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Abatement of the antibiotic levofloxacin in a solar photoelectro-Fenton flow plant: Modeling the dissolved organic carbon concentration-time relationship



Gabriela Coria ^a, Tzayam Pérez ^b, Ignasi Sirés ^{c, **}, Enric Brillas ^c, José L. Nava ^{a, *}

^a Universidad de Guanajuato, Departamento de Geomática e Hidráulica, División de Ingenierías, Av. Juárez 77, Col. Centro, C.P. 36000 Guanajuato, Gto, Mexico

^b Universidad de Guanajuato, Departamento de Ingeniería Química, División de Ciencias Naturales y Exactas, Norial Alta S/N, C.P. 36050 Guanajuato, Gto, Mexico

^c 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

- Mineralization of levofloxacin solutions at pH 3.0 by SPEF in a flow plant.
- Total abatement of the antibiotic and its by-products upon action of $\cdot\text{OH}$ and UV light.
- Mineralization current efficiencies >100% were found, attaining 1500% as maximum.
- 5 Cyclic derivatives and 3 aliphatic carboxylic acids, along with NO_3^- and F^- ions.
- SPEF plant modeled during the oxidation of levofloxacin by a parametric approach.

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ABSTRACT

The degradation of solutions of the antibiotic levofloxacin (LVN) in sulfate medium at pH 3.0 has been investigated at pre-pilot scale by solar photoelectro-Fenton (SPEF) process. The flow plant included an FM01-LC filter-press cell equipped with a Ti|Pt anode and a three-dimensional-like air-diffusion cathode, connected to a compound parabolic collector as photoreactor and a continuous stirred tank under recirculation batch mode. The effect of volumetric flow rate on H_2O_2 electrogeneration from O_2 reduction was assessed. Then, the influence of initial LVN concentration and Fe^{2+} concentration as catalyst on dissolved organic carbon (DOC) removal was thoroughly investigated. LVN was gradually mineralized by SPEF process, with faster DOC abatement at 0.50 mM Fe^{2+} , yielding 100% after 360 min at applied cathodic potential of -0.30 V/SHE . The high mineralization current efficiency (MCE) and low specific energy consumption (EC_{DOC}) revealed the extraordinary role of homogeneous hydroxyl radicals and natural UV light, which allowed the degradation of the antibiotic and its by-products with MCE values greater than 100%. Five cyclic by-products, *N,N*-diethylformamide and three short-chain linear carboxylic acids were detected by GC-MS and HPLC analyses. A parametric model to simulate the DOC decay versus electrolysis time was implemented for the SPEF pre-pilot flow plant, showing good agreement with experimental data.

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1. Introduction

Quinolones are broad-spectrum antibacterial drugs and, in

modern therapeutics, almost all of them belong to the class of fluoroquinolones. Levofloxacin (LVN, see structure in Table 1) is one of the most popular fluorinated quinolones, being used for the treatment of infectious diseases like pneumonia and abdominal infections (Mandell et al., 2007; Nasuhoglu et al., 2012; El Najjar et al., 2013; Epold et al., 2015). The occurrence of antibiotics in water bodies as a result of their massive and uncontrolled use has raised serious concerns worldwide due to the proliferation of

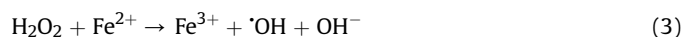
* Corresponding author.

** Corresponding author.

E-mail addresses: i.sires@ub.edu (I. Sirés), jlnm@ugto.mx (J.L. Nava).

antibiotic-resistant bacteria, so-called superbugs, which are responsible for killing an estimated 700,000 people each year (Williard, 2017). Therefore, it is urgent to develop more efficient treatments to transform the antibiotics into less active and more biodegradable molecules (Michael et al., 2013; Blair et al., 2015; Brillas and Sirés, 2015). The ability of several advanced oxidation processes (AOPs) to remove LVN from water has been recently investigated, including ozonation (Witte et al., 2009), photocatalysis (Sturini et al., 2012), conventional Fenton (Wang et al., 2016) and sonochemical AOPs (Guo et al., 2010; Wei et al., 2015). These methods are characterized by the in-situ production of hydroxyl radical ($\cdot\text{OH}$) at ambient conditions, giving rise to effective, efficient, safe and eco-friendly treatments that may allow the complete mineralization of the organic matter (Dirany et al., 2012; Oturan and Aaron, 2014).

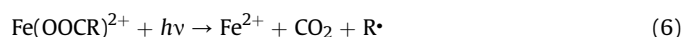
Among the electrochemical AOPs, the performance of electro-Fenton (EF) process with carbon felt and activated fiber cathodes to degrade LVN has been recently reported (Gong et al., 2016; Yahya et al., 2016; Liu et al., 2017). In general, these systems allowed a fast decay of LVN concentration and a final mineralization >90% at 360–480 min. However, current efficiencies were very low, attaining 40–50% as maximum (Yahya et al., 2016; Liu et al., 2017). In EF with large 3D-like cathodes, Fenton's reagent ($\text{Fe}^{2+} + \text{H}_2\text{O}_2$) can be continuously generated upon two-electron reduction of gaseous or dissolved O_2 by reaction (1) and mono-electronic conversion of Fe^{3+} to Fe^{2+} by reaction (2), thus yielding large amounts of free $\cdot\text{OH}$ in the bulk from Fenton's reaction (3) at optimum pH near 3 (Brillas et al., 2000; Sirés et al., 2014; Sopaj et al., 2015; Lanzalaco et al., 2017).



In undivided electrolytic cells, adsorbed hydroxyl radicals ($\text{M}(\cdot\text{OH})$) are formed at the surface of active and non-active anodes (M) from water oxidation via reaction (4) (Panizza and Cerisola, 2009; Labiadh et al., 2016). Hence, organic molecules are destroyed by both, free $\cdot\text{OH}$ and adsorbed $\text{M}(\cdot\text{OH})$, although the former radical has much higher oxidation ability to promote combustion (Sirés et al., 2014; Martínez-Huitle et al., 2015).



The decontamination treatment can be significantly accelerated by illuminating the solution with UVA light from either a commercial lamp in photoelectro-Fenton (PEF) or natural sunlight in solar PEF (SPEF). This high energy radiation causes the photoreduction reaction (5) that transforms the main Fe(III) species at acidic pH into Fe^{2+} , as well as the photolysis of some refractory intermediates. A good example of this latter phenomenon is the photodecarboxylation of stable complexes of linear carboxylic acids with Fe(III) from reaction (6) (Sirés et al., 2014; Martínez-Huitle et al., 2015).



In previous works, we have shown some of the interesting features of the SPEF approach to efficiently degrade pesticides (Flox et al., 2007b), pharmaceuticals (Pérez et al., 2017), dyes (Thiam

et al., 2015) and industrial additives (Flox et al., 2007a; Steter et al., 2018). On the other hand, we have studied the cathodic two-electron reduction of oxygen at different carbonaceous substrates, highlighting that graphite felt enhances the H_2O_2 electro-generation owing to its large volumetric area (Coria et al., 2015).

Within the chemical engineering field, several studies have been devoted to modeling the degradation of persistent organic pollutants upon application of AOPs (Royae and Sohrabi, 2012). In contrast, modeling of SPEF treatment of organic contaminants is rather limited, which is mainly due to the very recent demonstration of its great potential. In particular, in a previous work we described, for the first time, a mathematical model to simulate the treatment in a SPEF flow plant. The suggested parametric model to simulate the dissolved organic carbon (DOC) decay of erythromycin versus time showed a good agreement between experimental and theoretical data (Pérez et al., 2017). In such mathematical model, the reaction term implemented to the compound parabolic collector (CPC) used as photoreactor obeyed a zero-order kinetics because of the complex formula of erythromycin having 37 carbon atoms. However, the robustness of our mathematical model needs to be verified for other molecules.

This manuscript reports a study on the SPEF treatment of acidic synthetic solutions of LVN in a pre-pilot flow plant of 6 L capacity. The plant arrangement included an FM01-LC filter-press cell equipped with a Ti|Pt anode and an air-diffusion cathode. The reactor was connected in series with a CPC and a continuous stirred tank (CST). The influence of catalyst and LVN concentrations on the degradation rate, mineralization current efficiency and energy consumption for total mineralization was assessed. Higher drug concentrations than those found in the aquatic environment were tested aiming to know the oxidation ability of the SPEF process. The simulation of DOC decay versus time was performed by using the aforementioned parametric model. The evolution of intermediates was followed by chromatographic techniques.

2. Experimental

2.1. Reagents

All the chemicals used in this study were of analytical grade and were used without further purification. LVN (purity 98%) was obtained from Sigma Aldrich. Heptahydrate ferrous sulfate (purity 99%), anhydrous sodium sulfate (purity 99%), sulfuric acid and sodium hydroxide were supplied from J.T Baker and Fermont. Chromatographic grade acetonitrile and formic acid were purchased from Sigma-Aldrich. Synthetic solutions were prepared with deionized water.

2.2. Flow plant

2.2.1. Description of the SPEF plant

Fig. SM-1 shows the setup of the SPEF pre-pilot plant that combines an FM01-LC filter-press reactor in series with a CPC photoreactor and a mixing tank that contains 6 L of solution. The plant was operated under recirculation batch mode. The undivided electrochemical reactor was equipped with a platinized Ti plate anode (64 cm^2), which was made following the Pechini method, and an unmodified graphite felt pressed on top of carbon cloth as air-diffusion cathode (0.15 cm thickness, 64 cm^2 cross-sectional area). The carbon cloth and graphite felt were provided by ROE Group. The dry face of the cathode was in contact with an air chamber fed with atmospheric air under overpressure regulated with a back-pressure gauge to continuously electrogenerate H_2O_2 from reaction (1). A Dewalt® D55168 air compressor was used for

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