



The effect of the supporting electrolyte on the electrooxidation of enrofloxacin using a flow cell with a BDD anode: Kinetics and follow-up of oxidation intermediates and antimicrobial activity

Jussara F. Carneiro^{a, **}, José M. Aquino^a, Adilson J. Silva^b, Juliana C. Barreiro^c, Quezia B. Cass^a, Romeu C. Rocha-Filho^{a, *}

^a Departamento de Química, Universidade Federal de São Carlos, C.P. 676, 13560-970 São Carlos, SP, Brazil

^b Departamento de Engenharia Química, Universidade Federal de São Carlos, C.P. 676, 13560-970 São Carlos, SP, Brazil

^c Instituto de Química de São Carlos, Universidade de São Paulo, Avenida João Dagnone 1100, 13563-120 São Carlos, SP, Brazil

HIGHLIGHTS

- Use of NaCl led to a significantly faster removal of the fluoroquinolone enrofloxacin.
- Similar TOC removal rates were attained with the five supporting electrolytes.
- With NaCl, most initial intermediates detected by LC–QqTOF were chlorinated.
- Inhibition of antimicrobial activity was not affected by presence of organochlorines.
- Cleavage of fluoroquinolone structure is essential to inhibit antimicrobial activity.

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ABSTRACT

The role of the supporting electrolyte – SE (Na₂SO₄; NaCl; Na₂CO₃; NaNO₃; Na₃PO₄ – 0.1 M ionic strength) in the galvanostatic (10 mA cm⁻²) electrochemical degradation of the fluoroquinolone antibiotic enrofloxacin (ENRO; 100 mg L⁻¹) using a filter-press flow cell with a boron-doped diamond anode was investigated (flow rate, solution volume, and temperature were kept fixed at 420 L h⁻¹, 1.0 L, and 25 °C, respectively). The electrochemical degradation performance with the different SEs was assessed by following up [ENRO], total organic carbon concentration (TOC), oxidation intermediates (detected by LC and LC–QqTOF), and antimicrobial activity towards *Escherichia coli* as the electrolyses progressed. With NaCl as SE, complete removal of ENRO was attained ~10 times faster than with the other salts. The determination of terminal oxidation intermediates (short-chain carboxylic acids) produced during the electrolyses allowed concluding that their nature and number is indeed affected by the salt used as SE, most probably due to distinct electrogenerated oxidants. With NaCl, the antimicrobial activity of the electrolyzed solution decreased gradually (to ~20%) from 8 to 16 h of electrolysis due to the cleavage of the fluoroquinolone structure. On the other hand, with Na₂SO₄, Na₂CO₃ and NaNO₃ as SEs the growth of *Escherichia coli* cells was observed only after ~14 h, whereas it was completely inhibited with Na₃PO₄. Clearly, the electrooxidation and mineralization of ENRO is strongly affected by the SEs used, which determine the degradation mechanism and, consequently, the removal rates of the solution's organic load and antimicrobial activity.

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1. Introduction

Surface and groundwater contamination by pharmaceutical compounds and their metabolites have been reported in numerous

* Corresponding author.

** Corresponding author.

E-mail addresses: jussarafcarneiro@gmail.com (J.F. Carneiro), romeu@ufscar.br (R.C. Rocha-Filho).

studies in the literature (see e.g. Zuccato et al., 2000; Le et al., 2012). Antibiotics are an important class of pharmaceuticals among these environmental contaminants (Klatte et al., 2017), especially the fluoroquinolones (Frade et al., 2014), which are increasingly used because of their broad-spectrum antimicrobial activity. Thus, enrofloxacin (ENRO), a second-generation fluoroquinolone, is widely used in both human and veterinary medicine (Bogaard and Stobberingh, 2000). Fluoroquinolones, similarly to many pharmaceuticals, are only partially metabolized in the body; consequently,

a fraction of the matrix and its metabolites are excreted in urine and feces, thus contaminating the environment (Frade et al., 2014; Klatte et al., 2017). The wide use of antibiotics and their consequent presence in the environment have led to the development of antibiotic resistance by several pathogenic bacteria, a serious problem that has prompted the World Health Organization and other health organs to launch specific action plans to tackle it (Singer et al., 2016). On the other hand, as noted by Lofrano et al. (2017), these antibiotics cannot be efficiently eliminated by conventional wastewater treatment systems. Therefore, several authors have reported on degradation studies of these drugs by Electrochemical Advanced Oxidation Processes (EAOPs) (e.g. Guinea et al., 2009, 2010; Babić et al., 2013; Antonin et al., 2015; Coledam et al., 2016; Lan et al., 2017; Wang et al., 2017).

It is well known that electrochemical oxidation using a boron-doped diamond (BDD) anode represents a potential EAOP technique for the treatment of wastewater due to the electrogeneration of oxidant species, particularly hydroxyl radicals (HO^\bullet) (Panizza and Cerisola, 2005; Martínez-Huitle et al., 2015). Electrochemical oxidation processes depend on various operational parameters such as the initial organics concentration, supporting electrolyte, temperature, pH, liquid flow rate, electrode material, current density and others (Moreira et al., 2017). Among these variables, the use of distinct supporting electrolytes can lead to the generation of oxidant species that react with pollutants in the solution bulk (Lan et al., 2017; Moreira et al., 2017), the so-called mediated oxidation (indirect oxidation) (Panizza and Cerisola, 2009; Sirés et al., 2014; Martínez-Huitle et al., 2015). In this context, anions such as sulfate, carbonate and phosphate are directly oxidized to radical anions on the BDD surface, according to Eqs. (1)–(3). Subsequently, these radicals can combine to produce the strong oxidants persulfate, percarbonate and perphosphate in the reaction media (Eqs. (4)–(6)) (Sirés et al., 2014; Moreira et al., 2017).



Active chlorine species (Cl_2 , HOCl , and ClO^-) can also be produced by direct oxidation of chloride ions on the anode surface or their indirect oxidation by hydroxyl radicals to yield chlorine (Cl_2) (see Eqs. (7)–(9)). Depending on the solution pH, in the bulk of the solution Cl_2 disproportionates yielding hypochlorous acid, which can lead to hypochlorite ions (Eqs. (10) and (11)) (Moreira et al., 2017).



At solution pH values > 7.5 , ClO^- is the predominant active

chlorine species. For pH values < 7.5 , HOCl is the predominant species; for low values of $[\text{Cl}^-]$, this predominance of HOCl is extended to quite low pH values (Cheng and Kelsall, 2007).

These oxidant species can affect the mechanisms of organic oxidation, eventually leading to the formation of degradation intermediates or final products (especially organochlorines) that can be even more harmful than the original pollutant, as noted e.g. by Sirés et al. (2014). Furthermore, those oxidants can also affect the degradation kinetics since they can scavenge the HO^\bullet radicals, as shown above. Recently, Lan et al. (2017) investigated the effect of two salts (potassium sulfate and potassium chloride) on the electrooxidation of three pharmaceuticals (ciprofloxacin, sulfamethoxazole, and salbutamol) using a BDD anode in a one-compartment filter-press reactor. Specifically for ciprofloxacin, they reported that a higher concentration of sulfate led to faster removal of both the organic molecule and the solution's total organic carbon concentration (TOC). When chloride ions (at a low concentration: 2.25 mM) were added to the sulfate solution (20 mM), even faster removal rates were attained (Lan et al., 2017); however, degradation intermediates were not identified. Similar results were reported by Wang et al. (2017) for the electrooxidation of ENRO using a $\text{Ti/SnO}_2\text{-Sb/La-PbO}_2$ anode; significantly faster removal rates were attained when NaCl was added to the sulfate supporting electrolyte, whereas the opposite happened when NaNO_3 was added (these authors did report on initial oxidation intermediates, but only for the electrolysis in sulfate medium). Hence, further studies on the influence of distinct supporting electrolytes on the removal of organic compounds are still of great importance and need to be carried out.

Considering the above context, the aim of the present work is to compare the effect of distinct supporting electrolytes (Na_2SO_4 , NaCl , Na_2CO_3 , NaNO_3 , and Na_3PO_4) on the electrooxidation and mineralization of ENRO using a BDD anode in a filter-press flow cell. That effect will be compared through the removal rates of ENRO and TOC, which will also be compared to those from a theoretical model based on a mass transport controlled process. Furthermore, initial and terminal oxidation intermediates will be investigated using Liquid Chromatography coupled to Quadrupole Time of Flight Tandem Mass Spectrometry (LC–QqTOF) and LC analyses, respectively. Finally, the evolution of the antimicrobial activity (toxicity) of the electrolyzed solutions to *Escherichia coli* (*E. coli*) bacteria will be assessed along the electrolyses using the distinct supporting electrolytes.

2. Experimental

2.1. Chemicals

All chemicals, including enrofloxacin (98.0%, Sigma Aldrich), Na_2SO_4 (Qhemis), NaCl (Qhemis), Na_2CO_3 (Synth), NaNO_3 (Synth), Na_3PO_4 (Synth), $\text{Na}_2\text{S}_2\text{O}_8$ (Sigma Aldrich), yeast extract (Sigma Aldrich), tryptone (Sigma Aldrich), KH_2PO_4 (Synth), H_3PO_4 (85%, Mallinckrodt), H_2SO_4 (98%, JT Baker), methanol (HPLC grade, Tedia), formic acid (HPLC grade, JT Baker) and carboxylic acids (Sigma Aldrich), were used as received. All solutions were prepared using ultrapure water (Millipore Milli-Q, $\rho > 18 \text{ M}\Omega \text{ cm}$).

2.2. Electrochemical degradation experiments

The electrochemical degradation experiments were carried out in a one-compartment filter-press flow cell using a BDD anode (B content of 100 ppm; for specifications, see Coledam et al. (2016)) and an AISI 304 stainless steel plate as cathode. The exposed area of each electrode was $3.54 \text{ cm} \times 6.71 \text{ cm}$. Details on the setup of the assembled electrochemical system and flow cell are found

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