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Light-induced catalytic transformation of ofloxacin by solar Fenton in various water matrices at a pilot plant: Mineralization and characterization of major intermediate products☆

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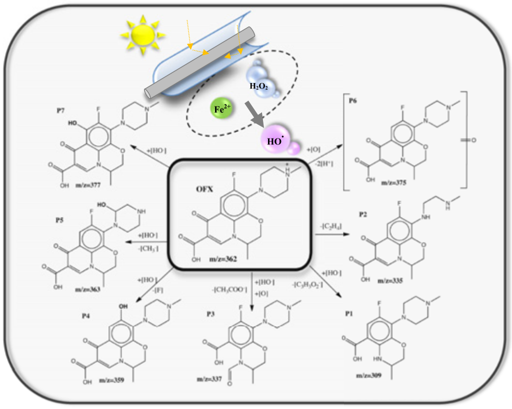
HIGHLIGHTS

- The pilot-scale solar Fenton degradation of ofloxacin was studied.
- Mineralization was lower in the wastewater matrices due to the presence of organics.
- Toxicity was found to originate from the oxidation of DOM present in the RE.
- The transformation of OFX proceeded through the formation of seven intermediates.
- The degradation pathway exhibited differences among the four matrices.

GRAPHICAL ABSTRACT



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ABSTRACT

This work investigated the application of a solar driven advanced oxidation process (solar Fenton), for the degradation of the antibiotic ofloxacin (OFX) in various environmental matrices at a pilot-scale. All experiments were carried out in a compound parabolic collector pilot plant in the presence of doses of H_2O_2 (2.5 mg L^{-1}) and at an initial Fe^{2+} concentration of 2 mg L^{-1}. The water matrices used for the solar Fenton experiments were: demineralized water (DW), simulated natural freshwater (SW), simulated effluent from municipal wastewater treatment plant (SWW) and pre-treated real effluent from municipal wastewater treatment plant (RE) to which OFX had been spiked at 10 mg L^{-1}. Dissolved organic carbon removal was

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Abbreviations: AOPs, Advanced oxidation processes; CPCs, Compound parabolic collectors; DOC, Dissolved organic carbon; DOM, Dissolved organic matter; DW, Demineralized water; FQs, Fluoroquinolones; HPLC-DAD, High performance liquid chromatography with diode array detector; LC–ToF-MS, Liquid chromatography–time of flight-mass spectrometry; MWTP, Municipal wastewater treatment plant; NDIR, Non-dispersive infrared detector; OFX, Ofloxacin; RE, Pre-treated real effluent from municipal wastewater treatment plant; SW, Simulated natural freshwater; SWW, Simulated effluent from municipal wastewater treatment plant; TOC, Total organic carbon; TPs, Transformation products.

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found to be dependent on the chemical composition of the water matrix. OFX mineralization was higher in DW (78.1%) than in SW (58.3%) at 12 mg L^{-1} of H_2O_2 consumption, implying the complexation of iron or the scavenging of hydroxyl radicals by the inorganic ions present in SW. On the other hand, the presence of dissolved organic matter (DOM) in SWW and RE, led to lower mineralization per dose of H_2O_2 compared to DW and SW. The major transformation products (TPs) formed during the solar Fenton treatment of OFX, were elucidated using liquid chromatography–time of flight-mass spectrometry (LC–ToF-MS). The transformation of OFX proceeded through a defluorination reaction, accompanied by some degree of piperazine and quinolone substituent transformation while a hydroxylation mechanism occurred by attack of the hydroxyl radicals generated during the process leading to the formation of TPs in all the water matrices, seven of which were tentatively identified. The results obtained from the toxicity bioassays indicated that the toxicity originates from the DOM present in RE and its oxidation products formed during the photocatalytic treatment and not from the TPs resulted from the oxidation of OFX.

1. Introduction

Antibiotics have been detected in various compartments of the aquatic environment worldwide (Fatta-Kassinos et al., 2011; Jeong et al., 2010). This indicates the ineffectiveness of the currently most frequently applied conventional biological treatment processes to remove such compounds adequately from the domestic wastewaters (Michael et al., 2013). Looking into the transformation of the antibiotics in the environment is very important for understanding the fate and behavior of these compounds. The presence of antibiotics and their transformation products (TPs) in low concentrations has been associated to chronic toxicity and the prevalence of resistance to antibiotics in bacterial species (Le-Minh et al., 2010). The consequences are particularly worrying in aquatic organisms as these are subjected to multigenerational exposure (Rosal et al., 2010). Although antibiotics are found in the environment at sub-inhibitory levels, relatively low concentrations of them can still promote bacterial resistance (Castiglioni et al., 2008). Indeed, antibiotic-resistant bacteria have been detected in wastewater effluents (Guardabassi et al., 2002; Akiyama and Savin, 2010; Novo and Manaia, 2010), surface water (Ash et al., 2002) and drinking water (Schwartz et al., 2003).

Fluoroquinolones (FQs) are broad-spectrum antibacterial agents widely used for treating bacterial infections (Paul et al., 2007). Their major mode of action is the inhibition of DNA replication in bacteria via interference of the normal function of DNA topoisomerase (Lhiaubet-Vallet et al., 2009). Although conventional activated sludge treatment can remove a significant fraction of FQs primarily by adsorption to sludge, their removal is incomplete, and FQs are discharged in treated wastewater (Paul et al., 2010). A representative example is ofloxacin (OFX) that has been frequently detected in various environmental compartments (Miao et al., 2004; Lin et al, 2009; Fatta-Kassinos et al., 2010; Zuccato et al., 2010). Regarding its environmental effects, Kümmerer et al. (2000) have found OFX to be genotoxic at environmentally-relevant concentrations while its phototransformation products were found to induce genotoxic effects (Vasquez et al., 2012). OFX was also categorized as posing a high hazard in the aquatic system due to the reuse of biosolids on agriculture land (Langdon et al., 2010).

Promising technologies for the treatment of non-biodegradable and/or toxic compounds are the advanced oxidation processes (AOPs), involving the in situ production of hydroxyl radicals (HO•HO•). Photo-Fenton has gained increasing attention due to its environmentally friendly application and the prospect of operating under solar irradiation hence, lowering the operation cost considerably (Malato et al., 2009; Mendez-Arriaga et al., 2010). The Fenton process consists of the use of ferrous iron salts and hydrogen peroxide in acidic medium. The combination of both reagents (in the presence of UV–vis irradiation) has a very strong synergetic effect because irradiation with light up to 580 nm leads to photoreduction of dissolved ferric iron to ferrous iron producing additional hydroxyl radicals. The mechanism, via which this process mainly occurs, has been comprehensively presented in the literature (Buda et al., 2001; Malato et al., 2009).

In a previous study, the pilot-scale solar degradation of trimethoprim in different water matrices was investigated (Michael et al., 2012), while the current work entailed the investigation of OFX during solar Fenton treatment at a pilot scale. OFX was selected in the present study due to its high photoactivity, its high consumption and presence in wastewater effluents and the aquatic environment. The degradation of OFX induced by various AOPs at a bench scale has been investigated under different experimental conditions: photocatalysis in the presence of TiO_2 (Calza et al., 2008; Michael et al., 2010; Vasquez et al., 2012), solar Fenton (Michael et al., 2010), sonophotocatalysis (Hapeshi et al., in press), photolysis (Wammer et al., 2012) and γ-radiolysis (Santoke et al., 2009). The photocatalytic transformation mechanisms of OFX during solar Fenton oxidation have not been published yet, even if studies relating to its environmental risks are reported in the literature (Albini and Monti, 2003; Park et al., 2002).

With this aim in mind, attention was paid to: (i) determining the effect of the composition of various aqueous matrices on the mineralization; (ii) elucidating the major transformation products (TPs) formed during the solar Fenton treatment of OFX; and (iii) assessing the acute toxicity of OFX and its oxidation products as a whole mixture generated during the treatment process. According to the authors' knowledge the current work, although its general methodology has been presented in various other publications (Klamerth et al., 2009, 2010; Sirtori et al., 2010), is the first one revealing data regarding the pilot-scale solar Fenton oxidation of OFX in four water matrices of different compositions, the elucidation of the main TPs and finally the acute toxicity of OFX and its TPs.

2. Materials and methods

2.1. Chemicals

High purity (>98.5%) OFX standard (CAS number 82419-36-1) was purchased from Sigma-Aldrich. The reagents used in the solar Fenton experiments were iron sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) and hydrogen peroxide (H_2O_2 30%, w/w) both provided by Panreac. The pH of the matrix under investigation was adjusted (around 2.8–2.9) by 2 N H_2SO_4 supplied by Panreac. The treated solutions were neutralized by 2 N NaOH (Panreac) for toxicity analyses. HPLC-grade acetonitrile (Panreac) and formic acid (Fluka) were used for the chromatographic analysis. Calcium sulfate dehydrate ($CaSO_4 \cdot 2H_2O$, Panreac), magnesium sulfate ($MgSO_4$, Sigma-Aldrich) and potassium chloride (KCl, J.T. Baker) were used for the simulated natural freshwater (SW) preparation. Peptone (Biolife), meat extract (Biolife), urea (Fluka), magnesium sulfate heptahydrate ($MgSO_4 \cdot 7H_2O$, Fluka), dipotassium phosphate (K_2HPO_4, Riedel-de Haën), calcium chloride