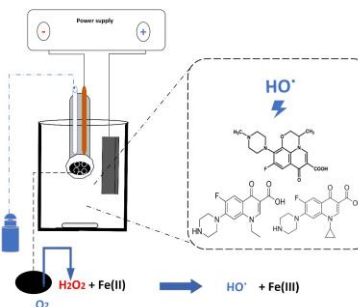


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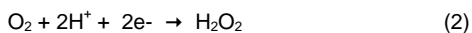
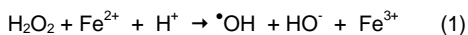
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In this work, an optimized EFP process is performed as pretreatment for the degradation and mineralization of three fluoroquinolones (FQs) drugs: ofloxacin (OFL), norfloxacin (NOR), and ciprofloxacin (CIP). Faster and complete degradation of the drugs mixture was achieved in 90 min and 61% of mineralization after 180 min, under the optimized conditions: $j = 244.0 \text{ mA/cm}^2$, $[\text{Fe}^{2+}] = 0.31 \text{ mM}$, and $[\text{FQs}] = 87.0 \text{ mg/L}$. Furthermore, a low toxicity effluent was achieved in 90 min of the experiment, according to bioassay toxicity with *Vibrio fischeri*. Five short-chain carboxylic acids, including oxalic, maleic, oxamic, formic, and fumaric acids, were detected and quantified, in addition to F^- and NO_3^- inorganic ions. The inhibition of the reactive oxygen species with scavenger proof was also evaluated.

Introduction

Pharmaceuticals are a common type of emerging pollutant found in several bodies of water or effluent of wastewater treatment plants in concentrations from ng/L to $\mu\text{g/L}$. Fluoroquinolones (FQs) are the most common family of antibiotics used nowadays. However, they cause ecotoxicity in aquatic species and contribute to the development of antibiotic-resistant bacteria [1-3]. On the other side, the electro-Fenton is an advanced oxidation process that is effective in degrading diverse emerging pollutants. It is based on the reaction of Fe^{2+} and H_2O_2 producing free radicals $\cdot\text{OH}$, see reaction 1. The H_2O_2 is generated electrochemically by the partial oxygen reduction reaction on a carbonaceous cathode in acidic media, according to the reaction 2.



This research aimed to degrade the mixture of FQs of ofloxacin (OFL), norfloxacin (NOR), and ciprofloxacin (CIP) by EFP and identify the final by-products.

Material and Methods

The degradation experiments were carried out in a 250 mL two-electrode electrolytic cell, where an air diffusion was the cathode and diamond boron-doped was the anode, and Na_2SO_4 0.5 M at pH 3 was the supporting electrolyte. The degradation conditions were: $[\text{Fe}^{2+}] = 0.31 \text{ mM}$, $[\text{FQs}] = 87.0 \text{ mg/L}$, and $j = 244 \text{ mA/cm}^2$ obtained from a Box-Behnken design [4]. The chromatographic

separation of the antibiotics was carried out by reverse-phase HPLC using a System Agilent (YL9100, Young Lin) with a diode array detector and a column C18 Luna Phenomenex (250 \times 4.6 mm, 5 μm , 100 \AA). The mobile phase was 5:5:90 (v/v) of ACN: THF: KH_2PO_4 at 30 mM.

Ion chromatography was used to determine inorganic ions, and exclusion chromatography was used to determine short-chain carboxylic acid. The mineralization of the mixture was evaluated based on total organic carbon quantification using a Shimadzu TOC VSCH analyzer. The toxicity was evaluated with bio-model bacteria *Vibrio fischeri* (Delta Tox II, Modern Water).

Results and Discussion

The EFP was capable of completely degrading the three antibiotics in 60 min Fig. 1 (a). The degradation velocities (k_{app}) were 0.0921, 0.0859, and 0.1131 min^{-1} for OFL, NOR, and CIP, respectively, obeying a pseudo-first order kinetics.

As can see in Fig. 1 (b) The maximum mineralization achieved was 61%; this incomplete mineralization is attributed to the formation of Fe (III) complexes with final short-linear carboxylic acids. These species are well known to be highly resistant to oxidation by hydroxyl radicals.

The mineralization current efficiency (MCE) is shown in Fig. 1(c). The highest efficiency was 13.45% at 40 min of experiment and a progressive diminution until it reached 9.17% after 180 min. This trend indicates an effort of $\cdot\text{OH}$ radicals to lead to the oxidation into CO_2 due to the generation of recalcitrant short-chain carboxylic acids and other by-products [5].

To identify the final by-products of degradation, carboxylic acids were determined during degradation. Oxalic acid, which is in ferric-oxalate form, has a rapid formation within the early times of the experiment, reaching a maximum concentration of 34 mg/L after 180 min of electrolysis.

Also, small amounts of formic and fumaric acids were observed at the beginning of the degradation, with the elimination of both in 90 min. Also, the liberation of oxamic and maleic acids was observed. In this case, the presence of ferric oxalate, oxamate, and malate has probably led to the incomplete mineralization of the FQs mixture.

Inorganic ions liberation is considered another support indicator of mineralization because it confirms molecule cleavage. Fluoride (F⁻) and nitrate (NO₃⁻) are presented as heteroatoms in the three molecules. The F⁻ liberation achieved a maximum accumulation of 9.77 mg/L, which represents 64.13% of the total stoichiometric fluorine in the three molecules. Also, 11.58 mg/L of NO₃⁻ ions were detected (23.8% of the total stoichiometric N).

Fig 1 (d) shows the toxicity of the solution conducted with *Vibrio fischeri*; as you can see, the toxicity of the effluent tends to decrease over time. Initially, the toxicity was so high that it caused over 100% bacterial inhibition. However, after only 90 minutes, the inhibition dropped to 14.0±9.8%. Inhibition below 20% represents a non-toxic effluent. A scavenger proof was carried out to determine the principal oxidant species that conduct the degradation and mineralization of the FQs mix. In these tries, 1,4-benzoquinone (BQ) 0.4 mM was used to provoke the inhibition of the superoxide radical (O₂^{•-}) and tert-butanol (TBT) (5%) for the

inhibition of the •OH radical. In the presence of TBT, a degradation-inhibition of the mix of FQs was observed, causing a partial degradation of only 75.03% of the FQs mix in 180 min.

These results indicated that the degradation of FQs is mainly carried out by •OH radical.

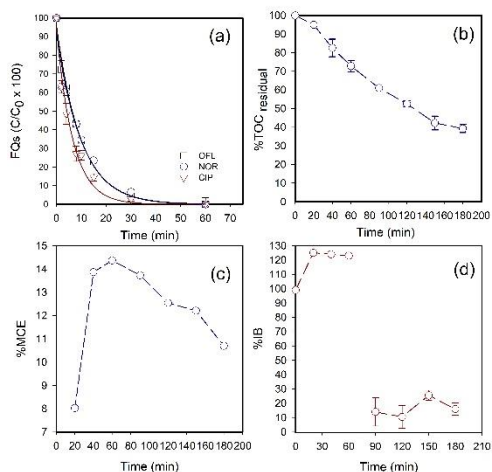


Figure 1. a) Degradation of the FQs mixture by EFP, b) TOC removal, c) Mineralization current efficiency (%MCE), d) bioluminescence inhibition employing toxicity assays with *V. fischeri* (%IB)

Conclusions

The electro-Fenton process allowed 100% of degradation of the mixture (29 mg/L each) in 60 min of treatment and 61% of mineralization after 180 min. The remaining organic carbon content is attributed to carboxylic acids, mainly oxalic acid and others such as oxamic, fumaric, formic, and maleic, which form oxalate complexes with Fe-III.

Based on the bioassays conducted with *V. fischeri*, the effluent's toxic effect was reduced to non-toxic after 90 min. The scavenger proof test confirmed that the mixture was primarily degraded by de •OH radicals. Considering all the results from this work, the electro-Fenton process is a successful alternative for the degradation of pharmaceutical compounds in a nonselective degradation.

Acknowledgments

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