



Electrochemical mineralization of the antibiotic levofloxacin by electro-Fenton-pyrite process



Natija Barhoumi^a, Lazhar Labiadh^a, Mehmet A. Oturan^{b,*}, Nihal Oturan^b, Abdellatif Gadri^a, Salah Ammar^{a,c}, Enric Brillas^{d,*}

^a Département de chimie, Faculté des Sciences de Gabès, Université de Gabès, Cité Erriadh, 6072 Gabès, Tunisia

^b Université Paris-Est, Laboratoire Géomatériaux et Environnement, EA 4508, UPEM, 5 Bd Descartes, 77454 Marne-la-Vallée Cedex 2, France

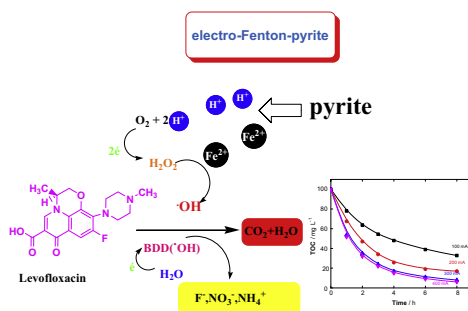
^c Faculté des Sciences de Bizerte, Université de Carthage, Tunisia

^d Laboratori d'Electroquímica dels Materials i del Medi Ambient, Departament de Química Física, Facultat de Química, Universitat de Barcelona, Martí i Franquès 1-11, 08028 Barcelona, Spain

HIGHLIGHTS

- Degradation of levofloxacin by electro-Fenton-pyrite using a BDD/carbon-felt cell.
- Pyrite powder in suspension regulates pH 3.0 and a catalytic Fe^{2+} content of 0.2 mM.
- Almost total mineralization at low levofloxacin concentration and high current.
- Oxalic and oxamic acids as main final products upon prolonged electrolysis.
- Release of F^- and NO_3^- as pre-eminent ions with a lesser proportion of NH_4^+ ion.

GRAPHICAL ABSTRACT



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ABSTRACT

Levofloxacin is a large spectrum antibiotic from fluoroquinolones family, widely used and detected in natural waters. Here, this drug was degraded by a novel heterogeneous electro-Fenton (EF) process, so-called EF-pyrite, in which pyrite powder in suspension regulates the solution pH to 3.0 and supplies 0.2 mM Fe^{2+} as catalyst to the solution. Trials were performed with a stirred boron-doped diamond (BDD)/carbon-felt cell under O_2 bubbling for cathodic H_2O_2 generation. Hydroxyl radicals formed from water oxidation at the BDD anode and in the bulk from Fenton's reaction between Fe^{2+} and H_2O_2 were the main oxidizing agents. The effect of applied current and antibiotic concentration over the mineralization rate and degree, mineralization current efficiency and specific energy consumption was studied. An almost total mineralization was achieved for a 0.23 mM drug solution operating at 300 mA for 8 h. The kinetic decay of the drug was followed by reversed-phase HPLC and obeyed a pseudo-first-order reaction. Ion-exclusion HPLC analysis of treated solutions revealed that oxalic and oxamic acids, the most persistent final products, were the predominant pollutants remaining in solution at long electrolysis time. Ion chromatography analysis confirmed the release of F^- , NO_3^- and NH_4^+ ions during levofloxacin mineralization.

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* Corresponding authors. Tel.: +33 149 32 90 65 (M.A. Oturan), +34 93 40 21 223 (E. Brillas).

E-mail addresses: mehmet.oturan@univ-paris-est.fr (M.A. Oturan), brillas@ub.edu (E. Brillas).

1. Introduction

The growing presence of antibiotic drugs in natural waters is an emerging environmental issue due to their potential bioactivity (Kümmerer, 2009; Sirés and Brillas, 2012). Pharmaceuticals industries, hospitals and urban wastewater effluents represent important points of antibiotics discharge into the aquatic environment leading to a significant effect on the physical, chemical and biological composition of receptor water bodies. Antibiotics are ineffectively removed in wastewater treatment plants (WWTPs) because of their recalcitrance to conventional physicochemical methods (Stackelberg et al., 2004; Klavarioti et al., 2009; Homem and Santos, 2011). The biotic/abiotic degradation of such drugs leads to the formation of toxic and persistent chemicals, which are accumulated in aquatic organisms (Dirany et al., 2012; Laurencé et al., 2014). It has been documented that some antibiotics cause long-term, irreversible changes to micro-organisms genome, affect the endocrine systems of fishes and invertebrates and are toxic on algae and small invertebrates (Crane et al., 2006; Fent et al., 2006; Pomati et al., 2008). The development of powerful oxidation technologies is then needed for the remediation of wastewaters containing antibiotics to prevent their harmful effects on living beings.

Over the last 15 years, ozonation and advanced oxidation processes (AOPs) have shown their potentiality to effectively remove organic pollutants from waters (Rosal et al., 2008; Klavarioti et al., 2009; Sirés and Brillas, 2012). The common feature of EAOPs is the in situ generation of hydroxyl radical ($\cdot\text{OH}$), with so high standard reduction potential ($E^\circ = 2.80 \text{ V/SHE}$) that can oxidize most organics up to mineralization (Pignatello et al., 2006; Oturan and Aaron, 2014). Lately, electrochemical AOPs (EAOPs) based on Fenton's reaction chemistry have received great attention for wastewater remediation (Brillas et al., 2009; Sirés et al., 2014; Vasudevan and Oturan, 2014), because of their simplicity, great efficiency and relative low cost. The most ubiquitous of these EAOPs is electro-Fenton (EF), in which the weak oxidant H_2O_2 is continuously generated and supplied to an acidic contaminated solution from the two-electron cathodic reduction of O_2 gas as follows:



Reaction (1) is very efficient by using carbonaceous cathodes like carbon nanotubes (Khataee et al., 2013), activated carbon fiber (Yamanka et al., 2008), graphite felt (Panizza and Oturan, 2011), carbon felt (Oturan et al., 2012; El-Ghenymy et al., 2014; Yahya et al., 2014; Ammar et al., 2015), carbon-polytetrafluoroethylene O_2 or air diffusion (Ammar et al., 2006; Guinea et al., 2010; Moreira et al., 2013) and boron-doped diamond (BDD) (Cruz-González et al., 2010; Daskalaki et al., 2013).

In EF, the oxidation power of generated H_2O_2 is strongly enhanced by adding Fe^{2+} ion to form Fe^{3+} ion and $\cdot\text{OH}$ in the bulk through Fenton's reaction (2). The generation of $\cdot\text{OH}$ is continuous since Fe^{3+} ion formed in reaction (2) is concomitantly reduced to Fe^{2+} ion by reaction (3) at the cathode, thereby making the process catalytic (Brillas et al., 2009).

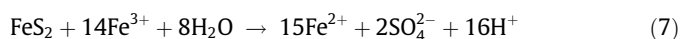
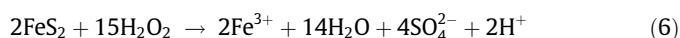
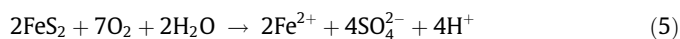


When an undivided cell with a high O_2 -overpotential anode (M) is used in EF, organics can be destroyed not only by $\cdot\text{OH}$ formed in the bulk from Fenton's reaction (2), but also by physisorbed $\text{M}(\cdot\text{OH})$ produced as intermediate from water oxidation by reaction (4) (Panizza and Cerisola, 2009; Rodrigo et al., 2010; Sirés et al., 2014):



The BDD thin-film electrodes are preferred in EAOPs because of their greater production of reactive BDD($\cdot\text{OH}$) than other common anodes like Pt and PbO_2 (Ciríaco et al., 2009; Cavalcanti et al., 2013; Ferreira et al., 2013), making the process significantly more performing and allowing to mineralize aromatic and aliphatic organic pollutants in much larger extent (Mhemdi et al., 2013; El-Ghenymy et al., 2014).

The classical EF process has some critical limitations like the need of operating at pH 3 for an optimum run and the precipitation of soluble iron species used as catalyst (Sirés et al., 2014). These drawbacks could be overcome by using a Fe containing solid catalyst as source of Fe^{2+} ion instead of a soluble iron salt. In previous work, we have tested that pyrite can act as heterogeneous catalyst in EF, so-called EF-pyrite process, to enhance the degradation of tyrosol, a phenolic component of olive oil mill wastewaters, using a BDD/carbon-felt cell (Ammar et al., 2015). Pyrite is a low-cost and abundant natural iron sulfur mineral, which can provide iron ions from reactions 5–7. It seems then a good candidate to be employed as heterogeneous catalyst in EF because we proved that it self-regulated the Fe^{2+} content and the solution pH in solution in the presence of dissolved O_2 through reactions 5–7. Moreover, after the treatment, pyrite can be easily recovered from filtration and reused.



To gain a better knowledge on the oxidation ability of this novel EF-pyrite process over complex molecules, we have undertaken a study on the oxidative degradation of synthetic aqueous solutions of levofloxacin ($\text{C}_{18}\text{H}_{20}\text{FN}_3\text{O}_4$, see molecular structure in Fig. SM-1). This drug is a recently developed large spectrum antibiotic, very active against gram-negative and gram-positive bacteria, which belongs to the fourth generation of the fluoroquinolones family. Levofloxacin has been chosen because there is scarce information about the destruction power of EAOPs over fluoroquinolones (Guinea et al., 2010). In view of its widespread use, levofloxacin has been detected at low levels of ng L^{-1} – $\mu\text{g L}^{-1}$ in surface waters (Sturini et al., 2012) and WWTPs effluents (Lindberg et al., 2014). Recent studies have reported its degradation by photolysis (Ge et al., 2015), $\text{S}_2\text{O}_8^{2-}/\text{Fe}^{2+}$, $\text{S}_2\text{O}_8^{2-}/\text{H}_2\text{O}_2$ and $\text{S}_2\text{O}_8^{2-}/\text{OH}^-$ (Epold and Dulova, 2015), sonolysis (Guo et al., 2010), ozonation (Nasuhoglu et al., 2012; Hamdi El Najjar et al., 2013) and TiO_2 photocatalysis (An et al., 2010; Nasuhoglu et al., 2012). Table SM-1 collects the main results for the EF and related treatments of pharmaceuticals in waters.

This paper presents the results obtained for the electrochemical mineralization of 200 mL of acidic aqueous solutions of levofloxacin by EF-pyrite using a stirred BDD/carbon-felt cell. Antibiotic concentrations higher than those found in natural waters were used to check the oxidation ability of this EAOP for wastewater treatment. The influence of applied current and antibiotic content on the mineralization rate and degree and the mineralization current efficiency (MCE) was examined. Comparative experiments with a Pt anode were performed to better clarify the role of oxidizing hydroxyl radicals generated. UV-vis spectrometry, high-performance liquid chromatography (HPLC) and ion chromatography were used to follow the levofloxacin abatement and the evolution of aromatics products, generated carboxylic acids and released inorganic ions.

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