artificial or solar) that produce additional $HO^{\bullet}$ (Pignatello, 1992), thus increasing the efficiency of the process.

OFX is a second generation fluoroquinolone antibiotic (Okeri and Arhewoh, 2008). It is an orally administered broad spectrum antibacterial drug active against most Gram-negative bacteria, many Gram-positive bacteria (staphylococci and enterococci) and some anaerobes (Nau et al., 1994). TMP belongs to a family of synthetic 2,4-diaminopyrimidines and is used either alone or in combination with sulfonamides for the treatment of specific bacterial infections (Li et al., 2005). It is a broad-spectrum antimicrobial agent which inhibits the enzyme dihydrofolate reductase (Barbarin et al., 2002). OFX and TMP have been reported in many environmental monitoring studies, detected in wastewater treatment plant effluents and in natural waters worldwide at concentrations of $\mu g\ L^{-1}$ (Watkinson et al., 2009; Li and Zhang, 2011).

The overall aim of this work was to (i) investigate at a pilot-scale the degradation of OFX and TMP when present in secondary effluents at $\mu g\ L^{-1}$ concentration level; (ii) determine the degradation kinetics for both compounds; (iii) assess the acute toxicity of the parent compounds and their oxidation by-products generated during the process using a set of bio- and phyto- assays and (iv) assess the efficiency of the process to remove the antibiotic resistant enterococci.

2. Materials and methods

2.1. *Chemicals*

The standards of antibiotics (OFX, Sigma Aldrich; TMP, Fluka) used were of high purity grade and were not subjected to any further purification. The reagents used in the solar photo-Fenton experiments were $FeSO_4 \cdot 7H_2O$ (Sigma Aldrich) and H_2O_2 (30% w/w, Merck). The pH of the wastewater was adjusted by 2 N H_2SO_4 (Merck). The Fenton reaction was terminated at specific time intervals by adding: (i) methanol (Fluka) for the chromatographic analysis, (ii) anhydrous Na_2SO_3 (Sigma Aldrich) for the DOC measurements and (iii) MnO_2 (particle size 10 μm, reagent grade $\geq$ 90%) (Sigma Aldrich) for the COD determination. LC/MS-grade solvents such as methanol (Fluka) and acetonitrile (Sigma Aldrich), formic acid (Fluka) and ammonium acetate (Sigma Aldrich) were used for the chromatographic analysis. Ultrapure water (Milli-Q) was also used. For toxicity and microbiological analyses the treated solutions were neutralized with 2 N NaOH (Merck) while the residual H_2O_2 was removed from the treated samples with commercially available catalase solution (*Micrococcus lysodeikticus* 170,000 U mL^{-1}, Fluka) (Zapata et al., 2009a).

2.2. *Experimental procedure*

The experiments were performed using a compound parabolic collector (CPC) pilot plant installed at the sewage treatment plant at the University of Cyprus (UCY), for solar photocatalytic degradation applications. The pilot plant is comprised of twelve borosilicate glass tubes (Ø 55 mm) and is mounted on curved polished aluminum reflectors. The reflectors are mounted on a fixed platform tilted at the local latitude (35°). Storage tank, flow meters, sensors (pH, DO and T), air blower, UV radiometer (UV_air_ABC), control panel, pipes, and fittings complete the installation. The storage tank of the pilot unit is directly connected to the main secondary tank of the sewage treatment plant at the UCY and was filled with 250 L of wastewater for each experiment. The plant was operated in batch mode. The wastewater flows directly from one tube to the other and finally to the reservoir tank. A centrifugal pump (600 L h^{-1}) returns the wastewater from the tank to the collectors in a closed circuit. The overall volume capacity of the reactor V_T is 250 L and the total irradiated volume V_i (tubes volume) is 85.4 L. The irradiated surface of the pilot plant is 5.65 m^2. The secondary effluent was analyzed before use for a number of quality characteristics (Table 1). Note that OFX and TMP were not detected in the secondary effluent by UPLC-MS/MS.

The secondary effluent before entering the tank passes through a cylindrical filter (200 μm pore size, Ø 25.4 mm, PALAPLAST, Greece) installed at the entrance of the storage tank. This is necessary to avoid fouling problems in the mechanical parts of the pilot plant. The temperature in the reactor as well as the UV solar radiation was continuously recorded. The UV radiometer is mounted on the platform of the CPCs. During the loading of the reactor with the