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Research article

Degradation of enoxacin antibiotic by the electro-Fenton process: Optimization, biodegradability improvement and degradation mechanism

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ABSTRACT

This study aims to investigate the effectiveness of the electro-Fenton process on the removal of a second generation of fluoroquinolone, enoxacin. The electrochemical reactor involved a carbon-felt cathode and a platinum anode. The influence of some experimental parameters, namely the initial enoxacin concentration, the applied current intensity and the Fe(II) amount, was examined. The degradation of the target molecule was accompanied by an increase of the biodegradability, assessed from the BOD_5 on COD ratio, which increased from 0 before treatment until 0.5 after 180 min of electrolysis at 50 mg L^{-1} initial enoxacin concentration, 0.2 mmol L^{-1} Fe(II) concentration and 300 mA applied current intensity. TOC and COD time-courses were also evaluated during electrolysis and reached maximum residual yields of 54% and 43% after 120 min of treatment, respectively. Moreover, a simultaneous generation of inorganic ions (fluorides, ammonium and nitrates) were observed and 3 short chain carboxylic acids (formic, acetic and oxalic acids) were identified and monitored during 180 min of electrolysis. By-products were identified according to UPLC-MS/MS results and a degradation pathway was proposed.

1. Introduction

In recent years, treating environmental hazards due to the significant detection of pharmaceutical compounds in wastewater became an area of interest for the scientific community worldwide (Ellis, 2006; Sui et al., 2011; Yoon et al., 2010). Excretion after administration and wastes in the production sites are the main causes of the presence of pharmaceutical compounds in the aquatic environment (Bound and Voulvoulis, 2005). This type of compounds has been recently classified as a priority risk pollutants (Hernando et al., 2006; Watkinson et al., 2009). Most of them are antibiotics. Their presence in wastewater is responsible for the development of antimicrobial resistance among microorganisms (Levy, 1998). Owing to their recalcitrance, the commonly employed treatment processes (biological processes) appear not effective enough for a complete removal of such species. The contamination by these micropollutants is observed not only in the received water but reached also surface waters. Their toxic and adverse effects were proven in previous studies (Daughton and Ternes, 1999; Giger et al., 2003).

Fluoroquinolones (FQs) are the third largest group of antibiotics with 17% of the global market share (Van Doorslaer et al., 2014). They are frequently detected with relatively high concentrations in hospital wastewaters (3 ng L^{-1}–240 μg L^{-1}), urban wastewaters (2 ng L^{-1}–14 μg L^{-1}) and in bulk drug producer wastewaters (6 ng L^{-1}–31 mg L^{-1} (Golet et al., 2002; Lin et al., 2008; Van Doorslaer et al., 2014). FQs are also observed in livestock and aquaculture wastewaters (Van Doorslaer et al., 2014). Their broad antimicrobial spectrum may lead to the proliferation of bacterial drug resistance (Watkinson et al., 2007). FQs are characterized by

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their chemical stability and their high resistance to hydrolysis and to high temperatures, due to their quinolone ring. Conventional water treatment plants show a high variation in FQ removal efficiency (between 47 and 77% on average) (Van Doorslaer et al., 2014). However, it is suggested by several authors that the predominant removal mechanism for FQ compounds is sorption to activated sludge rather than biodegradation (Hendricks and Pool, 2012; Lindberg et al., 2006; Van Doorslaer et al., 2014). A previous study reported that more than 80% of the total amount of ciprofloxacin and norfloxacin (FQ molecules) treated in a sewage treatment plant in Sweden was ultimately found in the digested sludge (Lindberg et al., 2006). This behavior is due to the high affinity of FQs for sludge, soils and sediments, through electrostatic and hydrophobic interactions (Lindberg et al., 2006).

Therefore, an effective strategy must be found to degrade these compounds from aquatic matrices and to enhance their biodegradability as a pretreatment before their discharge into sewage treatment plants.

Advanced Oxidation Processes (AOP) have received great interest in recent years as an alternative method to treat organic and recalcitrant molecules (Nasuhoglu et al., 2012). Some recent review papers reported the relevance of AOP on the degradation and the mineralization of residual molecules (Feng et al., 2013; Klavarioti et al., 2009; Pera-Titus et al., 2004; Sirés et al., 2014). These oxidative treatment processes can be classified into four categories: chemical oxidation processes in homogeneous phase (H_2O_2/Fe(II) and H_2O_2/O_3); photocatalytic processes in homogeneous phase and/or heterogeneous phase (H_2O_2/UV, O_3/UV, Fe(II)/H_2O_2/UV and TiO_2/UV); oxidation by sonochemical processes and electrochemical oxidation processes. AOP are characterized by the in-situ production of hydroxyl radicals (•OH) that are very strong oxidants (E° (•OH/H_2O) = 2.81 V/SHE at 25 °C) able to oxidize complex organic molecules such as pesticides (Guivarch et al., 2003), industrial dyes (Hammami et al., 2008) and pharmaceuticals (An et al., 2010; Guinea et al., 2010; Ikehata et al., 2006; Mansour et al., 2012; Rodrigues-Silva et al., 2013).

The electro-Fenton Process (EF) is one of the most efficient electrochemical AOP, which consists in the continuous production of hydroxyl radicals using electrogenerated Fenton reagent (H_2O_2/Fe(II)) according to the reactions below (El-Desoky et al., 2010; Xie and Li, 2006):

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (1)$$

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + {}^\bullet OH \quad (2)$$

$$Fe^{3+} + 1e^- \rightarrow Fe^{2+} \quad (3)$$

EF achieves high reaction yields and may be considered as an environmentally clean process (El-Desoky et al., 2010).

Studies dealing with FQ degradation using AOP are numerous. Flumequine degradation was investigated by EF and by photo-electro-Fenton (PEF) in a non divided electrochemical cell using a Carbon–PTFE-air diffusion cathode and a Boron Doped Diamond (BDD) anode. Results showed an almost total mineralization in 360 min at 300 mA current intensity for both EF and PEF (Garcia-Segura et al., 2012). Ciprofloxacin was completely degraded by EF within 8 min and reached 94% of mineralization after 360 min of treatment using a carbon felt cathode and Platinum (Pt) anode (Yahya et al., 2014). Its degradation was also studied by sono-chemistry (Xiao et al., 2014). Anodic oxidation and Solar-photo-electro-Fenton have been tested for Enrofloxacin elimination in an undivided filter press coupled to a photoreactor and using a batch recirculation flow plant. Investigations reported 28% and 86% of mineralization yields respectively after 300 min of treatment with a BDD anode and a Carbon PTFE gas diffusion cathode (Guinea et al., 2010). Nasuhoglu et al. demonstrated the efficiency of ozonation and TiO_2 photocatalysis to degrade Levofloxacin leading to maximal oxidation yields of 59% and 70% respectively after 300 min of treatment (Nasuhoglu et al., 2012). The efficiency of photocatalysis was also verified for moxifloxacin (Van Doorslaer et al., 2015).

However, there is a lack of studies dealing with the effectiveness of coupling AOP with a biological treatment for FQs. The effectiveness of this type of coupling has been proven with other classes of antibiotics such as sulfonamides (sulfamethazine) (Mansour et al., 2012), macrolides (tylosin) (Yahiat et al., 2011) and tetracycline (Ferrag-Siagh et al., 2013).

Therefore, the focus of this study is to evaluate the applicability of EF for the pretreatment of enoxacin (ENO), an oral broad-spectrum FQ antibacterial agent, used in the treatment of respiratory and urinary tract infections (Patel and Spencer, 1996) and to assess the possibility of coupling EF and a biological process for enoxacin mineralization. In this sense, the biodegradability of the degraded solution was examined. By-products and inorganic species were analyzed as well.

2. Materials and methods

2.1. Chemicals

Enoxacin (1-ethyl-6-fluoro-4-oxo-7-(piperazin-1-yl)-1,4-dihydro-1,8-naphthyridine-3-carboxylic acid) was generously provided by the LNCM (Laboratoire National de Contrôle des Médicaments – Tunis, Tunisia) (structure displayed in Fig. 1).

$FeSO_4 \cdot 7H_2O$ (purity 99%) and Na_2SO_4 (purity 99%) were used as catalyst and a supporting electrolyte respectively and were purchased from Acros Organics (Thermo Fisher Scientific, Illkirch, France). Acetonitrile (purity 99.9%) (HPLC grade) was obtained from Sigma–Aldrich (Saint Quentin Fallavier, France). The initial pH of the solutions was adjusted to 3, the optimal pH value for the electro-Fenton process (Diagne et al., 2007), by adding analytical grade sulfuric acid H_2SO_4 purchased from Acros Organics. All solutions were prepared with ultrapure water and all the other chemicals used for analysis were supplied from Acros Organics and Sigma Aldrich.

2.2. Electrochemical apparatus and procedures

Experiments were performed at room temperature (18 °C) with an undivided cylindrical glass cell containing 250 mL of solution. The cell was equipped with two electrodes, a tri-dimensional carbon felt piece (Carbone Lorraine RVG 4000 Mersen, Paris La Défense, France) as cathode (90 mm × 50 mm × 12 mm) and a cylindrical platinum (Pt) electrode (34.6 cm^2) as anode, located in the center of the electrochemical reactor to have a good potential distribution. Compressed air was bubbled for 10 min through the cell to saturate the solution prior to electrolysis. The treated

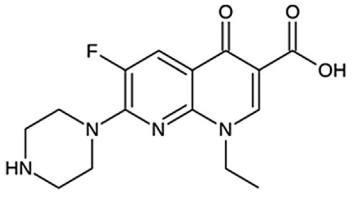

Fig. 1. Molecular structure of enoxacin.