



Electrochemical incineration of the antibiotic ciprofloxacin in sulfate medium and synthetic urine matrix



Vanessa S. Antonin^a, Mauro C. Santos^{a,*,**}, Sergi Garcia-Segura^b, Enric Brillas^{b,*}

^a Laboratório de Eletroquímica e Materiais Nanoestruturados (LEMN), Centro de Ciências Naturais e Humanas (CCNH), Universidade Federal do ABC (UFABC), Rua Santa Adélia, 166, 09210-170 Santo André-SP, Brazil

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

ARTICLE INFO

Article history:

Received 4 April 2015

Received in revised form

5 May 2015

Accepted 12 May 2015

Available online 20 June 2015

Keywords:

Ciprofloxacin

Electrochemical oxidation

Electro-Fenton

Photoelectro-Fenton

Sunlight

Wastewater treatment

ABSTRACT

The degradation of 100 mL of 0.245 mM of the antibiotic ciprofloxacin in 0.05 M Na₂SO₄ at pH 3.0 has been studied by electrochemical oxidation with electrogenerated H₂O₂ (EO-H₂O₂), electro-Fenton (EF), UVA photoelectro-Fenton (PEF) and solar PEF (SPEF). Electrolyses were performed with a stirred tank reactor using either a boron-doped diamond (BDD) or Pt anode and an air-diffusion cathode. In EF, PEF and SPEF, ciprofloxacin was rapidly removed due to its oxidation with •OH formed from Fenton's reaction between added Fe²⁺ and H₂O₂ generated at the cathode. The larger electrochemical incineration of the antibiotic was achieved by SPEF with BDD with 95% mineralization thanks to the additional attack by hydroxyl radicals formed from water oxidation at the BDD anode surface and the photolysis of final Fe(III)-oxalate and Fe(III)-oxamate species from sunlight. Up to 10 primary intermediates and 11 hydroxylated derivatives were identified by LC-MS, allowing the proposal of a reaction sequence for ciprofloxacin mineralization. A different behavior was found when the same antibiotic concentration was oxidized in a synthetic urine matrix with high urea content and a mixture of PO₄³⁻, SO₄²⁻ and Cl⁻ ions. Since Fenton's reaction was inhibited in this medium, only EO and EO-H₂O₂ processes were useful for mineralization, being the organics mainly degraded by HClO formed from Cl⁻ oxidation. The EO process with a BDD/stainless steel cell was found to be the most powerful treatment for the urine solution, yielding 96% ciprofloxacin removal and 98% mineralization after 360 min of electrolysis at optimum values of pH 3.0 and current density of 66.6 mA cm⁻². The evolution of released inorganic ions was followed by ion chromatography.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Pharmaceuticals have received increasing attention as potential bioactive chemicals in the environment (Kümmerer, 2009). Their recalcitrance to conventional physicochemical methods in wastewater treatment plants favors the accumulation of many drugs and their metabolites into natural waters (Homem and Santos, 2011), which represents a potential toxicity risk for ecosystems and living beings (Klavarioti et al., 2009). Some drugs cause long-term, irreversible changes to micro-organisms genome, even at low content in water, being more resistance to them (Mutiyar and

Mittal, 2014; Tang et al., 2015). To avoid the potential hazardous effects of these pollutants over living beings in the environment, powerful oxidation processes are being developed to remove synthetic drugs from wastewaters.

Over the last decade, electrochemical advanced oxidation processes (EAOPs) have received great attention for the remediation of waters contaminated with organic pollutants (Özcan et al., 2009; Sirés et al., 2014; Brillas and Martínez-Huitle, 2015). These treatments generate in situ reactive oxygen species (ROS) like hydroxyl radical (•OH), which have so high standard reduction potential ($E^\circ = 2.80$ V/SHE) that can mineralize most organics. The most common EAOP is electrochemical oxidation (EO), where organics are directly oxidized at the surface of the anode M and/or much more quickly attacked by physisorbed hydroxyl radical M(•OH) formed as intermediate from water oxidation to O₂ via reaction (1) at high current (Flox et al., 2006; Panizza and Cerisola, 2009).

* Corresponding author.

** Corresponding author.

E-mail addresses: mauro.santos@ufabc.edu.br (M.C. Santos), brillas@ub.edu (E. Brillas).

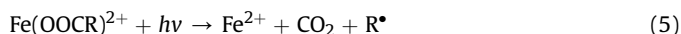


When an active anode like Pt is employed, the Pt($\cdot OH$) radical is converted into chemisorbed PtO species with weaker oxidizing ability leading to partial conversion of parent molecules into carboxylic acids (Panizza and Cerisola, 2009). Conversely, a non-active anode like a boron-doped diamond (BDD) thin film produces high amounts of physisorbed BDD($\cdot OH$) with ability enough to mineralize organics, even short-linear carboxylic acids (Ciriaco et al., 2009; Rodrigo et al., 2010; Garcia-Segura and Brillas, 2011; Sopaj et al., 2015). Due to its great oxidation power, the BDD electrode is currently preferred as anode for EO (Panizza and Cerisola, 2009).

Several EAOPs based on electrogenerated H_2O_2 have been developed (Sirés and Brillas, 2012; Sirés et al., 2014). They consist in the continuous supply of H_2O_2 to the medium from the two-electron reduction of O_2 gas at a carbonaceous cathode such as activated carbon fiber (Wang et al., 2008), carbon nanotubes (Khataee et al., 2013), carbon felt (Dirany et al., 2012; Oturan et al., 2012; El-Ghenymy et al., 2014), carbon sponge (Özcan et al., 2008), carbon modified with metals or metal oxides nanoparticles (Assumpção et al., 2013a, 2013b) and carbon-polytetrafluoroethylene (PTFE) gas (O_2 or air) diffusion (Guinea et al., 2010; Moreira et al., 2013; Florenza et al., 2014) by reaction (2):



In the EO process with electrogenerated H_2O_2 (EO- H_2O_2), organics are degraded pre-eminently by physisorbed $M(\cdot OH)$, although other ROS such as H_2O_2 and its oxidation product $HO_2\cdot$ may also contribute (Sirés and Brillas, 2012). The electro-Fenton (EF) process enhances the oxidization power of H_2O_2 by adding to the solution a small amount of Fe^{2+} to produce Fe^{3+} and $\cdot OH$ in the bulk from Fenton's reaction (3) at optimum pH near 3 (Dirany et al., 2012). Organics are then removed by both ROS, $M(\cdot OH)$ and $\cdot OH$. Other EAOPs like UVA photoelectro-Fenton (PEF) or solar PEF (SPEF) involve the simultaneous irradiation of the solution with either artificial UVA light or direct sunlight, respectively (Flox et al., 2007). This irradiation promotes: (i) the photoreduction of $Fe(OH)^{2+}$ to Fe^{2+} with $\cdot OH$ generation from reaction (4) and (ii) the photolysis of $Fe(III)$ -carboxylate products from reaction (5) (Sirés et al., 2014). SPEF is the most promising technology to be explored because it relies on sunlight as an inexpensive, renewable energy source.



The degradation of some pharmaceuticals by various EAOPs has been reported (Almeida et al., 2011; Isarain-Chávez et al., 2011; Dirany et al., 2012; El-Ghenymy et al., 2014), although less is known about the treatment of fluoroquinolones (Guinea et al., 2010). These papers have only considered the use of a sulfate medium without analyzing the influence of other organic matter with a complex mixture of inorganic ions, as is the case of urea present in diluted urine from hospital effluents. To gain a better knowledge on the application of EO, EF, PEF and SPEF to the electrochemical incineration of fluoroquinolones, we have undertaken a study on the removal of ciprofloxacin (1-cyclopropyl-6-hydroxy-4-oxo-7-(piperazin-1-yl)-1,4-dihydroquinoline-3-carboxylic acid, $C_{17}H_{18}N_3FO_3$) in a typical sulfate solution as well as in a synthetic urine matrix to clarify the effect of a complex organic electrolyte

over its mineralization. Ciprofloxacin is the most widely used antibiotic of the second generation of fluoroquinolones in medicine and veterinary with a broad spectrum of antibacterial activity including most strains of bacterial pathogens responsible for respiratory, urinary tract, gastrointestinal and abdominal infections. It has been found in relatively high levels of $\mu g L^{-1}$ in rivers (Conley et al., 2008; Ferrando-Climent et al., 2014) and lakes (Tang et al., 2015) and up to concentrations as high as $6.5 mg L^{-1}$ (Fick et al., 2009) and $31 mg L^{-1}$ (Larsson et al., 2007) in effluents of drug manufacturers. Its toxicity over aquatic organisms has been well-proven (Robinson et al., 2005; Hernando et al., 2007; Johnson et al., 2015). The oxidation of ciprofloxacin has been studied by a large variety of methods such as sonolysis (De Bel et al., 2009), $KMnO_4$ (Hu et al., 2010), UVC/peroxymonosulfate (Mahdi-Ahmed and Chiron, 2014), ozonation (De Witte et al., 2009; Bobu et al., 2013), photo-Fenton (Sun et al., 2009; Bobu et al., 2013; Giri et al., 2014), zero-valent iron (Perini et al., 2014), membrane anodic Fenton (Xiao et al., 2010) and EF with a carbon-felt cathode (Yahya et al., 2014).

This paper presents a careful study on the electrochemical incineration of ciprofloxacin by EAOPs using a stirring tank reactor with a Pt or BDD anode and an air-diffusion or stainless steel cathode. First, comparative electrolyses in 0.05 M Na_2SO_4 were performed under EO- H_2O_2 , EF, PEF and SPEF conditions to clarify their relative oxidation power and the role of the generated oxidizing agents for the antibiotic incineration. The drug decay and the evolution of short-linear carboxylic acids were followed by high-performance liquid chromatography (HPLC). The fate of inorganic ions was ascertained by ion chromatography. Aromatic products were identified by liquid chromatography-mass spectrometry (LC-MS), allowing the proposal of a reaction sequence for drug mineralization. In a second step, a synthetic urine matrix was used as electrolyte to know its influence over the performance of EAOPs. The effect of pH and current density (j) on the best treatment by EO with a BDD/stainless steel cell was examined.

2. Materials and methods

2.1. Chemicals

Analytical grade ciprofloxacin was purchased from Sigma and used as received. Heptahydrated iron(II) sulfate used as catalyst for Fenton's reaction and anhydrous sodium sulfate used as background electrolyte were of analytical grade supplied by Sigma–Aldrich and Fluka, respectively. Carboxylic acids, the components of the synthetic urine matrix, other chemicals and solvents were of HPLC, LC-MS and analytical grade purchased from Sigma–Aldrich, Lancaster, Merck and Panreac. All solutions were prepared with high-purity water obtained from a Millipore Milli-Q system (resistivity > 18 $M\Omega cm$ at 25 °C).

2.2. Synthetic urea matrix

A concentrated urine solution was prepared with 6.8 mM $CaCl_2 \cdot 2H_2O$, 51.3 mM NaCl, 14.2 mM Na_2SO_4 , 7.3 mM KH_2PO_4 , 26.8 mM KCl, 18.7 mM NH_4Cl and 0.42 M urea. This solution contained a high dissolved organic carbon (DOC) of about 5000 $mg L^{-1}$ and pH 4.9. To simulate the conditions of sewage effluents from hospitals (Dbira et al., 2015), the concentrated urine was diluted 20 times to obtain the urine matrix for the synthetic wastewater, which was then prepared by spiking 0.245 mM ciprofloxacin (50 $mg L^{-1}$ DOC) and H_2SO_4 for pH adjustment to 3.0. The starting wastewater then contained 300 $mg L^{-1}$ DOC with 0.37 mM PO_4^{3-} , 1.28 mM SO_4^{2-} , 5.49 mM Cl^- , 0.34 mM Ca^{2+} , 3.98 mM Na^+ , 1.70 mM K^+ , 0.94 mM NH_4^+ and 42 mM urea.

Download English Version:

<https://daneshyari.com/en/article/6365725>

Download Persian Version:

<https://daneshyari.com/article/6365725>

[Daneshyari.com](https://daneshyari.com)