



## Oxidative degradation study on antimicrobial agent ciprofloxacin by electro-fenton process: Kinetics and oxidation products



Muna Sh. Yahya<sup>a</sup>, Nihal Oturan<sup>b</sup>, Kacem El Kacemi<sup>a</sup>, Miloud El Karbane<sup>c</sup>, C.T. Aravindakumar<sup>d</sup>, Mehmet A. Oturan<sup>b,\*</sup>

<sup>a</sup> Laboratoire d'Électrochimie et Chimie Analytique (LECA), Université Mohammed V – Agdal, Rabat, Morocco

<sup>b</sup> Université Paris-Est, Laboratoire Géomatériaux et Environnement (LGE), EA 4506, 5 Bd Descartes, 77454 Marne-la-Vallée, France

<sup>c</sup> Physicochemical Service, Drugs Quality Control Laboratory, Division of Drugs and Pharmacy, Ministry of Health, Rabat, Morocco

<sup>d</sup> School of Environmental Sciences, Mahatma Gandhi University, Kottayam 686560, Kerala, India

### HIGHLIGHTS

- Degradation/mineralization of ciprofloxacin was investigated by electro-Fenton.
- Oxidation of ciprofloxacin by  $\cdot\text{OH}$  follows a pseudo-first order reaction kinetics.
- A quasi-complete mineralization (>94%) rate was obtained at 6 h treatment.
- A mineralization pathway is suggested based on identification of reaction intermediates.

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### ABSTRACT

Oxidative degradation of the antimicrobial agent ciprofloxacin hydrochloride (CIP) has been investigated using electro-Fenton (EF) treatment with a constant current in the range 60–500 mA. The process generates highly oxidant species  $\cdot\text{OH}$  in situ via electrochemically monitored Fenton reaction. The EF experiments were performed using cells with a carbon felt cathode and Pt anode. Effect of applied current and catalyst concentration on the kinetics of oxidative degradation and mineralization efficiency have been investigated. Degradation of CIP followed pseudo-first order reaction kinetics. The rate constant of the oxidation of CIP by  $\cdot\text{OH}$  has been determined to be  $(1.01 \pm 0.14) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  by using competitive kinetics method. An optimum current of 400 mA and a catalyst concentration of  $\text{Fe}^{2+}$  at 0.1 mM are found to be optimal for an effective degradation of CIP under our operating conditions. A remarkably high degree of mineralization (>94%) was obtained at 6 h of treatment under these conditions. A number of stable intermediate products have been identified using HPLC and LC-MS/MS analyses. Based on the identified reaction intermediates, a plausible reaction pathway was proposed for the mineralization process. The high degree of mineralization obtained in this work highlights the potential application of EF process in the efficient removal of fluoroquinolone based drugs in aqueous medium.

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### 1. Introduction

Fluoroquinolones (FQs) represent one of the most important classes of antibiotics based on their annual global sales and therapeutic versatility (Dodd et al., 2005). They are synthetically produced antibiotics, active against a broad spectrum of pathogenic gram-negative and gram-positive bacteria (Neu, 1992; Cardoza et al., 2003). Consequently, they are used as antibiotics of first choice for general bacterial infectious diseases, and its efficacies

are highly appreciated. Ciprofloxacin (CIP), a common FQ, is a primary degradation product of enrofloxacin, which is used worldwide in aquaculture and agricultural applications (Cardoza et al., 2003). Because of their continued use in both human and veterinary medicine, the environmental impact of such antibacterial agents is of serious concern for the public health. This concern arises from their potential for migration into the environment and the possible development of resistance in pathogens (Kidwai et al., 1998; Levy and Marshall, 2004). CIP is readily transported into the environment via discharge of wastewater and direct runoff. It has been detected at concentrations ranging from  $\text{mg L}^{-1}$  in untreated hospital sewage (Hirsch et al., 1998), to  $\text{ng L}^{-1}$  levels

\* Corresponding author. Tel.: +33 149329065.

E-mail address: [Mehmet.oturan@univ-paris-est.fr](mailto:Mehmet.oturan@univ-paris-est.fr) (M.A. Oturan).

in secondary wastewater effluents (Golet et al., 2002; Brown et al., 2006), and surface waters (Golet et al., 2002; Batt et al., 2006).

Research on the biodegradability of ciprofloxacin demonstrated that it is not “readily biodegradable” in water (Kummerer et al., 2000). Study on the behavior of fluoroquinolones during mechanical, chemical, and active sludge treatment of sewage water and digestion of sludge (Lindberg et al., 2006) showed that more than 70% of the total amount of ciprofloxacin and norfloxacin pass through the plant as digested sludge when they adsorbed to sludge during sewage treatment. Indeed, ciprofloxacin in water is mainly transferred from one phase to another but not really degraded after treatment by traditional wastewater treatment plants (WWTPs), which may cause the secondary pollution of environment. Therefore, the development of novel and cost-effective technologies to purify ciprofloxacin-contaminated wastewater is of primary interest.

At present, most of the WWTPs plants are not designed to completely remove pharmaceuticals, and consequently these compounds are released into receiving water bodies. Advanced oxidation processes (AOPs) are known as effective methods to remove non-biodegradable organic pollutants from ground, surface and wastewater (Ikehata et al., 2006; Saez et al., 2013; Oturan and Aaron, 2014). Their effectiveness depends on the in-situ generated  $\cdot\text{OH}$  which are able to oxidize organic molecules until their mineralization. These radicals can be produced by chemical, photochemical or electrochemical methods (Malato et al., 2002; Cañizares et al., 2005; Brillas et al., 2009; Panizza and Cerisola, 2009). A number of studies are available on the degradation of organic pollutants such as pesticides, dyes, pharmaceuticals, aromatic compounds, nitro phenols or surfactants by photo-Fenton oxidation (Bobu et al., 2006; Ikehata et al., 2006; Diagne et al., 2009; Kesraoui-Abdessalem et al., 2010; Oturan et al., 2012). Some studies have shown that AOPs and adsorption applications are viable treatment methods for degrading or removing CIP from water and wastewater (Vasconcelos et al., 2009; An et al., 2010; Paul et al., 2010). An et al. (2010) were determined the rate constant of CIP with different radical species generated in pulsed radiolysis method and studied its degradation by heterogeneous photocatalysis using  $\text{TiO}_2$ , however they are not investigated its mineralization ability which is important regarding toxicity assessment of treated solution”. CIP is susceptible to direct photochemical transformations by exposure to direct ultraviolet (UV) light in the presence of photocatalytic reagents such as  $\text{H}_2\text{O}_2$ ,  $\text{O}_3$  and  $\text{TiO}_2$ , in aqueous solutions (De Witte et al., 2009; Paul et al., 2010). CIP adsorption onto water sediment, soil and sludge is also reported (Carmosini and Lee, 2009). Its electrochemical oxidation using conductive diamond electrode was also studied (Guinea et al., 2009).

In a number of earlier studies, we have demonstrated the effectiveness of the electro-Fenton method in the degradation of persistent and/or toxic organic pollutants in aqueous medium (Oturan, 2000; Zhang et al., 2007; Brillas et al., 2009; Zhou et al., 2012). In this process,  $\cdot\text{OH}$  are produced through the electrochemically assisted Fenton's reaction in which the Fenton's reagent ( $\text{H}_2\text{O}_2 + \text{Fe}^{2+}$ ) is electrochemically generated or regenerated (Oturan et al., 1992; Wu et al., 2002; Oturan et al., 2009; Dirany et al., 2010; Garcia-Segura et al., 2011).

Although the degradation of CIP is studied using other AOPs, to the best of our knowledge, there is no study reported on its removal from water by electrochemical advanced oxidation processes. Therefore, the present contribution investigates the performance of the EF process for the efficient removal of CIP, which is chosen as a model fluoroquinolones, from water using Pt/carbon-felt cells. This study was carried out in deionized water to easier kinetics studies as well as identification and dosage of degradation products since these measurements measures could be disrupted

by organic matter present in natural (river or lake) or waste water. Thus the effect of operating parameters such as applied current and  $\text{Fe}^{2+}$  (catalyst) concentration on the decay kinetics of CIP was initially investigated. The mineralization of the treated solutions was simultaneously monitored from the abatement of the total organic carbon (TOC). The by-products and intermediates were identified by HPLC and MS/MS analyses. Based on these intermediates and TOC results a plausible mineralization pathway is proposed.

## 2. Experimental

### 2.1. Chemicals

Monohydrochloride monohydrate salt of Ciprofloxacin (1-cyclopropyl-6-fluoro-1,4-dihydro-4-oxo-7-(1-piperazinyl)-3-quinolinecarboxylic acid) ( $\text{C}_{17}\text{H}_{18}\text{FN}_3\text{O}_3 \cdot \text{HCl} \cdot \text{H}_2\text{O}$ ) was purchased from Sigma–Aldrich and used without further purification. Compounds A (7-chloro-1-cyclopropyl-6-fluoro-4-oxo-1,4-dihydroquinoline-3-carboxylic acid), C (7-[(2-aminoethyl)amino]-1-cyclopropyl-6-fluoro-4-oxo-1,4-dihydroquinoline-3-carboxylic acid) and D (7-chloro-1-cyclopropyl-4-oxo-6-(piperazin-1-yl)-1,4-dihydroquinoline-3-carboxylic acid) were obtained from LGC Luckenwalde, (Germany). Heptahydrated Ferrous sulfate, sulfuric acid, and KCl were obtained from Shanghai Chemical Reagents Co., (Shanghai, China). Other chemicals such as methanol (HPLC grade, Sigma–Aldrich), and phosphoric acid (Scharlau, Spain) were used as received. Benzoic acid (BA) used in competition kinetic experiments was provided by Sigma–Aldrich.

### 2.2. Electrolytic system

Electrolyses were performed in a cylindrical, one-compartment and open electrochemical cell of 6-cm diameter and 250-mL capacity in which CIP aqueous solutions were placed. A cylindrical Pt mesh of 5 cm height (i.d. = 3 cm) was used as anode, and a large surface area tri-dimensional carbon-felt (14 cm  $\times$  5 cm  $\times$  0.5 cm in width – Carbone-Lorraine) as cathode. In all cases, the anode was centred in the electrochemical cell and was surrounded by the cathode.

The aqueous solutions submitted to electrolysis contained 0.1 mM  $\text{Fe}^{2+}$  as catalyst and 0.05 M  $\text{Na}_2\text{SO}_4$  as supporting electrolyte and were investigated at room temperature ( $23 \pm 2$  °C) by applying a constant current in the range 60–500 mA. Indeed, pH 3.0 is considered as the optimum pH value for electro-Fenton process and the use of a  $\text{Fe}^{2+}$  concentration of 0.1 mM is recommended as the optimum amount of catalyst for electro-Fenton process (Brillas et al., 2009). All trials were performed with solutions of 230 mL, vigorously stirred by a magnetic PTFE follower during the treatment to enhance the mass transport towards electrodes.

### 2.3. Analytical procedures

The mineralization of treated solutions was assessed from the abatement of the total organic carbon (TOC). A Shimadzu VCSH TOC analyzer was used to measure this analytical parameter. Samples withdrawn from the treated solution at regular electrolysis time interval were microfiltered through a hydrophilic membrane (Millex-GV Millipore, pore size 0.22  $\mu\text{m}$ ) before analysis. Reproducible TOC values with  $\pm 2\%$  accuracy were found using the non-purgeable organic carbon method.

The time course of the concentration of CIP was followed by reversed-phase HPLC using a Merck Lachrom liquid chromatograph equipped with a L-7100 pump, fitted with a Purospher RP-18, 5  $\mu\text{m}$ , 25 cm  $\times$  4.6 mm (i.d.) column at 40 °C, and coupled with

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