



Structure-reactivity relationship in the degradation of three representative fluoroquinolone antibiotics in water by electrogenerated active chlorine



Efraím A. Serna-Galvis^a, Sindy D. Jojoa-Sierra^a, Karen E. Berrio-Perlaza^a, Franklin Ferraro^b, Ricardo A. Torres-Palma^{a,*}

^aGrupo de Investigación en Remediación Ambiental y Biocatálisis (GIRAB), Instituto de Química, Facultad de Ciencias Exactas y Naturales, Universidad de Antioquia UdeA, Calle 70 No. 52-21, Medellín, Colombia

^bDepartamento de Ciencias Básicas, Universidad Católica Luis Amigó, Transversal 51A No. 67B-90, Medellín, Colombia

HIGHLIGHTS

- Piperazyl on fluoroquinolones (FQ) is the most reactive moiety to active chlorine.
- Theoretical calculations predicted sites on FQ reactive to electrophilic attack.
- In the tested system neutral forms of FQ have higher degradation rate than cation.
- Transformations of FQ led to antimicrobial activity removal of treated solutions.
- Electrochemical system fastly removed antibiotic activity from a hospital wastewater.

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ABSTRACT

In this work electrogenerated active chlorine was used to treat fluoroquinolones, a class of antibiotics that is highly consumed and frequently found in waste and natural waters. Taking into account the structural variety and diverse molecular forms of these pharmaceuticals, their structure-reactivity relationship toward active chlorine was studied. Three representative fluoroquinolones: ciprofloxacin, norfloxacin and levofloxacin were considered. Despite structural differences, the primary by-products evidenced that the major reactive part of fluoroquinolones was the piperazyl ring. However, ciprofloxacin and norfloxacin were degraded faster than levofloxacin, due to the fact that secondary amines on ciprofloxacin and norfloxacin were more reactive toward active chlorine than tertiary amines on levofloxacin. The reactivity of cationic and neutral forms of the fluoroquinolones was also evaluated using both experimental and theoretical procedures. Experimental results evidenced that the neutral forms have higher degradation rates than the cationic structures. Theoretical analysis of net charge on atoms (obtained by the natural bonding orbitals method) indicated that the reactive moieties on the neutral form of antibiotics have a high nucleophilicity. Therefore, this form is more susceptible to electrophilic attacks by chlorine species than the cationic one. Additionally, the environmental impact was evaluated considering the evolution of antimicrobial activity and its correlation with the antibiotics transformations. Finally, simulated hospital wastewater containing norfloxacin was treated. The electrogenerated active chlorine removed 100% of the antimicrobial activity in a short period (40 min), indicating that this system is an interesting option for treating hospital wastewaters and decreasing the negative environmental impact of the input of fluoroquinolones into natural media.

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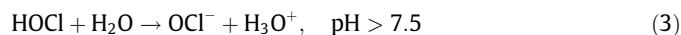
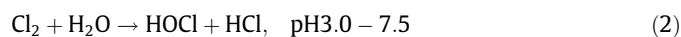
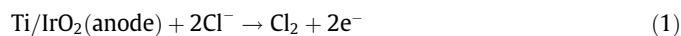
1. Introduction

Electrochemical oxidation based on the utilization of dimensionally stable anodes (e.g. Ti/IrO₂) has been shown to be a useful process for eliminating different kinds of pollutants from water [1,2]. These anodes are recognized as easily transforming chloride

* Corresponding author.

E-mail address: ricardo.torres@udea.edu.co (R.A. Torres-Palma).

ions into chlorine (Eq. (1)) [1–3]. In water, chlorine produces other active chlorine species (Eqs. (2) and (3), which act as degrading agents of pollutants (mediated route, Eq. (4)) [2,4,5]. Therefore, electrochemical processes using a Ti/IrO₂ anode in chloride media are becoming an interesting alternative for removing organic pollutants from water [5–9].



On the other hand, a current environmental problem is the continuous input of antibiotics into natural media. Antibiotics mainly enter the environment from livestock activities and wastewater treatment plant (WWTP) effluents, due to the absence (in the case of livestock) or failure of water treatment systems (in the case of WWTP) [10,11]. In fact, antibiotics are also able to inhibit the growth and activity of microorganisms used in biological processes of WWTP [12].

Fluoroquinolones are among the most common antibiotics found in different environmental waters. Fluoroquinolones are omnipresent due to their extensive use and high stability [13]. For example, ciprofloxacin, norfloxacin and levofloxacin have been found in raw water, tertiary effluents of WWTP and surface water [12,14]. Indeed, 7.0–56.4 μg L⁻¹ of ciprofloxacin have been reported in WWTP effluents, while ~0.030–0.050 μg L⁻¹ of norfloxacin have been detected in raw water [12]. Meanwhile, levofloxacin has been found in surface water at concentrations up to 0.087 μg L⁻¹ [14]. Moreover, these fluoroquinolones have a synthetic nature and high antibiotic potency [15,16]. Owing to such characteristics, even at very low concentrations they can negatively impact the environment through bacterial resistance development and toxic effect on other aquatic species [12,14,17].

Taking into account the high efficiency of Ti/IrO₂ anode in the presence of chloride ions for removing pharmaceutical compounds [1,5], this electrochemical treatment is an option to eliminate fluoroquinolones. In previous papers, the ability of this electrochemical system (or similar systems) to degrade fluoroquinolones has been reported [18–20]. Therefore, the effects of operational parameters (such as current density, supporting electrolyte and antibiotic concentrations) and/or water matrix components have been considered. However, a systematic study on the structure-reactivity is not undertaken in these works.

Due to the structural variety (similar core with different substituents) and diversity in molecular forms (anionic, cationic and neutral) of fluoroquinolones, the chemical behavior of such antibiotics is more complex than other substances. Thus, this work is focused on the structure-reactivity relationship in the degradation of representative fluoroquinolones in their different molecular forms during the treatment by electrogenerated active chlorine. Ciprofloxacin, norfloxacin and levofloxacin were selected because of their high consumption and presence in different kinds of water. Initially, the efficiency of the mediated route in the degradation of fluoroquinolones was established. Following this, the primary by-products were elucidated by HPLC-MS analysis and their evolution in the course of treatment. This was linked to theoretical analysis of net charge on fluoroquinolones atoms in order to determine the predominant pathways and the mechanistic aspects of antibiotic removal. Then, the reactivity of fluoroquinolones in cationic and neutral (or zwitterion) forms was also studied using both experimental information and computational chemistry. Finally, some environmental implications of the fluoroquinolones transfor-

mations were analyzed and connected to the evolution of antimicrobial activity.

2. Materials and methods

2.1. Reagents

Ciprofloxacin (CIP, purity of 99.0%) and norfloxacin (NOR, purity > 99%) were provided by Laproff laboratories. Levofloxacin (LEV, purity > 99%) was provided by Chemo laboratories. Sodium chloride, calcium chloride, potassium chloride, ammonium chloride, sodium sulfate, sulfuric acid, sodium hydroxide, potassium iodide, ammonium heptamolybdate, monopotassium phosphate, urea, acetonitrile and nutrient agar were provided by Merck. Potato dextrose agar was purchased from Oxoid. Formic acid was purchased from Carlo-Erba. All chemicals were used as received. The fluoroquinolones concentration was 40 μmol L⁻¹. The samples were prepared using distilled water and the pH was adjusted with sodium hydroxide or sulfuric acid.

2.2. Reactor and electrochemical conditions

The experiments were conducted in an electrolytic cell containing 150 mL of the fluoroquinolone sample. A Ti/IrO₂ electrode of 8 cm² (characterized previously in [21]) and a zirconium spiral electrode of 10 cm² were used as anode and cathode, respectively. The electrochemical system was operated under constant stirring conditions.

It has been reported that current densities (*j*) higher than 300 A m⁻² (30 mA cm⁻²) may lead to the formation of harmful chlorine species (e.g. ClO₃⁻ and ClO₄⁻) [22–24]. Therefore, in order to preclude the formation of such species, as well as to limit the cathodic reduction of the oxidative specie HOCl [25,26], a low value of *j* (5 mA cm⁻²) was chosen to develop the experiments. To establish the appropriate concentration of supporting electrolyte, a range from 0.01 to 0.05 mol L⁻¹ of NaCl was evaluated. It was found that chlorine formation increased and energy consumption decreased as NaCl concentration was augmented (Table S1 in the supplementary information). Thus, 0.05 mol L⁻¹ of NaCl was selected, because it represents a suitable concentration allowing a considerable production of active chlorine and low energy consumption; thus, avoiding an excessive use of NaCl. Meanwhile, at experimental conditions of 5 mA cm⁻² and NaCl 0.05 mol L⁻¹, the current efficiency for the active chlorine production was ~12%, which was calculated using the equation S1 (Supplementary information).

2.3. Analyses

The evolution of fluoroquinolones and their by-products was analyzed using an UHPLC Thermoscientific Dionex UltiMate 3000 instrument equipped with an AcclaimTM 120 RP C18 column (5 μm, 4.6 × 150 mm) and a diode array detector set at the maximum wavelengths of fluoroquinolones (270, 280, 290 nm for ciprofloxacin, norfloxacin and levofloxacin, respectively). The injection volume was 20 μL. The mobile phase was 10 mmol L⁻¹ formic acid (pH 3.0)/acetonitrile at 85/15 (% v/v), in isocratic mode (1 mL min⁻¹). The primary by-products were determined using a HPLC Agilent 1200 series coupled to an Agilent LC/MSD VL SQ mass spectrometer. The column and mobile phase were used at the conditions previously described for the antibiotics evolution analysis. The injection volume was 10 μL and the mass spectrometer was operated in positive ion mode.

The chlorine species electrogenerated during the process were determined by iodometry, as reported by Serna-Galvis, et al. [27].

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