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Mineralization of Ofloxcacin Antibiotic in Aqueous Medium by Electro-Fenton Process using a Carbon Felt Cathode: Influencing Factors

Muna Shueai Yahya,[1,2] Ghizlan Kaichouh,[2,*] Mariam Khachani,[2] Miloud El Karbane,[3] Mohammed Azeem Arshad,[4] Abdelkader Zarrouk,[2,*] and Kacem El Kacemi[2]

[1]Department of Chemistry, Faculty of Education, Hodeidah University, Hodeida, Yemen
[2] Laboratory of Materials, Nanotechnology and Environment, Faculty of Sciences, Mohammed V University, Av. Ibn Battouta, P.O. Box 1014 Agdal-Rabat, Morocco
[3]Laboratory Analytical Chemistry and Bromatology Laboratory, Faculty of Medicine and Pharmacy, Mohamed V University, Rabat, Morocco
[4]Laboratory of Composite Materials, Polymers and Environment, Department of chemistry, Faculty of Science, Mohamed V University, Rabat, Morocco

*Corresponding Author, Tel.: +212665201397, Fax.: +212537774261
E-Mail: azarrouk@gmail.com

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Abstract- The aim of this work is to study the degradation and mineralization of antibiotic ofloxacin in aqueous medium using the Electro-Fenton method as advanced oxidation technology. In this context, Pt/carbon-felt cell was used to investigate the influence of various parameters including initial pH, different supporting electrolytes, different metal ions as a catalyst and antibiotic concentration over the mineralization rate and instantaneous current efficiency. The chemical oxygen demand (COD) measurements during the electrolysis allowed the evaluation of the kinetic of organic matter decay and the mineralization efficiency reaches 90% COD removal at only 200 mA for 300 min of electrolysis.

Keywords- Antibiotic; Ofloxacin; Water treatment; Advanced electrochemical process; Electro-Fenton; Mineralization

1. INTRODUCTION

Antibiotic Ofloxacin (OFL), belonging to Fluoroquinolone (FQs) family, is a broad-spectrum antibacterial agent widely used for treating bacterial infections due to his strong antibacterial activity against the bacteria gram-positive and gram-negative [1]. FQs antibiotics are only partially (are not totally) metabolized when given to humans or livestock, thus, they can pass in agricultural runoff water and wastewater leading therefore to physiological teratogenesis of plants and algae. Among all antibacterial found in water, OFL is one of the main types [2] detected mostly in raw effluent [3,4], groundwater and surface water, with concentrations ranging from ng/L to mg/L [2,5-7]. Unlikely, FQs are weakly biodegradable and are genotoxic and carcinogenic for organisms [8]. Many authors have noted that OFL may pose a substantial risk to aquatic organisms because of their occurrence and toxicity [7,9-11].

In this fact, significant attention was extended in order to develop technologies for effective abatement of these toxic compounds [12] and their degradation by-products, which can be more harmful compared to the parent product. Recently, several studies have focused on the treatment of OFL degradation by application of advanced oxidation processes (AOPs) [5,13], including photodegradation with sunlight [8], photocatalysis with TiO_2 [14], UV/H_2O_2 [15], Fenton [16], photo-Fenton [17] and electrochemical oxidation [18]**.** However, up to now, there is no available information dealing with the application of Electro-Fenton (EF), an advanced electrochemical oxidation method, to the degradation and mineralization of OFL. Advanced electrochemical oxidation processes have proven their great ability to effectively destroy several toxic and bioreactive organic compounds [19-27]. It is an economical, efficient, and environmentally friendly process compared to conventional technologies [28]. The effectiveness of the EF process in the degradation and mineralization of persistent and poisonous pollutants, including pharmaceuticals in aqueous solutions was proved in some earlier works [29-31]. These processes are founded on the electrochemical production of hydroxyl radicals (•OH) produced either straight via the water oxidation at the anode or indirectly by total or partial *in-situ* production of the Fenton's reagents (H_2O_2 + Fe^{2+}). Besides, during these processes, a continuous and fast regeneration of Fenton's reagents accelerates the production of ($^{\bullet}$OH) in the bulk via Fenton's reactions (Eqs. 1,2,3) [32,33]:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (1)$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad (2)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \quad (3)$$

The principle of the electro-Fenton process nonetheless involves some experimental parameters whose optimization favors the effectiveness of the degradation of organic pollutants. These parameters include the type of electrode used (cathode, anode), the pH of the medium, the electrochemical factors (Current intensity, potential), electrolyte and catalyst type.

In this context, the objective of this work is to optimize the significant parameters for a great mineralization of aqueous medium charged by the pollutant Ofloxacin by EF using a Pt and carbon felt cell, trying to confirm the important oxidation power of this process to eliminate highly (bio) recalcitrant molecules.

2. EXPERIMENTAL

2.1. Chemicals

OFL ($C_{18}H_{20}N_3O_4F$ > 98% purity) was obtained from Sigma Aldrich. The pure compounds ferrous sulfate ($FeSO_4$), sulfuric acid (H_2SO_4) and potassium chloride (KCl) were purchased from Shanghai chemicals (Shanghai, China). Copper sulfate pentahydrate ($CuSO_4.5H_2O$, 99%) from Scharlau, Manganese sulfate monohydrate ($MnSO_4.H_2O$, 99%) from Sochid and Ferrous sulfate heptahydrate ($FeSO_4.7H_2O$) from Merck were used as catalysts sources. Anhydride sodium sulfate (Na_2SO_4) was used as background electrolyte was bought from Merck. Ultrapure water obtained from a Millipore Milli−Q system at room temperature and resistivity > 18 MΩ cm was used to prepare solutions.

2.2. Electrolytic system

Electrochemical treatments and consumed electrical charge measurements were conducted using a potentiostat-galvanostat PGZ301 from VoltaLab. Electrolysis was carried out in an open electrochemical system with 200 mL of capacity. Electro-Fenton treatment was applied with a large surface area of carbon felt (10 cm × 8 cm × 0.5 cm) cathode and platinum anode (5 cm^2) at room temperature (25 °C). Prior to the electrolysis, the initial pH of OFL solutions was measured with a Mettler-Toledo FE20 pH-meter and adjusted by sulfuric acid (H_2SO_4). Before starting electrolysis, compressed air was bubbled for 10 minutes to saturate the aqueous solution with oxygen.

2.3. Analytical studies

Mineralization capacity of OFL generated by this electrochemical technique was evaluated by the COD reduction during electrolysis. The dichromate method was used to determine this parameter. Thus, a proper quantity of sample was added to a commercial digestion solution containing potassium dichromate (KCr_2O_7), sulfuric acid (H_2SO_4) and mercuric sulfate ($HgSO_4$) (Hach Lange Europe, Belgium). Then, the mixture was incubated in the Lovibond® COD VARIO photometer at 150 °C for 2h. COD values were collected by colorimetry using a spectrophotometer DR/125 (Hach Company, USA).

The instantaneous current efficiency (ICE) can be defined as the part of the current directly used for the oxidation of the organic compounds. ICE for the oxidation of OFL was determined using the COD method.

The measurement of COD is conducted during electrolysis, while the instantaneous current efficiency is calculated by using the following relation [27]:

$$ICE = \frac{(COD_0 - COD_t) \times FV}{8 \times I \times t} \qquad (4)$$

where COD_0 and COD_t are chemical oxygen demand values at initial and final oxidation time, respectively. I is the current intensity (A), F is the Faraday constant (96487 C mol^{-1}), V is the volume of the electrolyte (in L), t is oxidation time (s) and 8 is a dimensional factor for unit consistency [(32 g of O_2 mol^{-1})/(4 mol of electron exchanged)].

3. RESULTS AND DISCUSSION

3.1. Effect of ofloxacin concentration

The OFL mineralization by Electro-Fenton process was evaluated using several OFL concentrations under the following conditions: a current of 200 mA at pH of 3.0, 50 mM of Na_2SO_4 as an electrolyte and Fe^{2+} catalyst with a concentration of 0.2 mM for 360 min of electrolysis (Figure 1).

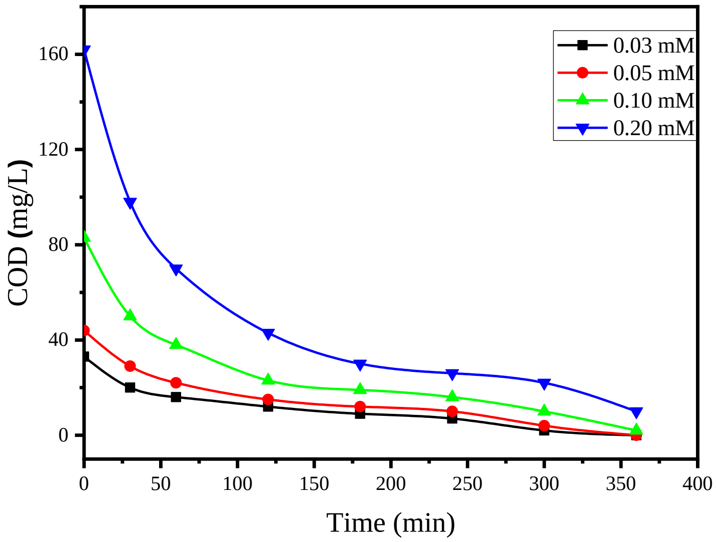

Fig. 1. Effect of different OFL concentrations on its mineralization under Electro-Fenton conditions: I = 200 mA, $[Fe^{2+}]$ = 0.2 mM and pH = 3

Figure 1 shows the efficiency of the electro-Fenton process for the removal of ofloxacin at different concentration ranges 0.03, 0.05, 0.1 and 0.2 mM corresponding respectively to 33, 44, 83 and 162 mg O_2/L. Under the same conditions, COD abatement exceeds 91% in all cases after 360 min of treatment (Figure 1).

The treatment time needed for total mineralization is dependent on the initial concentration. Therefore, at higher concentration, a longer electrolysis time is needed for quasi-totale mineralization. On the other hand, the higher rate of the mineralization observed at the beginning of the treatment decreases remarkably which means that the degradation by the electro-Fenton process generates aromatic intermediates. This latter are attacked by hydroxyl radicals which open the aromatic ring and form aliphatic organic companions with a short carbon chains such as carboxylic acids (oxalic acid, formic acid, glyoxylic acid, succinic acid, malic acid, maleic acid and malonic acid) [19,20]. The attack on aromatic rings is easier than aliphatic compounds due to their resistant to oxidation which significantly reduce the effectiveness of mineralization. Aliphatic compounds are very stable and low reactive with hydroxyl radicals [19,25].

3.2. Instantaneous current efficiency

Figure 2 presents the ICE evolution for each OFL concentration.

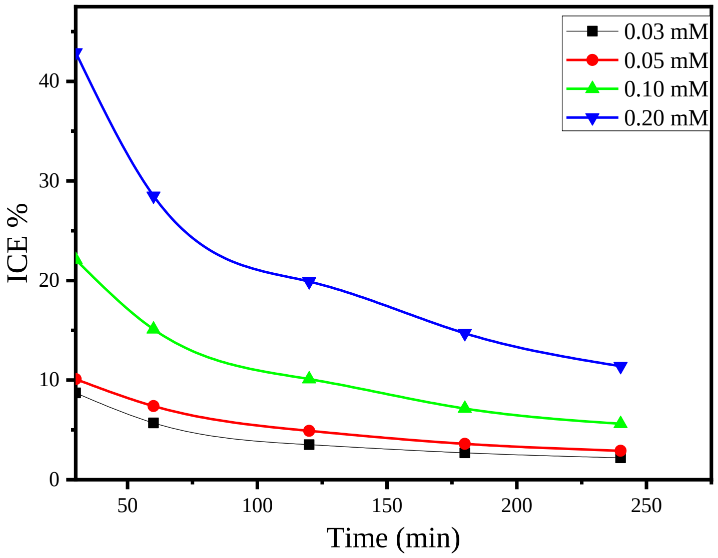

Fig. 2. ICE evolution along Electro-Fenton process at diverse Ofloxacin concentrations, $[Fe^{2+}]$ = 0.2 mM, I = 200 mA, pH = 3.0 and 50 mM Na_2SO_4

As presented in Figure 2, ICE values increase with OFL concentrations from 0.03 to 0.2 mM which means that a fast reaction in the solution has occurred between •OH radicals and molecule due to the important presence of OFL molecules, and therefore, the competitive non oxidizing reactions become slower which lead to raise the availability of •OH radicals to react with OFL. On the other hand, ICE values are lower at the beginning of the oxidation process with small OFL concentrations (from 0.03 to 0.05) and do not much change with time, whereas, it becomes very important at higher contents. In addition, the maximum efficiencies were obtained during the first 3 hours, and after that ICE slowly drops, which indicates that the by-products formed during this time are more easily degraded by •OH radicals than the generated intermediates [34,35].

3.3. Effect of different supporting electrolytes

Mostly, during electrochemical processes, the most common way for increasing the solution conductivity and facilitating the passage of the electrical current is to add a supporting electrolyte which leads to reduce the energy consumption. With a view to study the impact of the supporting electrolyte on OFL solutions mineralization, many experiments were realized in acidic medium (pH = 3.0) containing Na2SO4 (0.05 M) and NaCl (0.1 M) as supporting electrolytes (Figure 3) .

In order to study the effect of the support electrolyte on the mineralization of OFL solutions, after 4 hours of treatment (Figure 3), the COD removal efficiencies for OFL were 75.3% for Na_2SO_4 and 63.6% for NaCl after 300 min of treatment, thus, low mineralization was noted with NaCl, which means that the electrical conductivities of SO_4^{2-} solution is greater than that of equivalent-strength Cl^- [36]. This result is explained by the generation of active chlorine due to chloride ions oxidized of at Pt anode surface [35]. Consequently, a part of the provided electrical energy is lost.

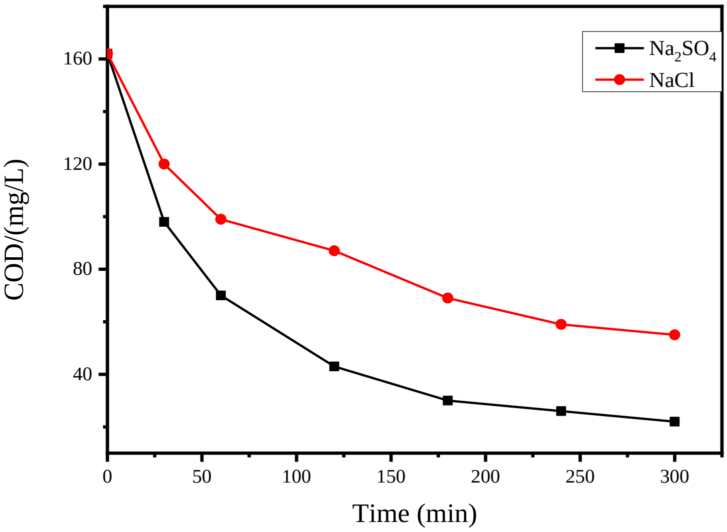

Fig. 3. Effect of electrolytes on the mineralization of OFL by EF process, [OFL] = 0.2 mM, NaCl = 0.1 M, Na_2SO_4 = 0.05 M, Fe^{2+} = 0.2 mM, pH = 3.0, I = 200 mA

Furthermore, the chlorine electrogenerated by the Electro-Fenton process can either react with Fe^{2+} (Eq. 5) or decompose peroxide hydrogen H_2O_2 (Eq. 6), which then reduce the production rate of •OH oxidant by Fenton's reaction. However, higher concentrations of

Na_2SO_4 could accelerate the generation of H_2O_2 and increased the pollutant removal efficiency [37,38].

$$2Fe^{2+} + Cl_2 \rightarrow 2Fe^{3+} + 2Cl^- \qquad (5)$$

$$2H_2O_2 + Cl_2 \rightarrow 2HCl + H_2O + O_2 \qquad (6)$$

3.4. Effect of pH solution

Impact of pH on the mineralization of 0.2 mM OFL was studied at initial pH values of 2.0, 3.0, and 4.0 as shown in Figure 4. It was observed that the mineralization of OFL was very fast at pH = 3.0 achieving 81 % at 180 min, whereas, it attains only 68% and 63% at pH = 4 and 2, respectively. This result confirmed that this process achieves maximum efficiency at the optimum pH of 2.8-3.0, thus, Fe^{2+}/Fe^{3+} catalytic couple kept the same comportment [39-45].

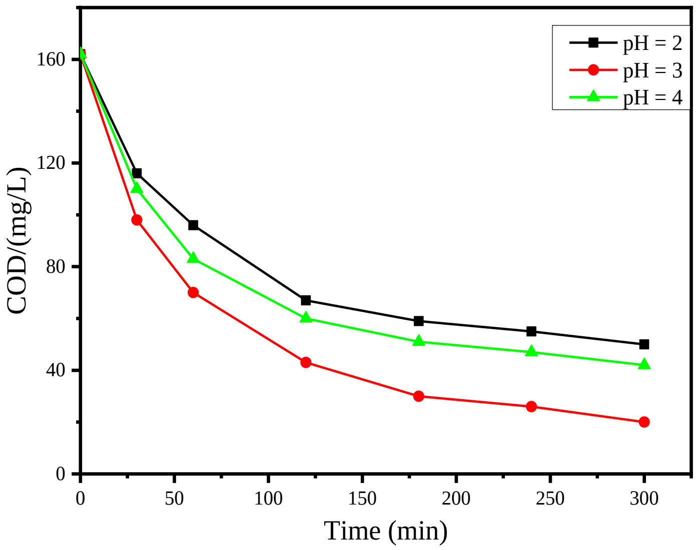

Fig. 4. Mineralization of OFL at different pH, [OFL] = 0.2 mM, [Na_2SO_4] = 0.05 M, [Fe^{2+}] = 0.2 mM and I = 200 mA

3.5. Comparative removal efficiency of each catalyst

The comparison of removal efficiency using three transition metals as catalysts (ferrous ion (Fe^{2+}), copper ion (Cu^{2+}) and manganese ion (Mn^{2+})) is illustrated in Figure 5. The experiments were conducted under the same operating conditions: [OFL]=0.2 mM, [Na_2SO_4] = 0.05 M, [Fe^{2+}] = 0.2 mM and I = 200 mA. As can be seen in Figure 5, the COD removal efficiency attained about 84% for Fe^{2+}, 64.2% for Cu^{2+} and 38% for Mn^{2+}.

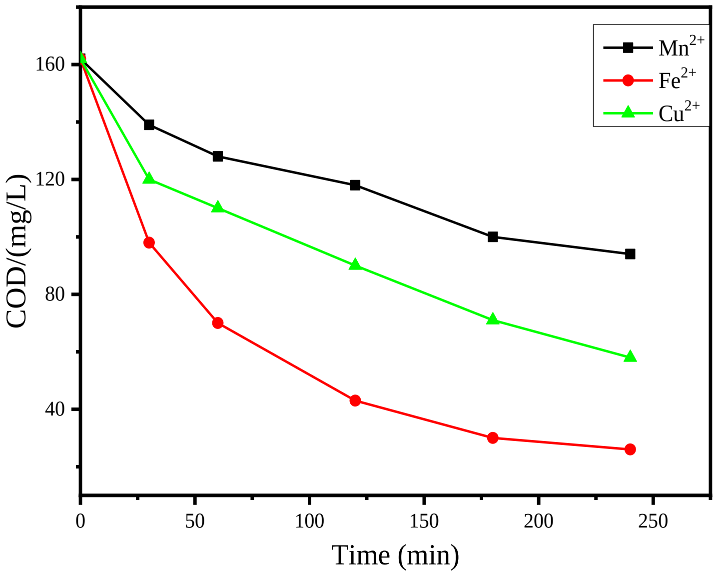

Fig. 5. COD evolution of OFL solution, with different catalysts: [OFL] = 0.2 mM, [Na_2SO_4] = 0.05 M, [Fe^{2+}] = 0.2 mM and I = 200 mA, pH = 3.0

The results showed that Fe^{2+} ions lead to the best mineralization rate compared to the catalysts Cu^{2+} and Mn^{2+} which could be related to the higher oxidizing power of Fe^{3+}/Fe^{2+} couple (E^0 = 0.77 V/ESH) versus Cu^{2+}/Cu^{+} (E^0 = 0.16 V/ESH) where the production of •OH through Fenton interaction between Cu^{+} and H_2O_2 is very low [46]. On the other hand, low effectiveness with Mn^{2+} may be ascribed to the electrode deposition reported in several electrochemical studies in acidic medium according to the reaction Eq. 7:

$$Mn^{2+} + 2H_2O \rightarrow MnO_2(s) + 4H^{+} + 2e^{-} \qquad (7)$$

With $MnSO_4$ molecule, the sulfate anion is exchanged with oxygen because the catalyst Mn^{2+} is oxidized from charge 2+ to 4+ [47].

3.6.Instantaneous current efficiency evolution using different catalysts

Figure 6 represents the evolution of ICE versus time for each electrolysis catalyst (Fe^{2+}, Cu^{2+}, and Mn^{2+}). It can be seen that the ICE behavior during the process differs from one catalyst to another. The highest ICE of 28.14% was obtained for the Electro-Fenton process catalyzed with Fe^{2+} ion after 1 hour of electrolysis. The values of ICE for Fe^{2+} were low in the beginning before increasing rapidly from 14.5% to 28.1%, then, sharply decreased to half after 3 hour and kept almost constant with a little diminution at the end of the electrolysis. These decreases may be due to the formation of some coordinated organic compounds with Fe^{2+}, either as Fe^{+2} or mostly as Fe^{3+} ions and so the recovery of the catalyst Fe^{2+} is impossible, therefore the catalytic decomposition of H_2O_2 into •OH radicals are limited. As a result, fewer oxidation procedures take place and may be the formed by-products are the most difficult to degrade [46]. On the other hand, for Cu^{2+}, the highest ICE values are noted at the beginning of Electro-Fenton process with 28.1%. After 180 minutes, the ICE sharply decreased and keep decreasing slowly along the process. This result can be attributed to the deposition of copper on the cathode. Otherwise, the lowest values of ICE were observed for Mn^{2+} catalyst. At the beginning of the Electro-Fenton process, ICE was a slightly higher, 12%, before attaining 6% where it stays at this value for the four hours of the process. This may be explained by the deposition of Mn^{2+}on the cathode occurring from the beginning of the process. During this deposition, the catalyst oxidation state change from Mn^{2+} to Mn^{4+} producing, therefore, to MnO_2 (Eq. 7). This result was confirmed by solution color change observed through the electrolysis [48].

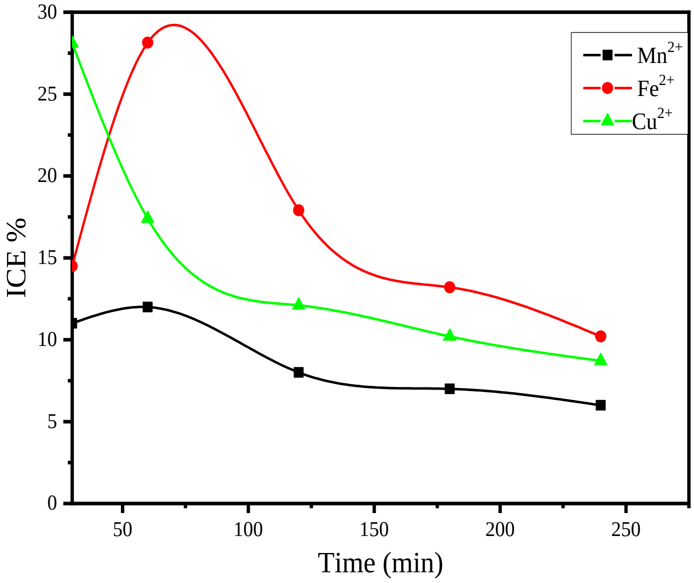

Fig. 6. ICE evolution for different catalysts with [OFL] = 0.2 mM, $[Fe^{2+}]$ = 0.2 mM $[Na_2SO_4]$ = 0.05 M, and I = 200 mA

3.7. Evolution of pH during the process with different catalyst

Throughout Electro-Fenton process, the initial molecule is broken into •OH radicals which lead to the formation of small carbon chains. These latter will be oxidized and converted to organic acids causing, thus, diminution of pH. Therefore, the pH evolution along the OFL oxidation, with different catalyst ions were investigated (Fig. 7).

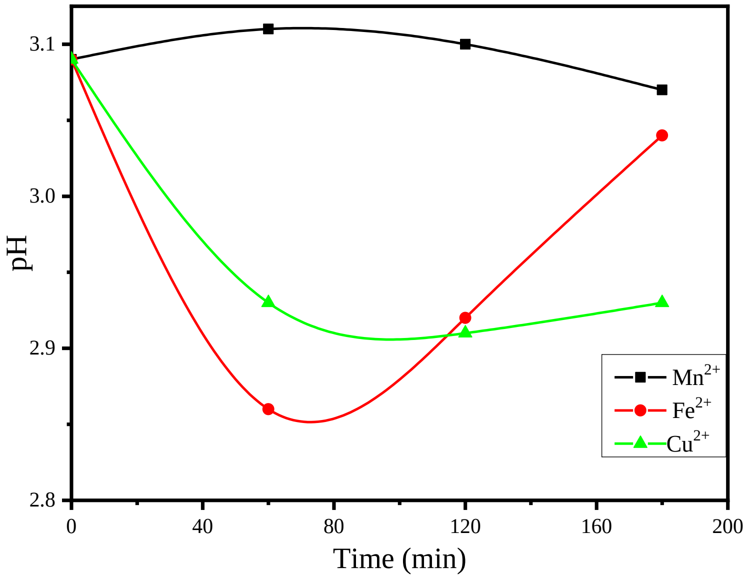

Fig. 7. pH evolution along of the Electro-Fenton process with different catalyst ions at 0.2 mM, [OFL] = 0.2 mM, I = 200mA

The larger pH changes were observed for Cu^{2+} where it decreases from 3.1 to 2.91. This variance compared to other catalysts could be attributed to the higher ammonia accumulation since the starting of electrolysis. And as well, the lowest pH variation was displayed for Mn^{2+} catalyst. This comportment is correlated to the lowest COD removal rate obtained for Mn^{2+} (Fig. 5). Besides, the optimal pH for Fe^{2+} is between 2.8 and 3.0 [40].

4. CONCLUSION

This study highlights the outcome of Electro-Fenton (EF) technique using a carbon felt cathode and a Pt anode as recommended advanced electrochemical oxidation for the treatment of water contaminated with the residues of Ofloxacin antibiotic. Changes in the parameters used, including different metal ions, initial pH, different supporting electrolytes and ofloxacin concentration illustrate significant changes on the efficiency of this method. Mineralization of 0.02 mM OFL achieves a maximum under optimal conditions. This parameters are Fe^{2+} catalyst concentration of 0.2 mM, Na_2SO_4 electrolyte concentration of 0.05 mM, initial pH of 3.0 and applied current of 200 mA.

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