

Elimination of gatifloxacin from water: Treatment by electro-Fenton process and highlighting of a biological post-treatment

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Abstract: This study concerns the oxidative degradation and mineralization of gatifloxacin in aqueous solution at pH = 3, and the presence of Fe²⁺ as a catalyst using electro-Fenton (EF) process, with carbon felt as a cathode and platinum as an anode. The chemical oxygen demand evaluates the mineralization by assessing the applied current value and concentration of catalyst Fe²⁺. Some stable by-products of gatifloxacin have been identified using high-performance liquid chromatography and liquid chromatography tandem mass spectrometry (LC-MS/MS). The second part of this paper concerns the study of the biodegradability in determining BOD₅/COD during the mineralization of gatifloxacin by EF in order to evaluate the possibility of coupling electro-Fenton process with the biological one. This leads to an efficient treatment of water contaminated by this antibiotic at a lower cost.

Keywords: treatment by electro-Fenton; gatifloxacin antibiotic; oxidative degradation; mineralization; biodegradation, essays in an aqueous medium.

Introduction

Given the fact that antibiotics are produced in order to cause pharmacological effects in organisms, it is not surprising that numerous studies have demonstrated that antibiotics have side effects on human health and the environment ¹. Also, the byproducts of these kinds of pharmaceutical substances are generally more toxic than the starting molecules during their oxidation in the ecosystem, thus causing a real danger on the environment. This situation has caused concern in public opinion about the hygienic and aesthetic quality of drinking water. Thus, scientists have had a challenge in order to eliminate antibiotics from water. They use some technics such as advanced oxidation processes (AOPs) including, ozonation ², photocatalysis ^{3,4}, electro-Fenton, Photo-Fenton ⁵⁻⁸, hybrid technique ⁹ etc. Indeed, AOP's principle of operation articulates on an in situ generations of hydroxyl radicals ·OH. These molecules have an oxidizing power more than the other molecules usually employed like H₂O₂, Cl₂,

ClO₂⁻ or O₃. So, these radicals arrive to mineralize the organic and organometallic substances totally or partially.

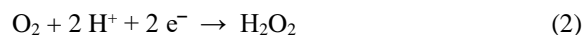
Among the pollutant antibiotics, there is gatifloxacin (destined to treat sensitive germ infections) where one study has clarified the aqueous photodegradation of this antibiotic, determining degradation kinetics and the formation of photoproducts ¹⁰. Another study has shown that the photodegradation of gatifloxacin in freshwater and seawater is not as faster as in pure water, so, there are the integrative effects of pH and dissolved substances in the solution, such as humic acids, on photodegradation ¹¹.

In the same context and electrochemistry, the efficacy of "Electro-Fenton" (EF) process in the mineralization of drugs part of the family of persistent organic pollutants in water was demonstrated.

The EF process articulates on the in situ generations of ·OH (reaction (1)) at pH = 3 ¹²⁻¹⁴.

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The reproduction of Fe^{3+} (reaction 3) from the reduction of Fe^{2+} produced by and the regeneration of H_2O_2 (reaction 2) ensure the generation of hydroxyl radicals $\cdot\text{OH}$ (reaction 2).

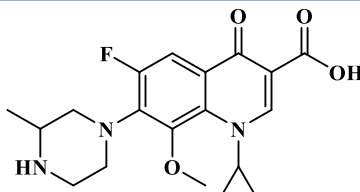
In acidic solution, the oxidizing power of $\cdot\text{OH}$ is very elevated (potential = 2.8 V/SHE), and with efficient reactivity. Thus, these radicals may degrade any organic molecule in an aqueous medium and leading in the end to the mineralization to CO_2 .

Overall, during mineralization of organic molecules by AOPs, the biorefractory molecules oxidize into small molecules biologically degradable. Thus, the coupling of AOPs with the biological process is strongly advised to eliminate efficiently and economically, the persistent organic pollutants from water ¹⁵⁻²⁰.

This paper clarifies the combination possibility of EF process and biological one for efficient

elimination of gatifloxacin in aqueous solution. The electrochemical cell employed in this study contains a carbon-felt cathode and a platinum anode. Different experimental tests have been realized on the aqueous medium of gatifloxacin at constant applied current, at pH = 3 and using Fe^{2+} as a catalyst. The first study concerns the effect of the applied current and the concentration of Fe^{2+} (catalyst) on the degradation and mineralization of gatifloxacin. Then, different concentrations of gatifloxacin were prepared in order to study their degradation and mineralization by monitoring the chemical oxygen demand (COD). The identification of the interaction of high-performance liquid chromatography (HPLC) and liquid chromatography-mass spectrometry (LC-MS / MS). On the other hand, the monitoring of the biodegradability with electrolysis allowed the estimation of the optimal time to pass from the electro-Fenton process (EF) to the biological process. In order to carry out the biodegradation tests, the domestic wastewater was used, knowing that the value of $\text{BOD}_5 / \text{COD}$ is the representative value of the biodegradability ²¹. This report gives information on the part of the organic substances present in the solution that can be biodegraded during five days

Table 1. Proprieties of gatifloxacin molecule.

Compound	Structure	Molecular Weight	wavelength of absorption	Water Solubility
Gatifloxacin		375.4	absorption maximum at 287.5 nm	40–60 mg/mL

Results and discussion

Influence of applied current on the oxidative degradation kinetics of gatifloxacin aqueous solution.

The primary factors which influence on EF process are applied current, catalyst concentration, solution pH and background electrolyte. In different researches, it is mentioned that the optimal pH value is about 3 ²²⁻²⁵ and the more appropriate supporting electrolyte is Na_2SO_4 ²⁶.

In order to study the effect of applied current on the degradation of gatifloxacin, 200 mL of 0.1 mM gatifloxacin solution with 0.1 mM Fe^{2+} at pH = 3 are used (Fig. 1).

The use of these data cited before determines the optimal applied current where oxidation of gatifloxacin is favored for which the oxidation of Gati.

The evolution of the concentration of gatifloxacin is followed using the high-performance liquid chromatography (HPLC).

Raising the applied current value from 100 to 500 mA carry on the accelerated oxidation kinetics of Gati. This behavior can be justified by the acceleration of the rate of electrochemical reactions (2) and (3), and thus, there is the production of more $\cdot\text{OH}$ radicals (reaction (1)).

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The complete degradation of Gati was checked at 6, 3, 2.5 and 3 min for the intensities of 100, 300, 400 and 500 mA, respectively. Thus, after 400 mA, the degradation rate of Gati was not significantly varied. Consequently, the optimal value of the applied current is 400 mA. Supplementary increase in this current carried on decreasing oxidative efficiency of Gati by dedicating a long time of electrolysis for the complete degradation of Gati.

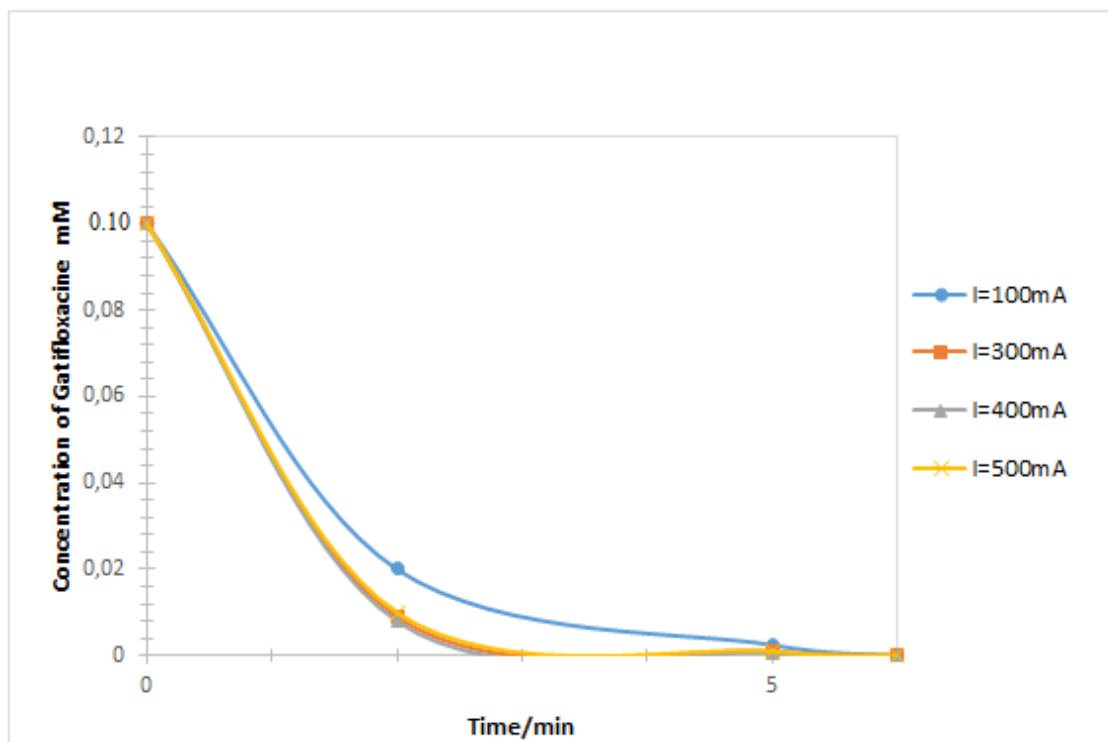


Figure 1. Effect of applied current on degradation of gatifloxacin during the electrolysis at pH3, $[Gati]_0 = 0.1$ mM, 0.05 M Na_2SO_4 , with $[Fe^{2+}] = 0.1$ mM, I (mA) = 100 (-•-), 300 (-■-), 400 (-▲-) and 500 (-×-)

Influence of the catalyst Fe^{2+} on the oxidative degradation kinetics of gatifloxacin in aqueous solution.

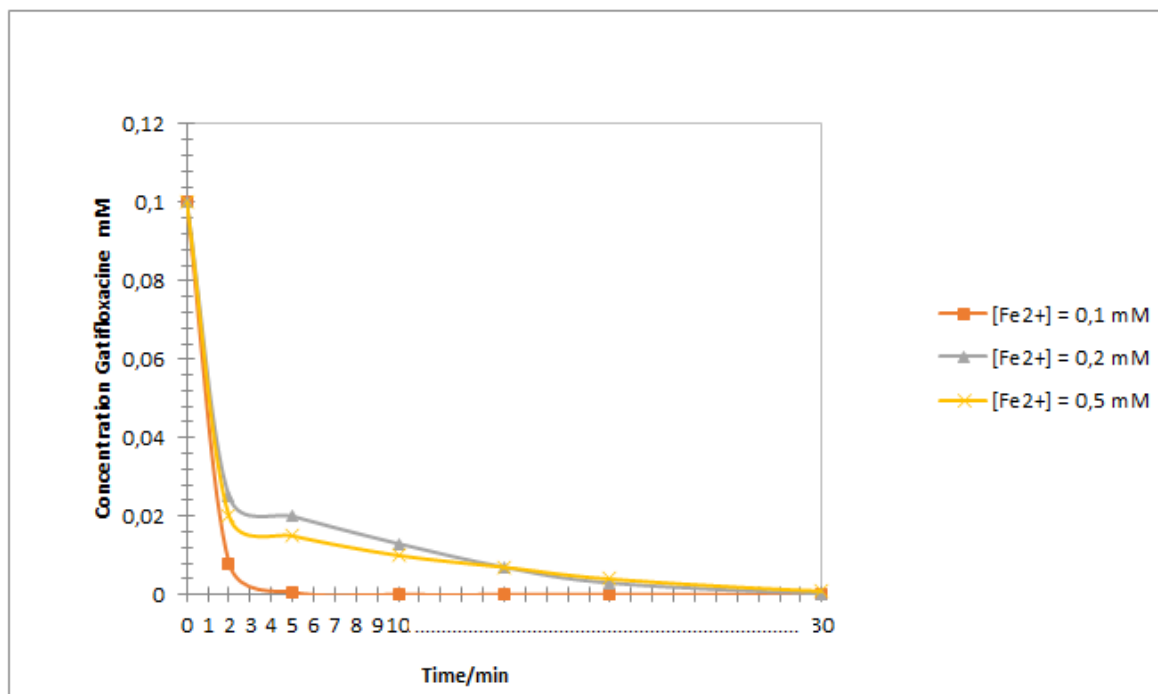
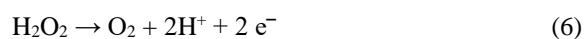
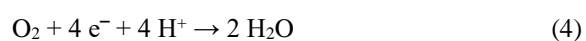


Figure 2. Effect of Fe^{2+} concentration on Gati concentration decay during the electrolysis at pH3 in $[Gati]_0 = 0.1$ mM and 0.05 M Na_2SO_4 solution at $I=400$ mA. $[Fe^{2+}]$ (mM) = 0.1 (-■-), 0.2 (-▲-) and 0.5 (-×-)

Higher applied current could be an origin for the speed-up of following wasting reactions:



In the objective to show the effect of Fe^{2+} concentration on oxidation of Gati, many experiments were realized by changing the concentration of the catalyst in the range of 0.1–0.5 mM with 400 mA as optimal current value as it is shown in Fig. 2. After the value 0.1 mM of the catalyst concentration, there is an inhibition of the degradation of the gatifloxacin solution, which explains the parasitic reaction between the Fe^{2+} ions and the radical hydroxyls (reaction (7)).

The time of the treatment by EF for the complete disappearance of Gati has been changed, so this elimination has been realized at 5, 30 and 30 min for 0.1, 0.2 and 0.5 mM of Fe^{2+} concentration, respectively.

We conclude that higher concentrations of catalyst reduce the process efficiency because of increase of the rate of its reaction with the hydroxyl radical (reaction (7))^{5,27}:

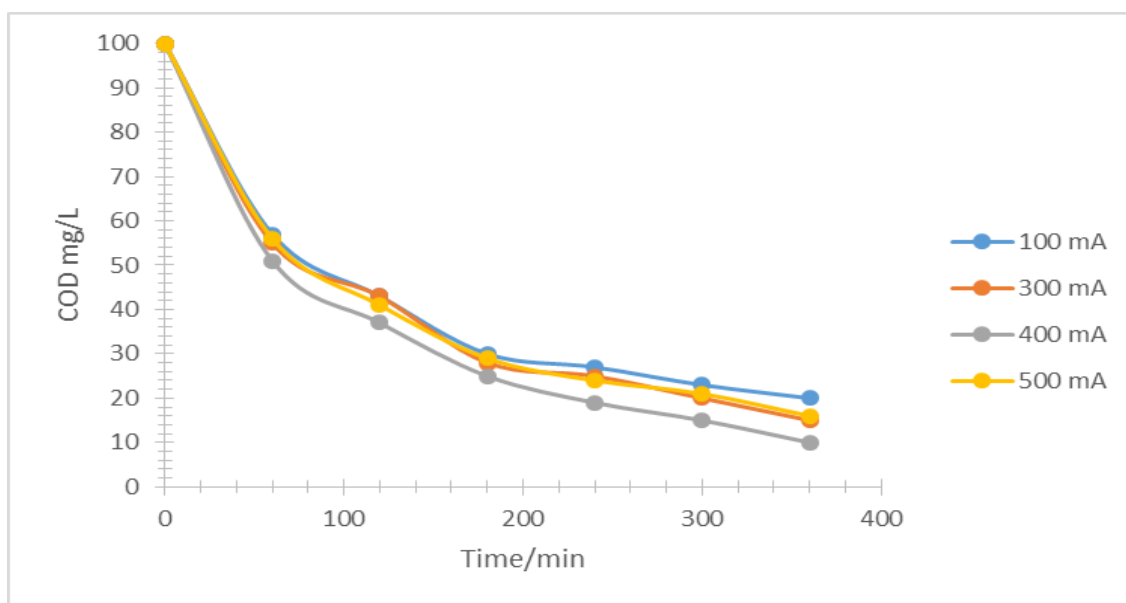


Figure 3. Effect of applied current on gatifloxacin (0.1 mM) mineralization during the electrolysis at pH 3 in 0.05 M Na_2SO_4 solution. $[\text{Fe}^{2+}]$ (mM) = 0.1. I (mA) = 100 (-•-), 300 (-•-), 400 (-•-) and 500 (-•-)

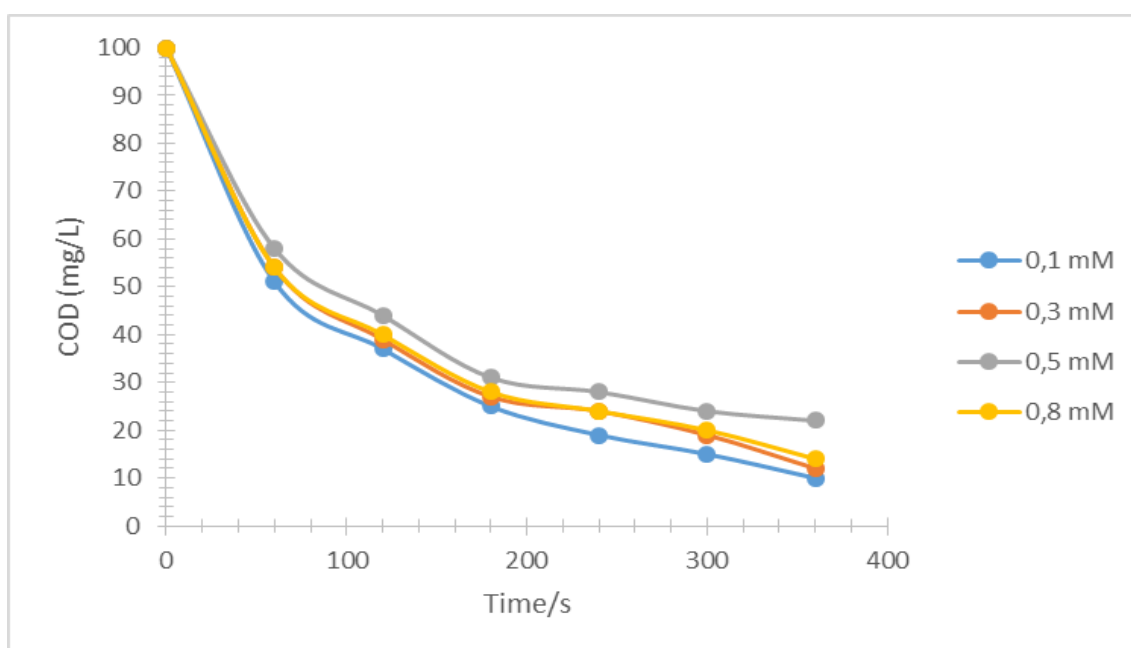


Figure 4. Effect of catalyst concentration on gatifloxacin (0.1 mM) mineralization during electro-Fenton treatment at pH 3 in 0.05 M Na_2SO_4 solution. I (mA) = 400 mA. $[\text{Fe}^{2+}]$ (mM) = 0.1 (-•-), 0.3 (-•-), 0.5 (-•-) and 0.8 (-•-)

Influence of operating parameters on the mineralization of gatifloxacin in an aqueous medium

Many experiments have been realized with various applied current values with a concentration of Fe^{2+} about 0.1 mM to study the mineralization of gatifloxacin in water by the electro-Fenton process (Fig. 3).

Indeed, during electrolytic treatment, the COD decreases in a continuous way showing the degradation of gatifloxacin as well as its by-products generated during the electrolysis. At high times of the treatment by EF, COD attained shallow values, indicating the complete mineralization of the polluted molecules. For example, the COD reduces, and we obtained 85% of its diminution after 6 hours of electrolysis for 300 mA.

According to Figure 3, the COD decay rate raises by raising the applied current value from 100 to 500 mA. After 400mA, a rise in the applied current did not present any positive effect on the COD decay rate. In consequence, this carried on weak COD values due to the acceleration of wasting reaction (4) that can disturb the production of Fenton's reagent.

Thus, the applied current of 400 mA may be considered as the optimum for a maximum mineralization rate. So, the mineralization degrees

after 6 hours of electrolysis about 80%, 85%, 90% and 84% for 100, 300, 400 mA and 500 mA, are respectively obtained.

Many essays have been realized by varying the catalyst concentrations (0.1 to 0.8mM) at 400 mA during electrolysis with EF (Fig. 4).

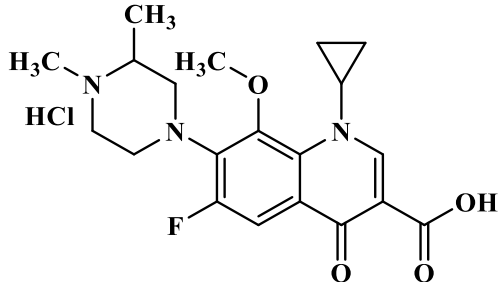
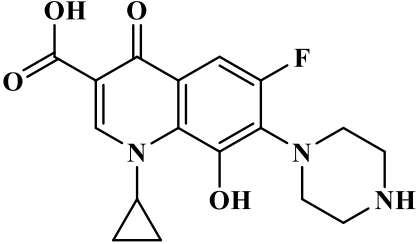
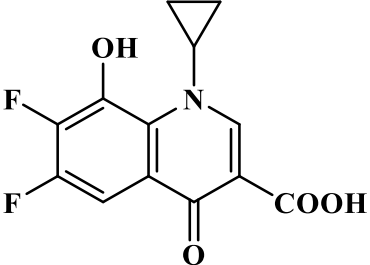
After the value 0.1 mM of the catalyst concentration, there is an inhibition of the removal rate of the gatifloxacin solution, which explains the parasitic reaction between the Fe^{2+} ions and the radical hydroxyls (reaction (7))²⁸. Similar results exist in the literature⁵. Thus, the parameter Fe^{2+} is very impacting in the electrolysis by EF.

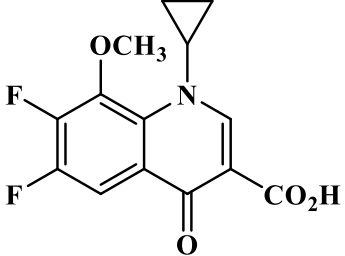
Identification of the reaction intermediates

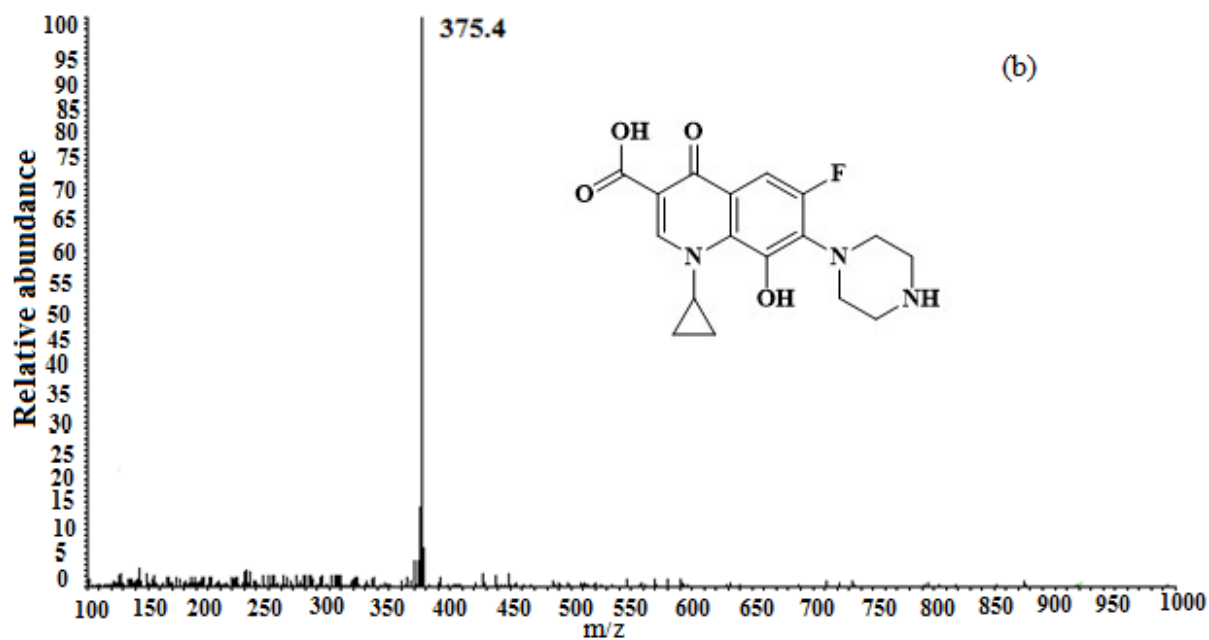
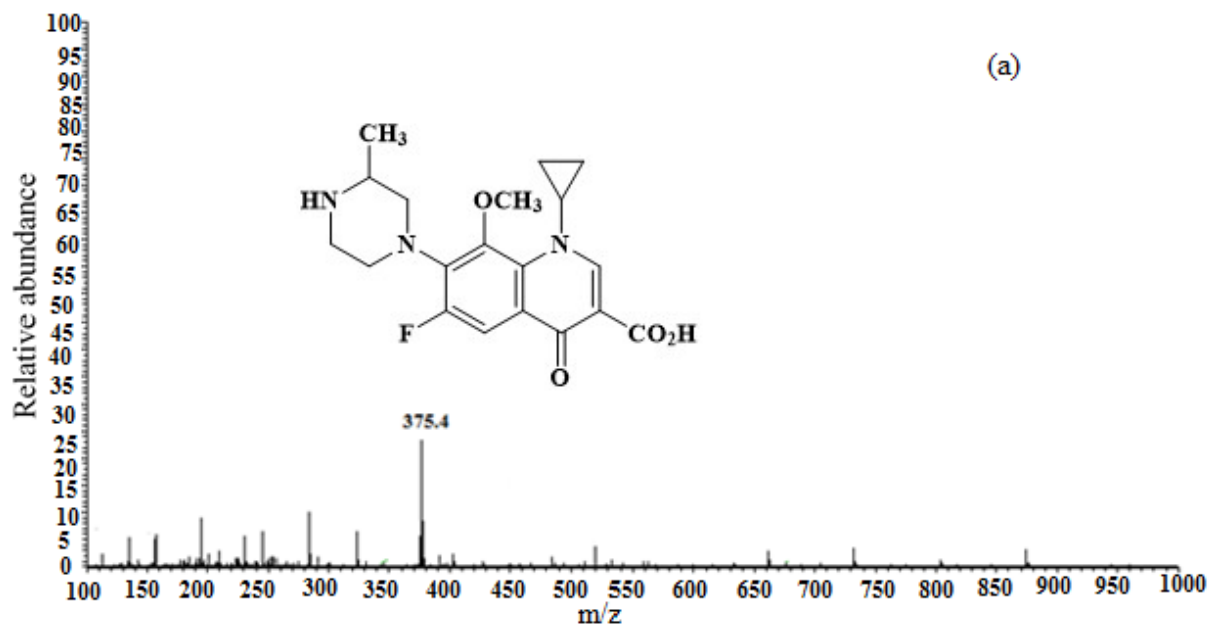
The stable by-products formed during the electrolysis are determined using LC/MS-MS analyses. The results correspond to the first 1 h (0 min, 15 min, 30 min and 1 h) of the treatment by the EF process showed an increasing disappearance of gatifloxacin and formation of some by-products. The concentration of these products goes to maxima and then decrease until full disappearance.

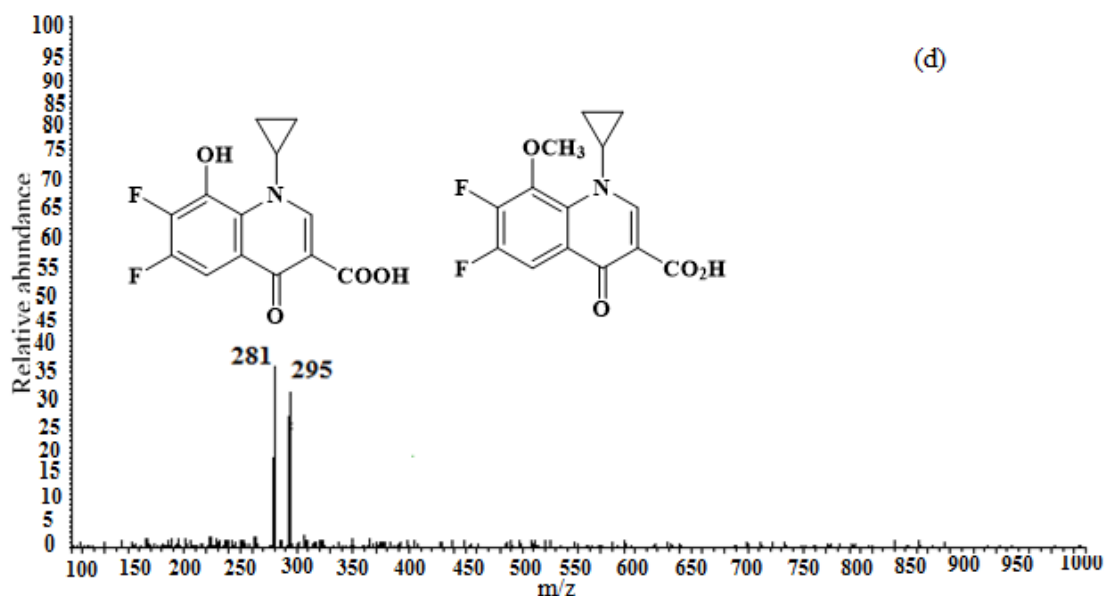
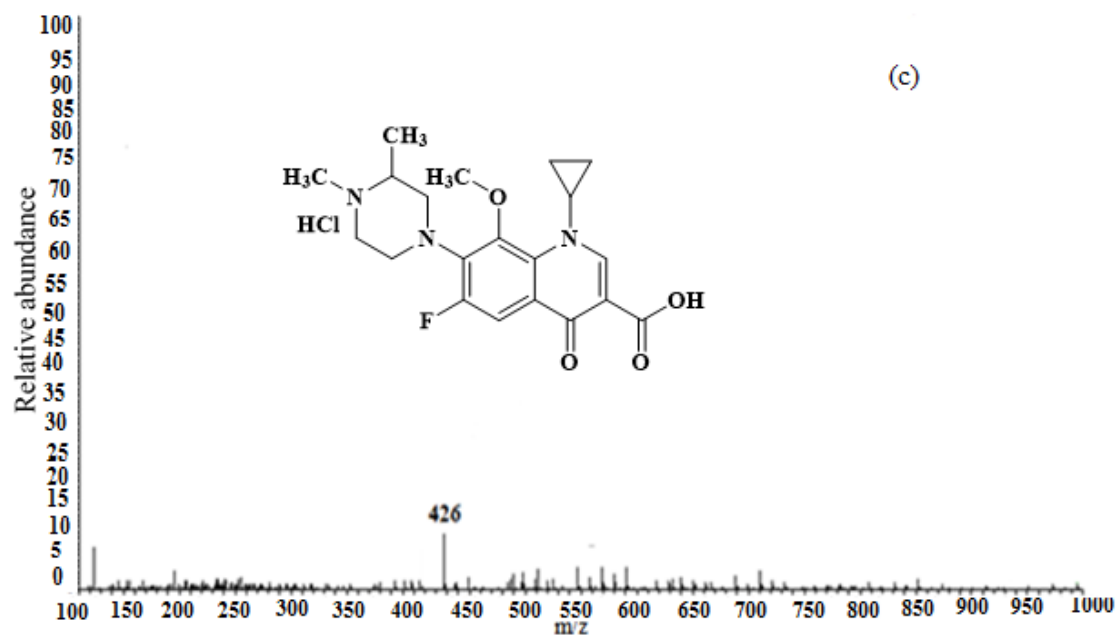
Table 2 represents the identified by-products, while mass spectra of these intermediates are shown in Fig. 5.

Table 2. The intermediates identified by LC/MS-MS during the mineralization of gatifloxacin by EF process.

Intermediates	Molecule name	m/z	References
	N-Methyl Gatifloxacin HCl	426	29,30
	Iso gatifloxacin	375	30
	1-cyclopropyl-6,7-difluoro-8-hydroxy-4-oxo-1,4-dihydroquinoline-3-carboxylic acid	295	30

	1-cyclopropyl-6,7-difluoro-8-methoxy-4-oxo-1,4-dihydroquinoline-3-carboxylic acid	281	30
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Figures 5. (a, b, c, d) spectra of by-products existing in the aqueous medium during 1 h of electrolysis of gatifloxacin. $[\text{Fe}^{2+}] = 0.1 \text{ mM}$, $I = 400 \text{ mA}$, $[\text{Na}_2\text{SO}_4] = 0.05 \text{ M}$, $\text{pH } 3$.

Biodegradability study

The biodegradation and mineralization of the samples are illustrated in Fig. 6 at an applied current of 400 mA and with Fe^{2+} as catalyst (0.1 mM).

The Figure 6 shows that the starting molecule (gatifloxacin) is non-biodegradable with BOD_5/COD has a value zero. Also, during 100 minutes of electrolysis, the primary intermediates (refractory aromatic molecules) are non-biodegradable since BOD_5/COD equal at zero. Then, the biodegradability

increases and at about $t = 150$ minutes of EF treatment, the BOD_5/COD attains the value 1.1. This shows that the molecules present in the water become biodegradables³¹. Therefore, biological treatment may be started. Then, between 150 and 300 min, the by-products from electrolysis still react with $\cdot\text{OH}$, and indeed there is a high biodegradability (it is small aliphatic molecules: short-chain molecules, as it is known in the literature).

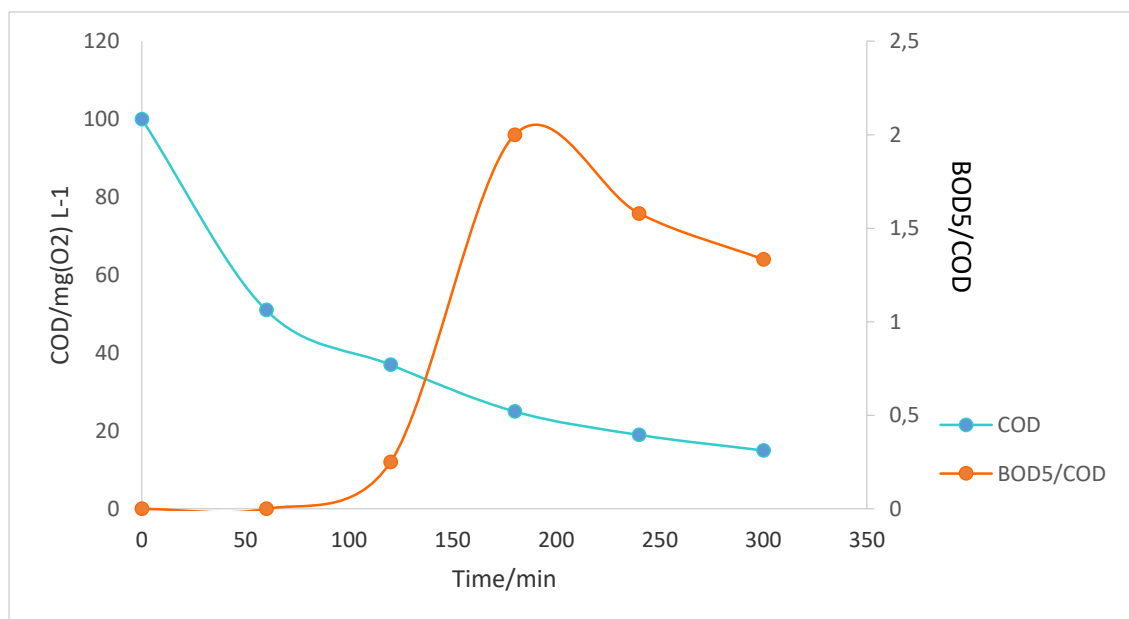


Figure 6. Biodegradability evolution and COD decay during the electrolysis ($I = 400$ mA and $[\text{Fe}^{2+}] = 0.1$ mM).

Comparison between the biodegradability of gatifloxacin and that of gentamicin

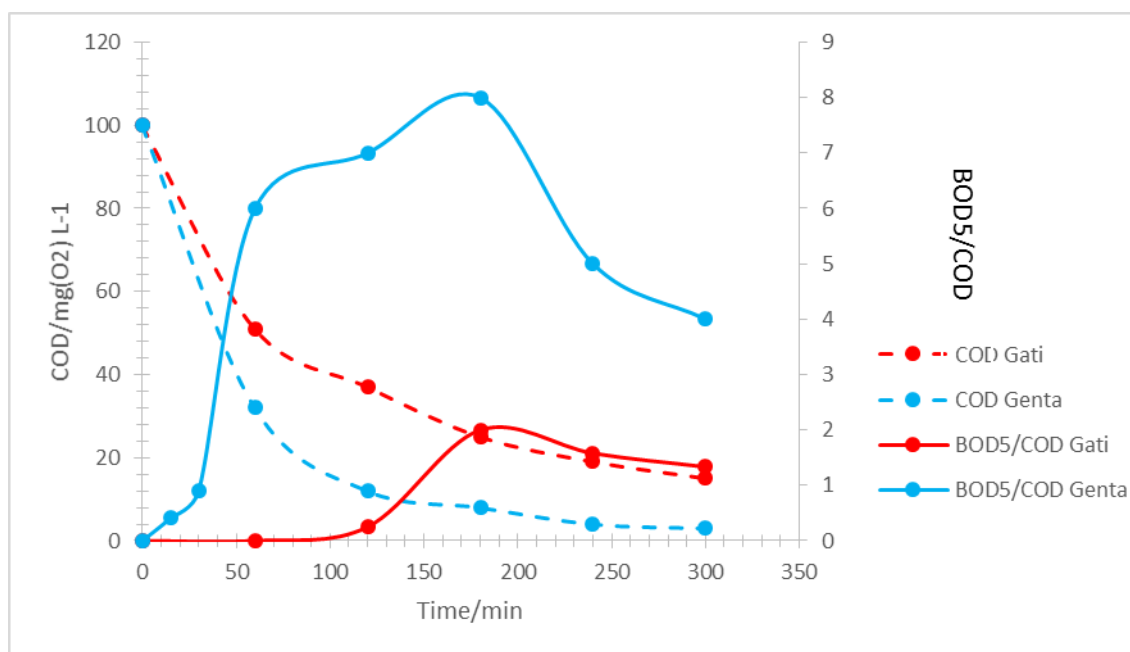


Figure 7. Comparison between the biodegradability of gatifloxacin and the biodegradability of gentamicin. Optimal operating parameters for Gati at $I = 400$ mA and concentration of Fe^{2+} of 0.1 mM and for Genta at $I = 100$ mA and concentration of Fe^{2+} of 0.1 mM.

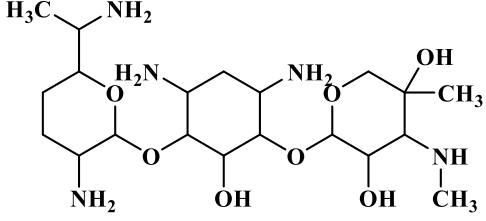
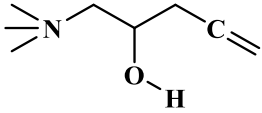
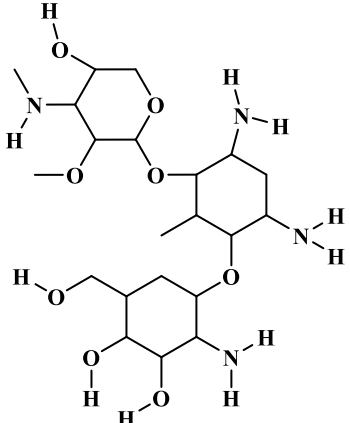
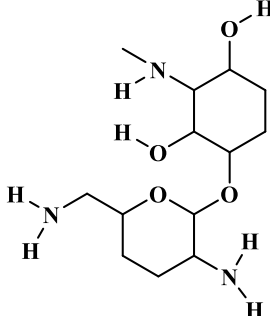
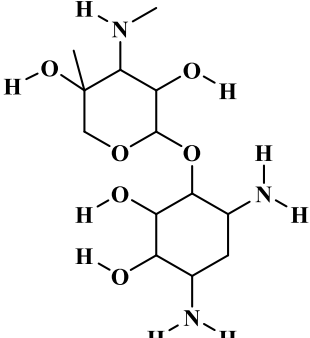
First, we have chosen the case of gentamicin for a comparison with the case of gatifloxacin since there is a significant difference concerning the behavior of both antibiotics in terms of biodegradability.

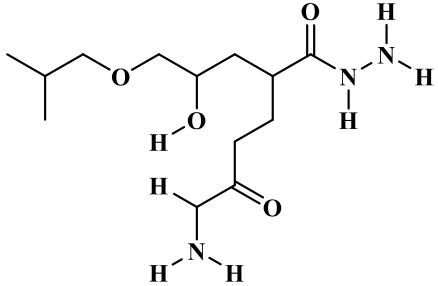
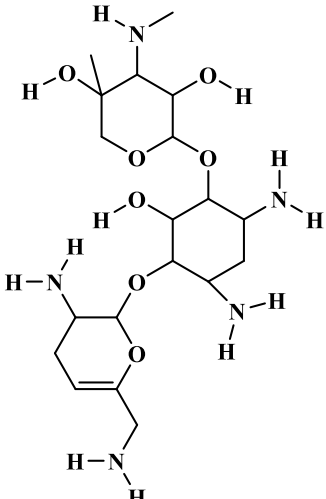
Second, according to the Figure 7, note that in the case of gentamicin, the solution becomes biodegradable after 30 min of treatment EF while for gatifloxacin is only biodegradable after 150 min.

For Gati, there is the formation of aromatic molecules (Table 2) between 0 min and 150 min of

electrolysis which are resistant for the biological treatment with BOD_5/COD equal to zero and easily degradable by the treatment EF. Also, between 150 min and 6 h of electrolysis, there is the formation of aliphatic molecules (with short chain) who are easily degradable biologically and resistant at the treatment EF. However, for gentamicin (Table 3), from the beginning (after 30 min) the molecules aromatics existing in the solution (Table 3) are biodegradables according to the literature³².

Table 3. The intermediates identified by LC/MS-MS during the mineralization of gentamicin by EF process.

Gentamicin and its intermediates	Structure	m/z	Reference
Gentamicin		477	---
1		142	33
2		468	34
3		305	35
4		322	33-36

5		291	33
6		447	33

Conclusion

It has been showed that for a 0.1 mM gatifloxacin concentration, $I = 400$ mA and $[Fe^{2+}] = 0.1$ mM constitute the optimum. Under these operational conditions, gatifloxacin disappears completely after 2 min of electro Fenton treatment, and the COD elimination attains 90% after 6 hours showing the mineralization of gatifloxacin in an aqueous medium.

The biodegradability study indicated that during 100 minutes of electrolysis, the BOD_5/COD ratio is equal to zero showing that the solution is non-biodegradable, thus indicating that gatifloxacin and its sub - aromatic products are biologically resistant. Next, the biodegradability improves and at about $t = 150$ minutes of EF electrolysis, the BOD_5/COD reaches the value 1.1, showing that the solution which contains the aliphatics principally, becomes biodegradable. This indicates that electro-Fenton pretreatments can enhance biodegradability by forming other biodegradable by-products that could be easily biodegraded.

So, a coupling between electrolytic treatment with a biological one could be seen as a perspective for determining the time in order to pass since the electrolysis to the biological process so that to minimize the cost of the global treatment. This leads to effective treatment of waters polluted with gatifloxacin at a lower cost.

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