Degradation and mineralization of moxifloxacin antibiotic in aqueous medium by electro-Fenton process: Kinetic assessment and oxidation products

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Abstract: Oxidation of moxifloxacin by electro-Fenton process (EFP) in acidic media at pH 3.0 is investigated. The influences of Fe2+ and current density have been assessed in order to determine the optimum operating parameters. Kinetic analysis of the degradation of initial moxifloxacin suggests a pseudo-first-order degradation reaction. The mineralization of the treated solutions is simultaneously monitored from the abatement of the chemical oxygen demand. The evaluation of the chemical composition and the characterization of the degradation products of moxifloxacin during electrolysis are carried out by high-performance liquid chromatography. The obtained results reveal the significant efficiency of EFP to degrade the moxifloxacin in the aqueous solution.

1. Introduction

Most of the fluoroquinolones (FQs) antibiotics are not fully metabolized in the body and are partially excreted in their pharmaceutically active forms (>50%) and in a lesser extent as phase I (addition of...
reactive functional groups through oxidation, reduction or hydrolysis) or phase II metabolites (cova-
lent conjugation to polar molecules, e.g. glucuronic acid, sulfate, acetic acid, or amino acid) (Stass,
1999; Watkinson, Murby, & Costanzo, 2007). FQs are a family of synthetic antibacterial agents with a
rising popularity. The total use of quinolones as well as that of second- and third-generation qui-

nolones is increasing in most of the European countries. One of those third-generation FQs is moxi-
floxacin, as shown in Figure 1. It is worldwide approved and represented 99.5% of the European
third-generation quinolone employed in 2003 (Ferech et al., 2006; Van Bambeke, Michot, Van Eldere,
Tulkens, & Quinolones, 2005). Removal of these persistent molecules in wastewater treatment
plants is mainly achieved by sorption processes, not by biodegradation (Fatta-Kassinos, Meric, &
Nikolaou, 2011; Kümmener, 2009; Li & Zhang, 2010; Speltini, Sturini, Maraschi, & Profumo, 2010). To
prevent resistance formation and toxic effects, the removal of these antibiotics is required by
physico-chemical techniques prior to discharge in the environment. Advanced oxidation processes
(AOPs) like heterogeneous photocatalysis, ozonation and sonification are promising techniques to
degradate persistent organic molecules (Abellán, Giménez, & Esplugas, 2009; De Bel, Dewulf, Witte,
Van Langenhove, & Janssen, 2009; De Witte et al., 2010; Heynderickx, Demeestere, Dewulf, De Witte,
& Van Langenhove, 2011; Vasconcelos, Kümmener, Henriques, & Martins, 2009). To evaluate the ef-
ficiency of an AOP, not only the kinetics and process parameters are of interest, but also it is equally
important to study the formed degradation products and residual antibacterial activity after an AOP
treatment (De Witte, van Langenhove, Demeestere, & Dewulf, 2011a; Fatta-Kassinos, Vasquez,
& Kümmener, 2011; Hapeshi et al., 2010; Nasuhoglu, Rodayan, Berk, & Yargeau, 2012; Paul, Dodd,
& Strathmann, 2010; Sirtori, Zapata, Gernjak, Malato, & Agüera, 2012). Full mineralization is not the
aim of an AOP treatment since it is not cost-effective (Doll & Frimmel, 2004). The focus is more on
the partial degradation of recalcitrant pollutants to deactivate their biological activity, and therefore
decreasing their toxicity, or increasing the biodegradability (de Witte, van Langenhove, Demeestere,
& Dewulf, 2011b; Van Doorslaer et al., 2013). Among others, commonly used AOPs for antibiotic

Figure 1. Effect of (a) applied current and (b) catalyst concentration on moxifloxacin concentration decay during electro-Fenton treatment at pH 3 and room temperature in 0.05 M Na2SO4 solution.
Notes: (a): I (mA) = 60 (■-●), 100 (- ▲-●), 300 (●.), 400 (●.), and 500 (●+) (mM) = 0.1
(- ▲-●), 0.2 (●-●), 0.5 (●.) and 1.0 (●+).
removal from wastewater are ozonation, sonolysis, (photo)-Fenton, and heterogeneous photocatalysis (De Bel, Dewulf, Witte, Van Langenhove, & Janssen, 2009; De Witte, Dewulf, Demeestere, & Van Langenhove, 2009; Homem & Santos, 2011; Paul, Miller, & Strathmann, 2007; Prieto-Rodríguez et al., 2012). A transition from synthetic matrices toward applications in effluent waters is ongoing (Dimitroula et al., 2012; Homem & Santos, 2011; Michael, Hapeshi, Michael, & Fatta-Kassinos, 2010; Prieto-Rodríguez et al., 2013; Sousa, Gonçalves, Vilar, Boaventura, & Alpendurada, 2012; Vasconcelos, Kümmener, Henriques, & Martins, 2009). In many of studies, we have demonstrated the effectiveness of the electro-Fenton (EF) method regarding the degradation of persistent and/or toxic organic pollutants and also pharmaceuticals in the aqueous medium (Brillas, Sirés, & Oturan, 2009; Oturan, 2000; Oturan, Peiroten, Chartrin, & Acher, 2000; Yahya et al., 2014; Zhang, Fei, Zhang, & Tang, 2007; Zhou et al., 2012).

In this process, ‘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 (Dirany, Sirés, Oturan, & Oturan, 2010; García-Segura et al., 2011; Oturan, Panizza, & Oturan, 2009; Oturan, Pinson, Deprez, & Terlain, 1992; Wu, Zhou, & Wang, 2002). Although the degradation of moxifloxacin has already been 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 moxifloxacin, which is chosen as a model fluoroquinolones, from water using Pt/carbon felt cells. This study was carried out in deionized water to ease the kinetics studies as well as identification and dosage of degradation products, since these measurements could be disrupted by the organic matter present in natural (river or lake) or wastewater. Thus, the effect of operating parameters such as applied current and Fe$^{2+}$ (catalyst) concentration on the decay kinetics of moxifloxacin was initially investigated. The mineralization of the treated solutions was simultaneously monitored from the abatement of the chemical oxygen demand (COD). The byproducts and intermediates were identified by HPLC and LC/MS analyses. The main objective of this study is the application of Electro-Fenton process (EFP) to degrade the moxifloxacin using hydroxyl radicals produced by Fenton’s reagent according to the reaction (2). The Fenton’s reagent is generated in situ by electrochemical treatment. The degradation was monitored by high-performance liquid chromatography (HPLC) analysis and COD measurements. The results demonstrate the efficacy of the EFP to degrade the moxifloxacin.

2. Experimental section

2.1. Chemicals

Moxifloxacin was obtained from GEMPHARMA ($C_{21}H_{24}N_3O_4F.\text{HCl}>98\%$ purity). Compounds 1, 2, 3, 4, and 5 were obtained from CRS.edqm. Ferrous sulfate, sulfuric acid, and KCl were obtained from Shanghai Chemical Reagents Co, Acetonitrile (HPLC grade), was obtained from Carlo ERPA; Triethylamine was obtained from Scharlau. Ammonium acetate and sodium perchlorate were obtained from Fluka. All the solutions were prepared with ultra-pure water obtained from a Millipore Milli-Q system with resistivity $>18\text{ M}\Omega\text{ cm}$, at room temperature.

2.2. Electrolytic system

Voltalab instrument for a Potentiostat/Galvanostat type PGZ 301 was used for electrochemical treatments and for measuring the consumed electrical charge. Electrolyses were performed in an open electrochemical cell of 200-mL capacity containing up to 0.15 mM moxifloxacin. A platinum ($5\text{ cm}^2$) as anode and a large surface area tri-dimensional carbon-felt as cathode ($10 \times 8 \times 0.5 \text{ cm}$) were used during the electro-Fenton treatment. The pH was maintained at 3.0 as the optimal pH value using $0.1\text{ M H}_2\text{SO}_4$. This value remained nearly constant during the entire treatment. Heptahydrated iron (II) sulfate used as catalyst source and anhydride sodium sulfate used as background electrolyte were of analytical grade, and were purchased from Merck. Applying a constant current in the range 60–500 mA, at room temperature.
2.3. Analytical procedures

Chemical oxygen demand removal was used as Mineralization efficiency, and was monitored by means of COD measurements. This parameter was evaluated by the dichromate method. The mixture was then incubated for 120 min at 150°C in the Lovibond® COD VARIO photometers. COD value was then measured colorimetrically using a DR/125 spectrophotometer (Hach Company, USA).

The time of the concentration of moxifloxacin and that of aromatic/cyclic intermediate compounds formed by its oxidation was followed by reversed-phase HPLC using a Waters 2695 coupled photodiode-array detector (PDA) 2998, selected at optimum wavelengths of 293 nm. Data acquisition was performed by the Empower 2 Software data registration, fitted with a thermo hypersil C18, 5 μm, 25 cm, 4.6 mm, column (Agilent zorbax phenyl) at 45°C. The analyses were carried out isocratically using a methanol/tetrabutylammonium hydrogen sulfate-potassium dihydrogen phosphate/phosphoric acid 28:72 (v/v) mixture as the mobile phase at a flow rate of 1.3 mL min⁻¹.

LC/MS studies were carried out with an LC surveyor HPLC system coupled with an LCQ Advantage triple quadrupole mass spectrometer equipped with a pneumatically assisted electro spray ionization source (ESI) in positive ion mode. A reverse phase Inertsil BDS Hypersil C18 (150 × 2.1) mm × 5 μm, column was used in the experiments. The column was placed in an oven which was thermostated at 35°C. The volume of the injections was 20 μL. The column was eluted with a mixture of water/formic acid-methanol/formic acid 0.1% with a flow rate of 0.2. min⁻¹. Detection was performed at 200–600 nm, with gradient program as following: 0 min 90% A; 1 min 90% A; 21 min 40% A, 26 min 0% A; 36 min 0% A; 37 min 90% A; 57 min 90% A. The flow rate was equal to 0.2 mL min⁻¹, and the injection volume was equal to 20 μL.

3. Results and discussion

3.1. Effect of experimental parameters on the degradation of MOXIFLOXACIN in aqueous solution

The influence of applied current on the degradation of moxifloxacin was investigated for 200 mL of 0.15 mM moxifloxacin solution in presence of 0.5 mM Fe²⁺ at pH value is about 3 (Figure 1(a)). The effect of applied current values (60, 100, 300, 400, and 500 mA) on the degradation rate of moxifloxacin has been examined and the obtained results are shown in (Figure 1(a)). This shows that the degradation rate of moxifloxacin increases by increasing the applied current value from 60 to 400 mA. It might be due to the proportionality of the amount of •OH production in the medium to the increasing generated H₂O₂ concentration, as current rises. This behavior can be explained by the acceleration of the rate of electrochemical reactions (1) and (2) leading to the generation of more •OH. The complete disappearance of moxifloxacin takes at 60, 30, 25, and 11 min for 60, 100, 300, and 400 mA current values, respectively. These results indicate that the degradation rate of moxifloxacin was not changed any more by increasing the applied current value after 400 mA.

\[
\begin{align*}
O_2 + 2e^- + 2H^+ & \rightarrow H_2O_2 \\
Fe^{3+} + e & \rightarrow Fe^{2+}
\end{align*}
\]

(1)

(2)

The decrease of moxifloxacin concentration indicates that its oxidative degradation by •OH follows a pseudo-first-order reaction kinetics. Similar results have been reported for the reaction of hydroxyl radicals with organic compounds (Boye, Dieng, & Brillas, 2002; Brillas, Banos, & Garrido, 2003; Oturan, Oturan, Lahitte, & Trevin, 2001; Ozcan, Ozcan, Ahin, & Oturan, 2010; Ozcan, Oturan, Oturan, & Ahin, 2009). The increase in the k_app value from 0.05 min⁻¹ for 60 mA to 0.64 min⁻¹ for 400 mA with R² > 0.99 is in agreement with the expected enhancement •OH production rate during Fenton reaction. The value of k_app for 500 mA is lower than that of 400 mA. The reasons of the moxifloxacin removal decrease at high applied current (or potential) values include, 4 e⁻ reduction of O₂ leading to the formation of H₂O (reaction (3) detriment of H₂O₂ formation, evolution of H₂ at the cathode (reaction (4), and the oxidation of H₂O₂ at anode (reaction (5) (Nasuhoglu et al., 2012).
The concentration of catalyst (Fe²⁺) is another important parameter related to the EFP. To determine the effect of catalyst concentration on the degradation of moxifloxacin, several experiments were carried out by varying Fe²⁺ concentration from 0.1 to 1.0 mM at the current value of 500 mA. The degradation rate was found to increase with increasing Fe²⁺ concentration from 0.1 to 0.5 mM. The electrolysis time required for complete disappearance of moxifloxacin varies from 20 min for 0.5 and 1.0 mM, and 30 and 40 min for 0.2 and 0.1 mM Fe²⁺ concentration, respectively, as can be seen from the inset of (Figure 1(b)). The degradation rate increases by increasing Fe²⁺ concentration from 0.1 to 0.5 mM. The degradation rate drastically decreases when the concentration value reaches 0.5 mM. On the other hand, in the case of the concentration between 0.5 and 1.0 mM, there was no considerable change in the degradation rate $k_{app}$, and the values were in agreement with the electrolysis durations (Figure 1(b)). Values showed variation for Fe²⁺ concentrations lower (0.102 s⁻¹ for 0.1 mM and 0.142 s⁻¹ for 0.2 mM). This behavior is particular to Fe²⁺ ion as catalyst. The apparent rate constant value obtained in the presence of different Fe²⁺ concentrations reached to its maximum (0.441 s⁻¹) in the presence of 0.5 mM Fe²⁺ at 500 mA.

3.2. Effect of experimental parameters on the mineralization of MOXIFLOXACIN in the aqueous solution

Several experiments were performed in the presence of constant Fe²⁺ concentration 0.2 mM in order to investigate the effect of different applied currents on the mineralization rate of moxifloxacin (Figure 2 (a)). COD rate increased by raising the applied current from 60 to 400 mA. On the other hand, the current value 500 mA led to a decrease of COD removal rate which was consequently responsible for weak removal kinetics. This loss of mineralization efficiency can be explained on the basis of the enhancement of wasting reactions (3). Therefore, we chose the value of 400 mA as the optimal applied current under the same conditions. Whereas, the mineralization degrees of moxifloxacin aqueous solution were 39.7, 51.77, 81.56, 90.78, and 87.9% after 6-h treatment.

The effect of catalyst concentration on the mineralization of moxifloxacin was investigated by performing the electrolysis, using different Fe²⁺ concentrations in the range of 0.1–1.0 mM at 500 mA, as shown in Figure 2 (b). The mineralization rate was decreased with the increase in the catalyst concentration to 1.0 mM. The mineralization rate slew down for 0.1 mM Fe²⁺ but greatly increased when the Fe²⁺ concentration was enhanced from 0.1 to 0.5 mM. After a certain value, an increase in the amount of Fe²⁺ concentration inhibits the removal rate of moxifloxacin because of the waste reaction between Fe²⁺ and hydroxyl radicals Equation (6) (Sun & Pignatello, 1993). This result has been frequently reported in the literature.

$$\text{Fe}^{2+} + \cdot \text{OH} \rightarrow \text{Fe}^{3+} + \text{OH}^- \quad (6)$$

The instantaneous current efficiency (ICE) for the oxidation of moxifloxacin has been calculated from the values of COD using the relation (7) (Brillas, Sirés, & Oturan, 2009):

$$\text{ICE} = \frac{(\text{COD}_0 - \text{COD}_t)FV}{8It} \quad (7)$$

COD₀ and CODₜ, respectively, refer to the initial and final COD values, I the applied current (A); F the Faraday constant (96,487 C mol⁻¹), V is the volume of the solution (L), and t is the treatment time (s).
Figure 2. Removal of solution COD as a function of applied current (a) catalyst concentration (b) on moxifloxacin during electro-Fenton treatment of 0.15 mM moxifloxacin in 0.05 mM Na₂SO₄ at pH 3 and room temperature.

Notes: Applied current (mA): I = 60 (■), 100 (▲), 300 (●●), 400 (●●●) and 500 (△△△). (b): [Fe²⁺] (mM) = 0.1 (■), 0.2 (▲), 0.5 (●●) and 1.0 (△△△).

Figure 3. Evolution of ICE % during electro-Fenton treatment of 0.15 Mm moxifloxacin in 0.05 mM Na₂SO₄ at pH 3 and room temperature with [Fe²⁺] = 0.5 mM.

Notes: Applied current (mA): I = 60 (■), 100 (▲), 300 (●●), 400 (●●●) and 500 (△△△).
Better ICE% values were obtained for 60 mA reaching 16.8% at 60 min followed by 100 mA (14.74% at 60 min). As shown in Figure 3, ICE increases by decreasing the applied current density up to 500 mA, that can be related to formation of short-chain carboxylic acids that are resistant to mineralization where was the decrease in concentration of aromatics in aqueous solution.

3.2.1. Effect of MOXIFLOXACIN concentration on the mineralization in aqueous solution
The COD removal values increase by increasing the initial COD of the moxifloxacin solution, where that initial concentrations of moxifloxacin solutions are 0.075, 0.12, 0.15, and 0.2 mM, respectively, decreases under the same conditions for initial COD values to 14, 22, 28, and 47 mg L⁻¹ after 3 h (Figure 4). This can be explained that where the increment was in the number of collisions between the antibiotic molecules with themselves where the probability of collisions was between the decreased moxifloxacin and •OH radicals. On the other hand, COD of all the systems at the end of 4-h electrolysis reached at almost the same value.

3.3. Identification of the reaction intermediates
A general reaction sequence for the mineralization of moxifloxacin in acidic medium is followed by the hydroxyl radicals. A number of intermediate products were identified by HPLC (using available...
standards) and LC/MS analyses. HPLC chromatograms of these products are given in Figure 5. Table 1 details the intermediates products identified by HPLC, LC/MS by comparing their retention time with the standard compounds and method EUROPAN PHARMACOPOEIA 8.0.

4. Conclusion
Catalyst concentration, applied current and moxifloxacin concentration strongly influence the oxidation and mineralization kinetics; a complete transformation of moxifloxacin into its oxidation intermediates takes place within 8 min. The mineralization of moxifloxacin is found to be achieved by multiple attacks of •OH with several intermediate products formed during the course of EFP. Based on intermediates identified by HPLC and LC/MS.

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