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Comparing the electrochemical degradation of the fluoroquinolone antibiotics norfloxacin and ciprofloxacin using distinct electrolytes and a BDD anode: evolution of main oxidation byproducts and toxicity

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1. Introduction

Fluoroquinolones (FQs), one of the most important classes of antibacterial agents [1,2], are widely used as drugs in human and veterinary medicine due to their broad activity spectrum against gram-positive and gram-negative bacteria [3]. However, as noted by Wang et al. [4], they are only partially metabolized by the body, and thus a large variety of these drugs and their pharmacologically active forms are discharged into municipal wastewater systems [1]. Since these pollutants cannot be efficiently eliminated by municipal wastewater treatment plants [5], they are frequently detected in waterbodies [2]. Even though FQs are usually detected at trace concentration levels [6], they can promote antibiotic resistance [7,8] and present toxic effects to aquatic biota [9]. Therefore, powerful oxidative methods to remove these pollutants from wastewater have been extensively investigated [4,6,10–28].

New advanced oxidation processes based on electrochemical technology, the so-called electrochemical advanced oxidation processes (EAOPs) [29], are based on the in-situ electrogeneration of hydroxyl radicals (HO•) as main oxidant agents, which are able to oxidize a wide variety of persistent organic pollutants (POPs) to CO2, H2O and inorganic ions [30–35]. The main disadvantages of these processes include the costs associated with the electrical energy supply as well as the low

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ABSTRACT

The effects of the supporting electrolytes (SEs) Na2SO4, NaCl, Na2CO3, NaNO3, and Na3PO4 on the anodic oxidation of norfloxacin (NOR) and ciprofloxacin (CIPRO), assessed by the respective degradation kinetics and byproducts and electrolyzed solution antimicrobial activity, are compared. Galvanostatic anodic oxidations were performed in a filter-press flow cell fitted with a boron-doped diamond anode. Removal rates higher than the theoretical one for a process purely controlled by mass transfer were found for all SEs, indicative of contribution by indirect oxidation processes. However, the removal rates for NaCl were about tenfold higher, with the lowest energy consumption per order (EC0) of targeted pollutant removal rate (ca. 0.7 kW h m−3 order−1), a very competitive performance. The TOC removal rates were also affected by the SE, but not as markedly. The antimicrobial activity of the electrolyzed solutions against Escherichia coli showed distinct temporal profiles, depending on the fluoroquinolone and SE. For instance, when Na3PO4 was used, the antimicrobial activity was completely removed for NOR, but none for CIPRO; conversely, when NaCl was used, complete removal was attained only for CIPRO. From LC-MS/MS analyses of Na3PO4 electrolyzed solutions, rupture of the fluoroquinolone ring leading to byproducts with no toxicity against E. coli occurred only for NOR, whereas exactly the opposite occurred for the NaCl solutions. Clearly, the nature of both the SE and the fluoroquinolone influence the oxidation steps of the respective molecule; this was also evidenced by the distinct short-chain carboxylic acids identified in the degradation of NOR and CIPRO.

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conductance of many effluents that thus require the addition of an electrolyte [30,36]. In this context, in anodic oxidation the nature of the supporting electrolyte can influence the degradation kinetics and oxidation mechanism of the targeted organic compound through indirect electron transfer involving the mediation of oxidants, such as the persulfate, percarbonate, perphosphate, and active chlorine species that are electrochemically generated by anodic oxidation of the electrolyte ions sulfate, carbonate, phosphate, and chloride, respectively [30,32,37].

Despite the fact that most of the published studies on the anodic oxidation of organics employed Na2SO4 as the supporting electrolyte, it has been reported by different laboratories that the removal of the organics occurs faster when NaCl is used (see e.g. [14,16,38–40]). This can be attributed to the degradation of the pollutants in the solution bulk by the pH-dependent active chlorine species Cl2, HOCl, and OCl− [32,41]. In addition, the scavenging of HO• by sulfate ions is reported to be higher than the one by chloride ions [32]. However, the use of chloride-containing electrolytes can lead to the formation of organochlorine byproducts, which may be more toxic than the parent molecules (see e.g. [42]).

Although a large number of studies reported on the effect of operational parameters on the removal rates of organics using EAOPs, further investigations regarding the influence of distinct supporting electrolytes on the toxicity of the electrolyzed solutions are still needed. Hence, the goal of the present work is to compare the effect of distinct supporting electrolytes – SEs (Na2SO4, NaCl, Na2CO3, NaN3, and Na3PO4) on the anodic oxidation (AO) of the FQs norfloxacin (NOR, C16H18FN2O3) and ciprofloxacin (CIPRO, C17H18FN2O3) using a filter-press flow cell fitted with a boron-doped diamond (BDD) anode, as assessed by the respective FQ degradation kinetics and byproducts, as well as the electrolyzed solution antimicrobial activity. These FQs exhibit a small difference in their molecular structure, which can play an important role in the degradation mechanism; as can be seen in Fig. 1, NOR presents an ethyl group bonded to the nitrogen atom of the fluoroquinolone group, whereas CIPRO presents a cyclopropyl group. The extent of mineralization of the NOR and CIPRO solutions throughout the electrolyses in the distinct SEs will be monitored by analyses of the total organic carbon concentration (TOC), whereas the toxicity, i.e. antimicrobial activity, of the electrolyzed solutions will be assessed by the inhibition index (Iind) using the bacterium Escherichia coli (E. coli) as the testing organism. Furthermore, the initial or terminal oxidation intermediates formed during electrolyses of the FQs will be investigated using liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS) or LC with an ultraviolet-visible absorbance detector, respectively.

2. Experimental

2.1. Chemicals

All chemicals, including norfloxacin (99.9% Vita Nova), ciprofloxacin hydrochloride (Vita Nova), Na2SO4 (Qhemis), NaCl (Qhemis), Na2CO3 (Synth), NaN3 (Synth), Na3PO4 (Synth), Na2S2O8 (Sigma Aldrich), yeast extract (Sigma Aldrich), tryptone (Sigma Aldrich), KH2PO4 (Synth), H3PO4 (85%, Mallinckrodt), H2SO4 (98%, JT Baker), methanol (HPLC grade, Tedia), formic acid (HPLC grade, JT Baker), and other carboxylic acids (Sigma Aldrich), were used as received. All solutions were prepared using deionized water (Millipore Milli-Q system, resistivity ≥ 18 MΩ cm).

The BDD electrode, purchased from NeoCoat (Switzerland), was a BDD film (thickness of 2.9 μm, boron doping of 100 ppm, and sp3/sp2 carbon ratio of 215 as determined by the manufacturer through Raman spectroscopy analyses) deposited by CVD on a p-doped monocrystalline Si substrate.

2.2. Electrochemical degradation experiments

The electrochemical degradation experiments were carried out in a one-compartment filter-press flow cell, with a BDD anode and a plate of AISI 304 stainless steel as cathode (the exposed area of each electrode was 3.54 cm × 6.71 cm). More details on the setup of the assembled recirculating electrochemical system and flow cell are found elsewhere - see the supplementary material of [12]. During the AO of the FQs, the influence of their molecular structure and the SE nature on the toxicity of the electrolyzed solutions was investigated; the following SEs were assessed at the 0.1 mol L−1 ionic strength: Na2SO4, NaCl, Na2CO3, NaN3, and Na3PO4. The initial mass concentration of the FQs ([NOR] and [CIPRO]) was 100 mg L−1 (0.313 and 0.301 mmol L−1, respectively). With the goal of attaining low energy consumption values, all the degradation experiments were performed at a fixed, low value of the temperature (j =10 mA cm−2). The flow rate, solution volume, and temperature were fixed at 420 L h−1, 1.0 L, and 25 °C, respectively, in accordance with previous works from the laboratory [12,14,16,39]. Previous to any of the degradation electrolyses, the BDD anode was electrochemically pretreated in a 0.1 mol L−1 Na2SO4 solution by applying 20 mA cm−2 for 20 min, to remove any incidentally adsorbed organics.

2.3. Analytical methods

The evolution of [NOR] and [CIPRO] was monitored by LC with an UV/Vis absorbance detector at (280 nm) as described in detail elsewhere [14]. Using these data, the electric energy consumption per order of targeted pollutant removal (EOd) was calculated according to eq. 1 [44–46], being defined as the electric energy (e.g. kW h) required to remove 90% of a contaminant per unit volume (e.g. 1 m3) of the aqueous solution that contains that contaminant.

$$E_{Od} = \frac{UIt}{V \log \left( \frac{c_0}{c_f} \right)}$$

where $U$ is the average cell potential (V), $I$ the applied electric current (A), $t$ the electrolysis time (h), $V$ the solution volume (m3), and $c_0$ and $c_f$ are the initial and final (after a decrease of one order of magnitude) contaminant concentration. When pseudo-first order kinetics is assumed for the oxidation process, eq. 1 can be simplified to eq. 2 since log $\left( \frac{c_0}{c_f} \right)$ = 0.4343 kr.

$$E_{Od} = \frac{UI}{0.4343 kV}$$
where \( k \) is the pseudo-first-order kinetic constant (h\(^{-1}\)).

The evolution of each electrolyzed solution TOC was monitored using a GE Analytical Instruments Sievers Innovox TOC analyzer, as described in detail elsewhere [12,47]. Using these data, the mineralization current efficiency (MCE) was determined as [48]:

\[
\text{MCE (\%)} = \frac{\Delta \text{TOC}_t}{\text{F} \times \frac{4.32 \times 10^4}{V} \times 100}
\]

(3)

where \( \Delta \text{TOC}_t \) (mg L\(^{-1}\)) is the removed TOC after a given treatment time \( t \) (h), \( n \) the number of electrons transferred for FQ mineralization (assumed as 90 for NOR or 94 for CIPRO – see Eqs. (4) and (5) below), \( F \) the Faraday constant (96485 C mol\(^{-1}\) h), \( V \) the solution volume (L), \( 4.32 \times 10^4 \) a conversion factor (3600 s h\(^{-1}\)), 12000 mg mol\(^{-1}\)) and \( y \) the number of carbon atoms of the FQ molecule (16 for NOR or 17 for CIPRO).

\[
\text{C}_2\text{H}_5\text{FNO}_3 + 38\text{H}_2\text{O} \rightarrow 16\text{CO}_2 + F^- + 3\text{NO}_3^- + 94\text{H}^+ + 90e^- \quad (4)
\]

\[
\text{C}_2\text{H}_5\text{FNO}_3 + 40\text{H}_2\text{O} \rightarrow 17\text{CO}_2 + F^- + 3\text{NO}_3^- + 98\text{H}^+ + 94e^- \quad (5)
\]

The energy consumption per unit mass of removed TOC (\( E_{\text{TOC}} \), kW h g\(^{-1}\)) after a given treatment time was calculated according to the following equation [49]:

\[
E_{\text{TOC}} = \frac{U I t}{\Delta \text{TOC}_t} \quad (6)
\]

where \( U \) is the measured cell potential (V) at the given treatment time.

The initial oxidation intermediates formed during the fluoroquinolones AO were determined by LC-MS/MS. The analyses were carried out using an Agilent 1200 Series HPLC system coupled to a SCIEX 3200 QTRAP LC-MS/MS system, operating in a positive mode and TurboIonSpray ionization. The special software LightSight 2.3 (Nominal Mass Metabolite ID Software, AB SCIEX) was used to investigate all possibilities of metabolites. The application of the software was performed for all ionization and fragmentation parameters optimized for the initial compound. The parameters were obtained using direct infusion of a solution containing NOR or CIPRO (1 mg L\(^{-1}\)) in MeOH:H\(_2\)O (1:1, V/V, containing 0.1% formic acid) at the rate of 10 \( \mu \)L min\(^{-1}\). The obtained conditions were: curtain gas, 20 psi; ion spray, 5500 V; gas 1, 50 psi; gas 2, 50 psi; temperature, 700 °C; declustering potential, 36 V (NOR) and 46 V (CIPRO); entrance potential, 10 V (NOR) and 4.5 V (CIPRO); interface heater, on. Selected reaction monitoring (SRM) optimized and full scan experiments were automatically performed using the LightSight software to investigate different kinds of possible reactions, such as oxidation, hydroxylation, reduction, C-C bond cleavage, and others. The chromatographic separation was achieved using a C-18 Kinetex column (150 × 4.6 mm, 5 μm, Phenomenex) and a gradient elution using H\(_2\)O (A) containing 0.1% formic acid (V/V) and methanol (B) as mobile phase. The gradient elution was programmed as follows: 0–0.5 min (10% B), 0.5–10 min (90% B), 10–12 min (90% B), and conditioned to the initial conditions up to 15 min. The column oven temperature was set at 25 °C, the flow rate was 1.0 mL min\(^{-1}\), and the injection volume was 20 \( \mu \)L. Before analysis, 2.5 mL samples extracted at the given treatment times were frozen in liquid nitrogen and then lyophilized for 20 h using a CHsetattr alpha 2-4 LD Plus freeze-dryer; subsequently, they were resuspended in 1 mL of methanol and filtered using a 0.22 μm cartridge.

Terminal oxidation intermediates (short-chain carboxylic acids) were determined by liquid chromatography coupled to UV/Vis detection at 210 nm (LC-UV/Vis) using a Phenomenex Rezex ROA-H-TM column as the stationary phase and an aqueous 2.5 mmol L\(^{-1}\) H\(_2\)SO\(_4\) solution as the mobile phase. The flow rate and injection volume were 0.5 mL min\(^{-1}\) and 25 \( \mu \)L, respectively. The carboxylic acids were identified by comparing their retention times with those of previously analyzed standards.

Finally, the antimicrobial activity of the NOR and CIPRO electrolyzed solutions against \( E. coli \) was evaluated after different electrolysis times, expressed as a percentage inhibition index \( I_{\text{ind}} \). Detailed description about this toxicity assay has been provided in an earlier study [39]. The values of \( I_{\text{ind}} \) after the different electrolysis times were determined according to the following equation [50]:

\[
I_{\text{ind}} = \left( \frac{A_0 - A}{A_0} \right) \times 100\%
\]

(7)

where \( A_0 \) and \( A \) are the absorbance values of samples in the absence (negative control) and in the presence of NOR or CIPRO and/or its degradation intermediates, respectively. Hence, \( I_{\text{ind}} = 0\% \) indicates that the solution has no antimicrobial activity against \( E. coli \).

3. Results and discussion

3.1. Influence of the nature of the supporting electrolyte

The decays of the relative concentration of NOR and CIPRO as a function of electrolysis time using the distinct SEs at the ionic strength of 0.1 mol L\(^{-1}\) are presented in Fig. 2. As can be inferred from the data in this figure, for both FQs the removal rate was significantly higher when the electrooxidation was performed using NaCl as the SE, with complete removals within only 1 h of electrolysis. This behavior is certainly due to the active chlorine species (Cl\(_2\), HOCI and OCI\(^{-}\)) produced as a result of the direct oxidation of chloride ions on the anode surface. In this process, Cl\(^{-}\) ions diffuse towards the anode surface and are oxidized to Cl, which combines with other Cl atoms to produce Cl\(_2\). Then, Cl\(_2\) diffuses from the anode surface to the solution bulk yielding HClO or OCI\(^{-}\) by a disproportionation reaction, depending on the solution pH [32]. Although these species present a lower standard reduction potential than the HO\(^{+}\) radicals [30,32], they are not limited by mass transfer [45] and do oxidize the FQs. It is interesting to observe that for the other SEs investigated, their nature does not significantly affect the NOR and CIPRO removal rate or extent.

![Fig. 2. Remaining NOR and CIPRO fraction vs. electrolysis time (t) for the degradation of these fluoroquinolones (C\(_0\) = 100 mg L\(^{-1}\)) using different salts as the supporting electrolyte at a constant ionic strength of 0.1 mol L\(^{-1}\): (n) Na\(_2\)SO\(_4\), (●) NaCl, (▲) Na\(_2\)CO\(_3\), (▼) NaNO\(_3\), and (▲) Na\(_2\)PO\(_4\). The insets present kinetic analyses assuming pseudo-first-order reaction kinetics. Electrolysis conditions: \( j = 10 \) mA cm\(^{-2}\), \( V = 1.0 \) V, \( q_F = 420 \) L h\(^{-1}\), and \( \theta = 25 \) °C.](image-url)
For all the investigated SE solutions, a linear regression was obtained for the ln(c(t)/c_0) vs. t plots (see insets in Figs. 2a and 2b), where c_0 is the initial concentration of the FQ and c its concentration after a given electrolysis time t (both expressed as the integrated area of the respective chromatographic peak areas). Thus, it can be concluded that the electrochemical oxidation processes followed a pseudo-first order kinetics (the values of the respective apparent rate constants, k_ap, are listed in Table S1 in the supplementary material file). As expected, the higher values of k_ap attained when NaCl is the SE corroborate the much faster (about tenfold) oxidation of the FQs mediated by active chlorine in the solution bulk compared with that mediated only by HO· electrogenerated on the BDD surface. Similar results were previously reported for the electrochemical oxidation of enrofloxacin [14,16].

The applied charge per unit volume of electrolyzed solution (Q_ap) needed the remove the FQs using NaCl was only ~0.24 A h L⁻¹, compared with ~1.9 A h L⁻¹ for the other electrolytes. Recently, Mora-Gomez et al. [51] reported on the removal of NOR (100 mg L⁻¹) from a sulphate medium (2 g L⁻¹ Na₂SO₄) using a BDD anode, comparing the performance of this anode with that of a novel Sn-doped SnO₂ ceramic anode in a stirred undivided or divided electrochemical cell (NOR solution volume: 0.25 L), at different j values. For the BDD anode in the undivided electrochemical cell and the lowest applied j value (33 mA cm⁻²), a higher value of ~5.5 A h L⁻¹ can be estimated for Q_ap. The comparatively improved performance attained in our work (Q_ap ~1.9 A h L⁻¹) highlights the importance of the mass transport conditions, which are significantly enhanced when a flow filter-press reactor is used instead of a stirred one-compartment cell, as previously noted [52,53].

The contribution of indirect, mediated oxidation processes for the increased removal rates of the FQs can be assessed by comparing the respective experimental data with the theoretical ones for a process purely controlled by mass transfer. In this context, the theoretical exponential concentration decay lines presented in Fig. 2 were determined according to the following equation:

\[
\frac{c_t}{c_0} = \exp \left( -\frac{A k_{ap} j}{V} t \right)
\]

(8)

where A is the geometric area (m²) of the BDD anode, V the electrolyzed solution volume (m³), and k_ap the mass transfer coefficient that is equal to 2.77 × 10⁻³ or 2.85 × 10⁻³ m s⁻¹ for NOR or CIPRO, respectively, at 25 °C. These k_ap values were calculated using the value of the limiting diffusion layer thickness (2.29 × 10⁻⁵ m) – obtained by a simple electrochemical assay based on the [Fe(CN)₆]⁴⁻/[Fe(CN)₆]³⁻ redox pair [54] – and the NOR or CIPRO diffusion coefficient (6.35 × 10⁻¹⁰ or 6.53 × 10⁻¹⁰ m² s⁻¹, respectively) – determined by the Wilke-Chang correlation equation [55]. As can be inferred from Fig. 2, for all the investigated electrolytes the attained NOR and CIPRO degradation rates are higher than the theoretically predicted ones. These results are related to indirect oxidation processes in the solution bulk mediated by electrogenerated oxidants such as persulfate, perphosphate, and active chlorine species. As can be seen in Fig. 2 and discussed above, the NOR and CIPRO degradation rates in the NaCl medium are considerably more pronounced than in the other electrolytes, thus leading to significantly greater pseudo-first-order kinetic constants. Other authors also reported markedly increased organics removal rates in solutions containing chlorine species [4,14,16,39,43], which can be explained by the ability of these species to promote electrophilic reactions on the organic molecules. However, the possible electrogeneration of organochlorine intermediates and their toxicity should be investigated.

Since electric energy significantly contributes to the operating costs of an EAO, the energy consumption per order of targeted pollutant removed (E_EO) was calculated using eq. 1 [44–46]. As can be inferred from the data presented in Fig. 3, no significant difference in the E_EO values was observed for the FQs in each SE. However, when the E_EO values for the distinct electrolytes are compared for the same FQ, the lowest values of E_EO were attained when NaCl was used, only ca. 0.7 kW h m⁻³ order⁻¹, being one order of magnitude lower in comparison with the values attained using the other SEs. These results were expected as both FQs were promptly oxidized by active chlorine (see Fig. 2). Previous studies have reported E_EO values for the electrochemical oxidation of different organic compounds, ranging from 10 to as high as 2300 kW h m⁻³ order⁻¹ for different anode materials, as noted by Lanzarini-Lopes et al. [45]. Specifically, Wang et al. [56] obtained an E_EO value of 31.6 kW h m⁻³ order⁻¹ for the degradation of CIPRO (c₀ = 100 mg L⁻¹) from a Na₂SO₄ SE, using a SnO₂-5H₂O anode at 30 mA cm⁻². Lanzarini-Lopes et al. [45], who employed a BDD anode at 16.6 mA cm⁻² for the removal of the p-chlorobenzoic acid (c₀ ≈ 188 mg L⁻¹) also from a Na₂SO₄ SE, reported an E_EO value of 39.3 kW h m⁻³ order⁻¹. In this context, by comparison the electrochemical system of the present work is very competitive in terms of energy consumption. However, it is important to note that E_EO depends on several operational parameters, such as the initial organics concentration and its nature, the temperature and pH, as well as mass and charge transfer limitations, among others.

As can be inferred from the data in Fig. 4, although the removal rates of NOR and CIPRO were markedly more pronounced using NaCl as the SE, their mineralization rates were similar to the ones attained using NaNO₃ (leading to ~80% mineralization within 8 h of electrolysis), but higher than the ones attained using the other SEs. Previously, Aquino et al. [43] reported that the electrochemical mineralization of the anthaquinonic dye Acid Blue 62 was increased when 20 mmol L⁻¹ NaCl was added to the 100 mmol L⁻¹ Na₂SO₄ SE. The contribution of indirect oxidation processes for the TOC removal was also assessed by comparing the experimental data with the theoretical ones based on a process purely controlled by mass transfer (see Fig. 4). In contrast to the comparison for the FQs removal (see Fig. 2), the attained mineralization rates are smaller than the theoretically predicted values. These results might be understood considering the different nature of the FQs removal and mineralization processes. The FQs removal can be limited to a simple modification (oxidation) step of the FQs molecular structure, whereas the complete mineralization process necessarily involves several oxidation steps. Furthermore, when BDD anodes are used [32], simple oxidation processes can take place both on the electrode surface and in the solution bulk, whereas the mineralization process occurs mostly on the electrode surface mediated by adsorbed HO·. As noted by Coledam et al. [39], this latter process is limited by mass transfer, i.e. by the transport of NOR, CIPRO, and their degradation intermediates to the anode surface. Once the mineralization process is dependent mostly on the extent of HO· electrogeneration on the BDD anode surface, similar mineralization rates can be expected irrespective of the SE because the applied current density, the hydrodynamic conditions, and other variables such as pH and temperature...
were kept constant. Therefore, the different attained TOC removal rates could be due to some scavenging of HO⁺ by SE ions, such as CO₃²⁻ and PO₄³⁻, according to eqs. 9 and 10 [30,32]. Here, it should be pointed out again that the pseudo-first-order kinetic constants for TOC removal, as well as those for the FQs removal (see Tables S1 and S2 in the supplementary material file), remained very close for both antibiotics, which suggests that the distinct substituents in the N atom of the fluoroquinolone ring have no significant effect towards their oxidation reactivity.

\[
\begin{align*}
\text{CO}_3^{2-} + \text{HO}^+ & \rightarrow (\text{CO}_3^\cdot)^+ + \text{OH}^- \quad (9) \\
\text{PO}_4^{3-} + \text{HO}^+ & \rightarrow (\text{PO}_4^\cdot)^+ + \text{OH}^- \quad (10)
\end{align*}
\]

As can be seen in the insets of Fig. 4, the mineralization current efficiency (MCE) decreased with the electrolysis time as a consequence of the organic-load removal and the production of recalcitrant final intermediates (see below). High MCE values are expected at the beginning of the AO process because the applied current density (10 mA cm⁻²) is not far from the initial limiting current density \(j_{\text{lim}}\), i.e. 7.5 or 7.8 mA cm⁻² for NOR or CIPRO, respectively. The values of \(j_{\text{lim}}\) were determined using this equation:

\[
j_{\text{lim}} = n F k_a c_0 \quad (11)
\]

where \(n\) is the number of electrons involved in the complete electro-oxidation process of NOR and CIPRO (see eqs. 4 and 5) and \(c_0\) is their initial concentration (mol m⁻³). According to this equation, \(j_{\text{lim}}\) decreases as the FQ concentration becomes smaller and, consequently, parasitic reactions (eqs. 12-14) [45] as well as oxidant regeneration from electrolyte ions become increasingly more predominant, leading to lower MCE values. As can be seen in Fig. S1 in the supplementary material file, an opposite profile was obtained for EC-TOC, which increases with TOC removal. To attain higher MCE values, other EAOPs could be used, such as Fenton-based or UV-coupled processes [32,35].

\[
\text{2H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \quad (12)
\]

A comparison of the attained MCE values for NOR mineralization from the Na₂SO₄ electrolyte solution (see inset in Fig. 4a) with the values reported by Mora-Gomez et al. [51] allows highlighting two important electrolys conditions that markedly determine performance: mass transport conditions and applied current density. Since those authors executed the NOR degradation electrolysis simply using a stirred one-compartment electrochemical cell and applying a higher current density (the lowest value was 32 mA cm⁻²), their attained MCE values were much lower: ≤10%, compared with ≥90% in this work accompanied by higher degrees of mineralization. Similar low MCE values (≤9%) where reported by Wachtler et al. [22] for CIPRO mineralization (for a lower value of \(c_0\), 50 mg L⁻¹) from a Na₂SO₄ electrolyte solution also in a filter-press reactor with a BDD anode, but with different flow conditions.

3.2. Assessment of the toxicity of the electrolyzed solutions

The organic load that remains as the electrolysis progresses (reflected as TOC) can be due to the presence of recalcitrant degradation intermediates, some of which may retain the antibiotic activity of the original FQ molecules. Thus, the toxicity of the electrolyzed solutions should be investigated to assess whether the electrochemical degradation process yields nontoxic (or less toxic) solutions. Consequently, the inhibition growth index \(I_{\text{ind}}\) of \(E.\ coli\) for the electrolyzed NOR and CIPRO solutions in the different SEs was determined for up to 16 h of...
electrolysis. As can be seen in Fig. 5, distinct electrolysis time profiles were obtained for ROH depending on the SE and FQ assessed. For NOR, complete removal of the antimicrobial activity, i.e., \( I_{\text{ind}} = 0 \%), could be attained when Na\(_2\)SO\(_4\), Na\(_2\)CO\(_3\), NaNO\(_3\) or NaPO\(_4\) was used as the SE; for NaCl, \( I_{\text{ind}} \) only started to decrease after \( \approx 11 \) h of electrolysis, but remained at \( \approx 35\% \) after \( 16 \) h of electrolysis. Conversely, for CIPRO \( I_{\text{ind}} = 0 \%) was attained only when NaCl was the SE, after \( 11 \) h of electrolysis; for Na\(_2\)SO\(_4\), Na\(_2\)CO\(_3\), and NaNO\(_3\), the antimicrobial activity was only partially removed, whereas no removal at all occurred for NaPO\(_4\). Very recently, Montanès et al. [28] reported that four-hour-long electrochemical oxidations (33 mA cm\(^{-2}\) \( \leq \) \( j \leq \) 8 mA cm\(^{-2}\)) of a 100 mg L\(^{-1}\) NOR solution (in 2 mg L\(^{-1}\) Na\(_2\)SO\(_4\)) using a BDD anode in an undivided cell led to increased toxicity of the solution against Lactuca sativa and Vibrio fischeri, despite 100% removal of NOR and \( \approx 50\% \) removal of TOC. The increase in toxicity, which was dependent on the value of \( j \), was attributed to the possible generation of persulfate ions.

In the present work, the persistence of the antimicrobial activity in some conditions might be related to two factors. First, traces of the original FQ may have remained in the electrolyzed solution at a concentration that could not be detected by LC-UV/Vis but was higher than the so-called minimum inhibitory concentration, MIC [57]; the MIC value for NOR is \( \approx 1 \) mg L\(^{-1}\) [58] and that for CIPRO is in the range of \( \leq 0.01 \)–0.2 mg L\(^{-1}\) [59].

### 3.3. Assessment of the degradation intermediates

#### 3.3.1. Initial intermediates

The initial intermediates were assessed by LC-MS/MS analyses only for electrolyzed solutions of the FQs in which NaPO\(_4\) or NaCl was used as the SE, as described in section 2.3. As can be inferred from the data in Table 1, for NaPO\(_4\) as the SE the majority of the initial oxidation and hydroxylation reactions of CIPRO occur only in the piperazine side-chain. When NOR undergoes AO under the same conditions, other reactions occur besides the attack by the oxidizing species on the piperazine sidechain: oxidation and hydroxylation of the ethyl group and of the fluoroquinolone ring were also proposed, as well as the rupture of the fluoroquinolone ring (see Table 2). As previously reported [12,14], the antimicrobial activity of FQs against E. coli can be related to the fluoroquinolone structure of their molecules, which corroborates the present results (Fig. 5). Here, when NaPO\(_4\) was used as the SE, a complete removal of the antimicrobial activity was attained for the electrolyzed NOR solution, whereas no decrease at all in the antimicrobial activity could be achieved for the electrolyzed CIPRO solution even after \( 16 \) h of electrolysis.

During the degradation of NOR using NaCl as the SE, initial hydroxylation reactions were also observed in the ethyl and piperazinyl groups of the molecule as well as in the fluoroquinolone ring, resulting in the rupture of these last two structures (see Table 3). In this condition, the \( m/z \) 354 compound (with the fluoroquinolone moiety intact) was detected up to the end of the electrolysis, which justifies the detected persistence of the antimicrobial activity, i.e., \( I_{\text{ind}} \) ca. 35%, even after \( 16 \) h of electrolysis. Conversely, as can be inferred from the data in Table 4, the cleavage of the fluoroquinolone ring was not identified in any of the initial intermediates detected by LC-MS/MS for the degradation of CIPRO using NaCl as the SE; however, the antimicrobial activity of the electrolyzed solution ceased in the earlier stages of the electrolysis (after \( 10 \) h). In this case, only four initial degradation intermediates were identified (see Table 4); among them, the \( m/z \) 314, 336, and 366 compounds were no longer detected after \( 3 \) h of electrolysis, whereas the \( m/z \) 361 compound was detected up to \( 10 \) h of electrolysis. Considering all these discussions, the faster removal of the antimicrobial activity of the CIPRO-in-NaCl solution might be due to a rapid initial oxidation of the CIPRO molecule (the cyclopropyl as well as the fluoroquinolone structure) and its intermediates, leading either to the complete removal of any antimicrobially active compound or the attainment of concentrations lower than the MIC. This could explain the detection of only four initial intermediates. Here it is important to note

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**Table 1**

| Molecular ion (m/z) | Retention time / min | Fragment ions (m/z) | Proposed chemical structure |
|--------------------|---------------------|---------------------|---------------------------|
| 320                | 8.90                | 302, 275, and 201   |                           |
| 334a               | 6.21                | 316, 289, 271, 217, and 220 |       |
| 334b               | 8.55                | 316, 302, 271, 244, and 217 |       |
| 346                | 6.57                | 328, 314, 302, and 231 |                           |
| 348a               | 8.45                | 330, 272, 245, and 174 |                           |
| 348b               | 6.91                | 330, 304, 294, 261, and 247 |       |
| 360                | 9.06                | 342, 272, 243, 230, and 215 |       |
| 361                | 9.11                | 343, 301, 274, 244, and 215 |       |
that other initial intermediates may have been produced in all the analyzed electrolysis conditions, but at concentrations that were too low to allow analysis by MS/MS.

The proposed fragmentation routes for all the initial intermediates detected during the electrochemical degradation of NOR and CIPRO using Na$_3$PO$_4$ or NaCl as the SE (shown in Tables 1 to 4) are presented in Figs. S2 to S28 in the supplementary material file. It is worthwhile mentioning that no chlorinated initial intermediates were identified in the NaCl electrolyzed solutions of both NOR and CIPRO, which is in contrast to results obtained for the fluoroquinolone enrofloxacin [14, 16].

Regarding their specific molecular structures, NOR has an ethyl group bonded to the nitrogen of the fluoroquinolone moiety, whereas CIPRO has a cyclopropyl group in that same position. Considering that only the piperazine ring is oxidized during the degradation of CIPRO

### Table 2

| Molecular ion (m/z) | Retention time / min | Fragment ions (m/z) | Proposed chemical structure |
|--------------------|----------------------|---------------------|-----------------------------|
| 240                | 4.17                 | 222 and 179         |                             |
| 269a               | 4.64                 | 251, 233, 190, and 123 |                             |
| 269b               | 4.99                 | 251, 233, 225, 208, and 153 |                             |
| 297                | 4.93                 | 279, 251, 233, 213, and 190 |                             |
| 322                | 8.17                 | 304, 276, 231, 217, and 205 |                             |
| 334                | 6.52                 | 316, 290, 233, 219, and 205 |                             |
| 336a               | 8.30                 | 318, 298, 273, 230, 203, and 187 |                             |
| 336b               | 6.97                 | 318, 292, and 185 |                             |
| 348                | 6.41                 | 330, 304, 273, and 245 |                             |

### Table 3

| Molecular ion (m/z) | Retention time / min | Fragment ions (m/z) | Proposed chemical structure |
|--------------------|----------------------|---------------------|-----------------------------|
| 285                | 5.23                 | 265 and 170         |                             |
| 324                | 6.77                 | 268 and 251         |                             |
| 334                | 8.77                 | 298, 275, and 247   |                             |
| 338                | 7.47                 | 320, 290, 265, and 237 |                             |
| 346                | 8.68                 | 329, 298, 275, 259, and 247 |                             |
| 348                | 8.68                 | 331, 277, 261, 249, and 212 |                             |
| 354                | 6.42                 | 336, 310, 290, 275, and 267 |                             |

### Table 4

| Molecular ion (m/z) | Retention time / min | Fragment ions (m/z) | Proposed chemical structure |
|--------------------|----------------------|---------------------|-----------------------------|
| 314                | 9.99                 | 272 and 245         |                             |
| 336                | 5.28                 | 318, 249, and 196   |                             |
| 361                | 0.15                 | 274                 |                             |
| 366                | 6.47                 | 348, 322, 279, and 223 |                             |
using Na₃PO₄ as the SE, the NOR ethyl group seems to be more susceptible to oxidation than the CIPRO cyclopropyl group.

Summarizing the results of the LC/MS-MS analyses, all the detected initial degradation intermediates resulted from three main electro-oxidation pathways in the FQ molecules, without defluorination: i) hydroxylation and/or oxidation reactions in the fluoroquinolone structure, ii) removal or hydroxylation of the piperazinyl group, and iii) removal or hydroxylation/oxidation of the ethyl group of NOR. No hydroxylation reactions in the CIPRO cyclopropyl ring were proposed in any of the fragmentation routes, except for the m/z 336 compound whose cyclopropyl ring is opened (see Table 4); the inertness of this group is present in many papers that reported FQs degradation by other AOPs, such as: ozonation [10]; electro-Fenton [31]; UV, H₂O₂, UV/H₂O₂, modified Fenton and modified photo-Fenton [18]; ferrous-activated peroxymonosulfate [20], photocatalysis [18]. The higher susceptibility of the piperazine moiety might be related to the oxidation reaction of the tertiary amine to produce anilinyl radicals that are in resonance with iminium ions, as discussed by Zhang and Huang [60]. Then, the latter ion can undergo hydroxylation or dealkylation reactions mediated by hydroxyl radicals to yield compounds such as m/z 320, 334b, 348a (from Table 1) or 269b and 297 (from Table 2).

### 3.3.2. Terminal intermediates

The terminal intermediates (short-chain carboxylic acids) were investigated by LC-UV/Vis for electrolyzed solutions of the FQs in the different SEs, as described in section 2.3. The chromatograms exhibited peaks corresponding to several carboxylic acids, including succinic, malic, propionic, and tartaric, which are formed from aromatic benzene cleavages [45]. These acids can be further oxidized to shorter-chain carboxylic acids [45], such as the oxalic, acetic, and formic acids that were also identified in the analyses.

As can be seen in Figs. 6 and 7, distinct carboxylic acids were detected for each electrolyte solution confirming that the electro-generated oxidants attack the FQs molecules at different functional groups according to the oxidant nature. Furthermore, the carboxylic acids identified for the NOR oxidation are not the same as those identified for the CIPRO oxidation in the same electrolyte solution despite the similarities in the molecular structure of these FQs (see Fig. 1). For instance, in the AO of CIPRO using NaCl as the SE (see Fig. 7b), malic acid accumulated in the beginning of electrolysis, reaching a maximum concentration of ~56 mg L⁻¹ at 3 h and being completely removed after 8 h of electrolysis, whereas no malic acid was identified in the AO of NOR (only low concentrations of glyoxylic and acetic acid were detected). It should be noted that for this SE, no chlorinated acids were identified along the electrolyses of both FQs. Interestingly, in the AO of NOR using Na₂SO₄ as the SE, succinic acid accumulated as the electrolysis progressed (see Fig. 6a); thus, at its end (after 8 h) most of the remaining TOC (see Fig. 4a) was contained in this acid. On the other hand, it is also interesting to note that succinic acid was not detected when the electrolysis was carried out at 40 °C [12].

The significant number of short-chain carboxylic acids detected, resulting from consecutive oxidation steps of the FQs, may be due to the low applied value of the current density, which is close to the limiting one [39]. It should be noted that despite the presence of some carboxylic acids at low concentrations during the AO process, these terminal intermediates are biodegradable and thus are considered to be environmentally innocuous species [45], as also predicted specifically for formic and oxamic acid in a previous work from our research group [23].

### 4. Conclusions

Total removal of NOR and CIPRO was attained in the electro-oxidation of these drugs using a flow cell with a BDD anode and distinct supporting electrolyte solutions (NaCl, Na₂SO₄, Na₂CO₃, NaNO₂, and Na₃PO₄). However, the electrooxidation of NOR and CIPRO in the NaCl medium is considerably more pronounced than in the other electrolytes, thus leading to the lowest value of electric energy consumption per order (E₉₀), ca. 0.7 kW h m⁻³ order⁻¹. By comparing the E₉₀ values obtained in this work with those from previous studies, the here-used electrochemical system proved to be very competitive in terms of energy consumption; nevertheless, it is important to note that attained E₉₀ values depend on several operational parameters. The influence of mediated oxidation in these processes can be appreciated through the
antimicrobial activity of NOR, CIPRO, and their byproducts against *E. coli*, and the terminal oxidation intermediates in the form of short-chain carboxylic acids, which show distinct profiles depending on the supporting electrolyte solution. For instance, the complete removal of the antimicrobial activity of CIPRO and its byproducts against *E. coli* was attained in the electrolysis of this FQ using NaCl, whereas no removal at all was attained when Na$_2$PO$_4$ was used. As shown by the LC-MS/MS analyses, the antimicrobial activity of the fluoroquinolones and their byproducts can be related to the rupture of the fluoroquinolone ring. Additionally, removal of the antimicrobial activity against *E. coli* was observed in the degradation of NOR using Na$_2$PO$_4$, evidencing that the molecular structure of the fluoroquinolones also plays a role in the oxidation steps. Clearly, the nature of both the supporting electrolyte and the fluoroquinolone influence the oxidation steps of the respective molecule; this is also supported by the terminal oxidation intermediates analyses, when a higher number of short-chain carboxylic acids were identified in the degradation of NOR. In all electrolyses, at the end there is some remaining TOC, but that is related to biodegradable innocuous compounds, i.e. short-chain carboxylic acids.

**Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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**Appendix A. Supplementary data**

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jece.2020.104433.

**References**

[1] M.C. Dodd, A.D. Shah, U. von Gunten, C.-H. Huang, Interactions of fluoroquinolone antibacterial agents with aqueous chlorine: reaction kinetics, mechanisms, and transformation pathways, Environ. Sci. Technol. 39 (2005) 7065–7076, https://doi.org/10.1021/es050504z.

[2] V.M.F. Frade, M. Dias, A.C.S.C. Teixeira, M.S.A. Palma, Environmental contamination by fluoroquinolones, Brazilian J. Pharm. Sci. 50 (2014) 41–54, https://doi.org/10.1590/1984-8520201101000904.

[3] S. Babic, M. Perisa, I. Storic, Photolytic degradation of norfloxacin, enrofloxacin and ciprofloxacin in various aqueous media, Chemosphere 93 (2013) 1635–1642, https://doi.org/10.1016/j.chemosphere.2012.10.072.

[4] C. Wang, L. Yin, Z. Xu, J. Niu, L.A. Hou, Electrochemical degradation of enrofloxacin by lead dioxide anode: kinetics, mechanism and toxicity evaluation, Chem. Eng. J. 326 (2017) 911–920, https://doi.org/10.1016/j.cej.2017.06.038.

[5] M.J. Shreve, R.A. Brennan, Trace organic contaminant removal in six full-scale integrated fixed-activated sludge (IFAS) systems treating municipal wastewater, Water Res. 151 (2019) 318–331, https://doi.org/10.1016/j.watres.2019.01.034.

[6] D.A.C. Coledam, J.M. Aquino, B.F. Silva, A.J. Silva, R.C. Rocha-Filho, Electrochemical mineralization of norfloxacin using distinct boron-doped diamond anodes in a filter-press reactor, with investigations of toxicity and oxidation by-products, Electrochim. Acta. 213 (2016) 856–864, https://doi.org/10.1016/j.electacta.2016.08.003.

[7] E. Guinea, J.A. Garrido, R.M. Rodríguez, P.-L. Cabot, C. Arias, F. Centellas, Electrochemical degradation of ciprofloxacin with highly ordered mesoporous MnCo$_2$O$_4$-CF cathode: enhanced redox capacity and accelerated electron transfer, Chem. Eng. J. 358 (2019) 299–309, https://doi.org/10.1016/j.chemosphere.2018.10.047.

[8] J. Carneiro, J.M. Aquino, S. Lin, W. Cao, Z. Li, W. Liu, Photocatalytic degradation of norfloxacin using N-doped TiO$_2$: optimization, mechanism, identification of intermediates and toxicity evaluation, Chemosphere 237 (2019) 124433, https://doi.org/10.1016/j.chemosphere.2019.124433.

[9] Y. Sun, D.-W. Cho, N.J.D. Graham, D. Hou, A.C.K. Yip, E. Khan, H. Song, Y. Li, D.C. W. Tsang, Degradation of antibiotics by modified vacuum-UV-based processes: mechanistic consequences of H$_2$O$_2$ and K$_2$S$_2$O$_8$ in the presence of halide ions, Sci. Total Environ. 664 (2019) 312–321, https://doi.org/10.1016/j.scitotenv.2019.02.060.

[10] N. Wachter, J.M. Aquino, M. Denadai, J.C. Barreiro, A.J. Silva, Q.B. Cass, N. Bocchi, R.C. Rocha-Filho, Electrochemical degradation of the antibiotic ciprofloxacin in a flow reactor using distinct BDD anodes: reaction kinetics, identification and toxicity of the degradation products, Chemosphere 234 (2019) 461–470, https://doi.org/10.1016/j.chemsus.2019.06.053.

[11] N. Wachter, J.M. Aquino, M. Denadai, J.C. Barreiro, A.J. Silva, Q.B. Cass, N. Bocchi, R.C. Rocha-Filho, Optimization of the electrochemical degradation process of the antibiotic ciprofloxacin using a double-sided µ-PbO$_2$ anode in a flow reactor: kinetics, identification of oxidation intermediates and toxicity evaluation, Environ. Sci. Pollut. Res. 26 (2019) 4438–4449, https://doi.org/10.1007/s11356-018-2349-8.

[12] Y. Wang, D. Tian, W. Chu, M. Li, X. Lu, Nanoscaled magnetic CuFe$_2$O$_4$ as an activator of peroxymonosulfate for the degradation of antibiotics norfloxacin, Sep. Purif. Technol. 212 (2019) 536–544, https://doi.org/10.1016/j.seppur.2018.11.051.

[13] X. Yu, J. Zhang, J. Zhang, J. Niu, J. Zhao, Y. Wei, B. Yao, Photocatalytic degradation of ciprofloxacin using ZnO-doped CuO$_2$ particles: analysis of degradation pathways and intermediates, Chem. Eng. J. 374 (2019) 316–327, https://doi.org/10.1016/j.cej.2019.05.177.

[14] G. Zhang, Y. Xue, Q. Wang, H. Yao, W. Zhang, J. Zhao, Y. Li, Photocatalytic oxidation of norfloxacin by ZnO, supported on Ni-foam under visible light irradiation, Chemosphere 230 (2019) 405–415, https://doi.org/10.1016/j.chemosphere.2019.05.015.

[15] Q. Huang, C. Fang, M. Muhammad, G. Yao, Assessment of norfloxacin degradation induced by plasma-produced ozone using surface-enhanced Raman spectroscopy, Chemosphere 230 (2019) 124618, https://doi.org/10.1016/j.chemosphere.2019.124618.

[16] M.T. Montañés, M. García-Gabaldón, L. Boca-Pérez, J.J. Giner-Sanz, J. Mora, Gómez, V. Pérez-Herranz, Analysis of norfloxacin ecotoxicity and the relation with its degradation by means of electrochemical oxidation using different anodes,
W. Wu, Z. Huang, T. Lim, A comparative study on electrochemical oxidation of bisphenol A by boron-doped diamond anode and modified SnO₂-Sb anodes: influencing parameters and reaction pathways, J. Environ. Chem. Eng. 4 (2016) 2807–2815, https://doi.org/10.1016/j.jece.2016.05.034.

J.M. Aquino, M.A. Rodríguez, R.C. Rocha-Filho, C. Siesz, P. Cañizares, Influence of the supporting electrolyte on the electrolyses of dyes with conductive-diamond anodes, Chem. Eng. J. 184 (2012) 221–227, https://doi.org/10.1016/j.cej.2012.01.044.

J.R. Bolton, K.G. Bircher, W. Tumas, C.A. Tolman, Figures-of-merit for the technical development and application of advanced oxidation technologies for both electric- and solar-driven systems (IUPAC Technical Report), Pure Appl. Chem. 73 (2001) 627–637, https://doi.org/10.1351/pac200173040627.

M. Lanzarini-Lopes, S. García-Segura, K. Hristovski, P. Westerhoff, Electrical energy per order and current efficiency for electrochemical oxidation of p-chlorobenzoic acid with boron-doped diamond anode, Chemosphere 188 (2017) 304–311, https://doi.org/10.1016/j.chemosphere.2017.08.145.

S. García-Segura, H.O.N. Tugaon, K. Hristovski, P. Westerhoff, Photon flux influence on photoelectrochemical water treatment, Electrochem. Commun. 87 (2018) 63–65, https://doi.org/10.1016/j.elecom.2017.12.026.

I.J.S. Monte, B.F. Silva, J.M. Aquino, On the performance of a hybrid process to mineralize the herbicide tetramisuron using a DSA®- anode and UVC light: a mechanistic study, Appl. Cat. B, Environ. 200 (2016) 237–245, https://doi.org/10.1016/j.apcatb.2016.07.003.

M. Skoumal, A. Arias, F.L. Cabot, F. Centellas, J.A. Garrido, R.M. Rodríguez, E. Brillas, Mineralization of the bicarbonate anion by electrochemical advanced oxidation processes, Chemosphere 71 (2008) 1718–1729, https://doi.org/10.1016/j.chemosphere.2007.12.029.

E. Brillas, I. Sirés, M.A. Oturan, Electro-Fenton process and related electrochemical technologies based on Fenton’s reaction chemistry, Chem. Rev. 109 (2009) 6570–6631, https://doi.org/10.1021/cr900363g.

S. Silambarasan, A.S. Vangal, Biodegradation of 4-nitroaniline by plant-growth promoting Azotobacter sp. AVLB2 and toxicological analysis of its biodegradation metabolites, J. Hazard. Mater. 302 (2016) 428–434, https://doi.org/10.1016/j.jhazmat.2015.10.010.

J. Mora-Gómez, E. Ortega, S. Mestre, V. Perez-Herranz, M. Garcia-Baboljov, Electrochemical degradation of norfloxacin using BDD and new Nb-doped SnO₂ ceramic anodes in an electrochemical reactor in the presence and absence of a cation-exchange membrane, Sep. Purif. Technol. 208 (2019) 68–75, https://doi.org/10.1016/j.seppur.2018.05.017.

G.P. Pereira, R.C. Rocha-Filho, N. Bocchi, S.R. Biaggio, Electrochemical degradation of bisphenol A using a flow reactor with a boron-doped diamond anode, Chem. Eng. J. 198–199 (2012) 282–288, https://doi.org/10.1016/j.cej.2012.05.057.

G.P. Pereira, B.F. Silva, R.V. Oliveira, D.A.C. Coledam, J.M. Aquino, R.C. Rocha-Filho, N. Bocchi, S.R. Biaggio, Comparative electrochemical degradation of the herbicide tebuconozole using a flow cell with a boron-doped diamond anode and identifying degradation intermediates, Electrochim. Acta 247 (2017) 860–870, https://doi.org/10.1016/j.electacta.2017.04.039.

P. Cañizares, J. García-Gómez, I.F. de Marcos, M.A. Rodríguez, J. Lobato, Measurement of mass-transfer coefficients by an electrochemical technique, J. Chem. Educ. 83 (2006) 1204–1207, https://doi.org/10.1021/ed083p1204.

C.R. Wilke, P. Chang, Correlation of diffusion coefficients in dilute solutions, Aiche J. 1 (1955) 264–270, https://doi.org/10.1002/aic.690010222.

W. Wang, C. Shen, M. Zhang, B. Zhang, Y. Yu, The electrochemical degradation of ciprofloxacin using a SnO₂-Sb/Ti anode: Influencing factors, reaction pathways and energy demand, Chem. Eng. J. 296 (2016) 79–89, https://doi.org/10.1016/j.cej.2016.03.093.

F. Pasqua, G. Manfreda, Mutant prevention concentration of ciprofloxacin and enrofloxacin against Escherichia coli, Salmonella Typhimurium and Pseudomonas aeruginosa, Vet. Microbiol. 119 (2007) 304–310, https://doi.org/10.1016/j.vetmic.2006.08.018.

S.R. Noorby, M. Jonsson, Antibacterial activity of norfloxacin, Antimicrob. Agents Chemother. 25 (1983) 15–18, https://doi.org/10.1128/AAC.25.1.15.

N. Chinn, H.C. Neu, Ciprofloxacin, a quinolone carboxylic acid compound active against aerobic and anaerobic bacteria, Antimicrob. Agents Chemother. 25 (1984) 319–326, https://doi.org/10.1128/ AAC.25.3.319.

H. Zhang, C.-H. Huang, Oxidative transformation of fluoroquinolone antibacterial agents and structurally related amines by manganese oxide, Environ. Sci. Technol. 39 (2005) 4474–4483, https://doi.org/10.1021/es048166d.

J.F. Carneiro et al., Oxidative degradation study on antimicrobial agent ciprofloxacin by electrochemical advanced oxidation processes: today and tomorrow, Environ. Sci. Pollut. Res. 24 (2017) 6470–6479, https://doi.org/10.1002/acs.69001319.

O. Scialdone, S. Randazzo, A. Galia, G. Silvestri, Electrochemical oxidation of organic in water: role of operative parameters in the absence and in the presence of NaCl, Water Res. 43 (2009) 2260–2272, https://doi.org/10.1016/j.watres.2009.02.014.

D.A. Coledam, M.M.S. Pupo, B.F. Silva, A.J. Silva, K.I.B. Eguiluz, G.R. Salazar-Banda, J.M. Aquino, Electrochemical mineralization of ciprofloxacin using a conductive diamond anode: a mechanistic and toxicity investigation, Chemosphere 168 (2017) 638–647, https://doi.org/10.1016/j.chemosphere.2016.11.013.

Y. Lan, C. Coetsier, C. Causerand, K.G. Serrano, On the role of salts for the treatment of wastewaters containing pharmaceuticals by electrochemical oxidation using a boron doped diamond anode, Electrochem. Acta 231 (2017) 309–318, https://doi.org/10.1016/j.electacta.2017.01.160.

A.H. Degaki, G.F. Pereira, R.C. Rocha-Filho, N. Bocchi, S.R. Biaggio, Effect of specific active chlorine species and temperature on the electrochemical degradation of the Reactive Blue 19 dye using a boron-doped diamond or DSA anode in a flow reactor, Electrochimica Acta 5 (2014) 8–15, https://doi.org/10.1016/j.electacta.2009.01.056-z.

W. Wu, Z. Huang, T. Lim, A comparative study on electrochemical oxidation of bisphenol A by boron-doped diamond anode and modified SnO₂-Sb anodes: influencing parameters and reaction pathways, J. Environ. Chem. Eng. 4 (2016) 2807–2815, https://doi.org/10.1016/j.jece.2016.05.034.

J.M. Aquino, M.A. Rodríguez, R.C. Rocha-Filho, C. Siesz, P. Cañizares, Influence of the supporting electrolyte on the electrolyses of dyes with conductive-diamond anodes, Chem. Eng. J. 184 (2012) 221–227, https://doi.org/10.1016/j.cej.2012.01.044.