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EFFECT OF THE CATHODE MATERIAL ON THE EFFICIENCY OF THE ELECTRO-FENTON PROCESS TO REMOVE PEFLOXACIN. KINETICS AND OXIDATION PRODUCTS

The effect of the electro-Fenton process depends on the ability of the cathode material to produce H_2O_2, a primary oxidizing agent that is responsible for destroying organic pollutants. The study aimed at the impact of various cathode materials, including carbon felt, carbon graphite, and stainless steel, as well as current density on the electrochemical oxidation of pefloxacin (PEF) in water. The electro--Fenton technique was applied for the first time on the PEF employing various cathodes with a platinum anode. HPLC and LC-(MS-MS) studies have been utilized to determine intermediate compounds. Using ion chromatography, inorganic ions released in the solution as a final stage of the mineralizing process were determined. Finally, we assessed the viability of fusing the biological process with the electro-Fenton one. As a result, PEF-contaminated water can be treated effectively and cheaply.

1. INTRODUCTION

Quinolone antibiotics are frequently utilized, and much attention has been paid to their environmental migration and modification. The most widely used third-generation medications are pefloxacin, norfloxacin, ciprofloxacin, and levofloxacin, which differ from one another in their antibacterial capabilities [1, 2]. Antibiotic misuse has been serious in recent years [3, 4]. Such medications are common in municipal and industrial wastewater, as well as surface water [5, 6] because they cannot be completely digested after consumption by organisms.

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Efficient water treatment techniques such as advanced oxidation processes (AOPs) have been developed during the past few decades [7–12]. The ability of AOPs to oxidize organic micropollutants to their maximum degree of oxidation or mineralization is based on the in situ formation of powerful oxidants with high reactivity and extremely high oxidation power such as the hydroxyl radicals ($OH^{\bullet}$), with oxidation potential $E^{\circ} = 2.8$ V/SHE known as the electro-Fenton method [13, 14].

By creating H_2O_2 in situ by reducing dissolved oxygen with two electrons on a cathode, Fenton's reagent ($H_2O_2 + Fe^{2+}$) hydroxylation of organic compounds occurs; as a result, the radicals produced have a very high reaction rate with the hydroxylated organic contaminants [15–17]. The electro-Fenton (EF) treatment efficiency is affected by several operational elements such as electrode material, catalyst, current density, concentration, and pH [18]. Among these variables, the cathode type plays a critical role in the electro-Fenton treatment efficiency because, according reaction

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + OH^{\bullet} \tag{1}$$

it affects the H_2O_2 yield, which has an impact on how quickly $OH^{\bullet}$ is formed [19]. According to the Fenton reaction (Eq. (1)), an increase in H_2O_2 concentration causes an increase in the rate of $OH^{\bullet}$ production.

The purpose of this research was to examine and compare the performance of three cathode materials: felt cathode (CF), carbon-graphite (CG), and stainless steel (SS) in the electro-Fenton treatment with platinum anode. The present research focuses on how the cathode material and current used affect the electro-Fenton process' efficiency, which is based on the mineralization and oxidative degradation of an intended pollutant called pefloxacin (PEF). This study was the first for PEF as a pollutant model to assess the performance of various cathode materials in terms of production capacity, oxidation capacity, and mineralization in the electro-Fenton process in function of the current.

2. EXPERIMENTAL

Pefloxacin (PEF, $C_{17}H_{20}FN_3O_3$, 333.4 $g \cdot mol^{-1}$) was acquired from the Shanghai Jining Industrial (Shanghai, China). Compound A ($C_{14}H_{16}FN_3O_3$, 322 $g \cdot mol^{-1}$) was purchased from LGC Luckenwalde, Germany. KCl, H_2SO_4, and ferrous sulfate were purchased from Shanghai Chemical. Triethylamine, sodium perchlorate, and ammonium acetate were provided from Fluka. Acetonitrile, HPLC grade, was provided from Carlo ERPA. All solutions were created with ultra-pure water using a Millipore MilliQ system at room temperature.

Electrolytic system. The electrochemical parameters were measured using Voltalab equipment for a Potentiostat/Galvanostat type (PGZ 301). A 200-cm^3 open electrochemical cell with a maximum PEF concentration of 0.149 mM was used for the electrolyses.

All cathodes were made of commercially accessible materials such as stainless steel (SS), Goodfellow, France, carbon graphite (CG), and carbon felt (CF), Mersen, France. Both big-surface (14×5 cm^2) and small-surface (6×5 cm^2) cathodes, CF(l) and CF(s), respectively, were employed whereas only small-surface CG and SS cathodes were used. The anode (with a surface of 5 cm^2) was made of platinum (PLATECXIS, France). Using 0.1 M H_2SO_4, the pH was kept at 3.0. Both anhydride sodium sulfate utilized as electrolyte background and heptahydrate iron(II) sulfate, employed as the catalyst source, were bought from MERCK. A continuous current characterized by a current density in the range of 80–500 mA/cm^2 was applied when the device was at room temperature.

Analytical methods. The performance of the kinetics and decay of PEF was examined over, where the degradation of PEF occurred within a period not exceeding 50 min. To calculate the apparent rate constant (k_{app}), the time from 1 to 15 min was taken. To establish the rate of degradation of PEF, a minimum time of 350 minutes was required.

COD was determined by the dichromate technique. The analyzed mixture was placed in the Lovibond® COD VARIO photometer and incubated for 120 min at 150 °C, and then a spectrophotometer was used to determine the value of COD.

Time dependences of PEF intermediate products' concentrations were examined using a Waters 2695 coupled photodiode-array detector (PDA 2998) by reversed-phase HPLC at 274 nm. Data were collected using the Empower 2 Software. The system was fitted with a 45 °C thermal hypersil C18, 5 μm, 4.6 mm, 25 cm column from Agilent. A 28:72 (v/v) mixture of $CH_3OH/C_{16}H_{37}NO_4S–KH_2PO_4/H_2SO_4$ was used as the mobile phase.

LCQ advantage triple quadrupole mass spectrometer with LC Surveyor HPLC system was used to LC/MS investigations. The ESI source was operated in positive ion mode. The studies were conducted using an Inertsil BDS Hypersil C18, 150×2.1 mm^2 ×5 μm column in reverse phase, which was kept at 35 °C. The injections had a 20 μL in volume. Solution of water and methanol with formic acid was used to eluate the column at the flow rate of 0.2 min^{-1}. At 200–650 nm, detection was carried out using a gradient program.

By injecting 25 μL into a Dionex (ICS-1000) basic ion chromatograph GC, inorganic ions formed in the solutions were identified. The system was equipped with an Ion AG4A-SC Pac, 5 cm×5 mm column guard, and an Ion AS4A-SC Pac, 25 cm×5 mm for the determination of fluoride and nitrate anions. A combination of 1.8 mM Na_2CO_3 and 1.7 mM $NaHCO_3$ was introduced into the mobile phase, which was cycling at a flow rate of 2 cm^3/min. An IonPac CS12A (25 cm 4 mm) cation-exchange column connected to an IonPac (5 cm×4 mm) CG12A column was used to determine the concentration of ammonium ions. Operating software for Chromeleon SE was used to manage the system, which included a DS6 conductivity detector with a 35 °C heated cell.

Utilizing a respirometric assessment approach for 5 days, the BOD was measured with an OxiDirect (BOD_5) at 20 °C. pH between 6.5 and 7.5 is the operating environ-

ment for this technique. N-allylthiourea was the nitrification inhibitor. Potassium hydroxide was added to the bottles to trap carbon dioxide. Through residential wastewater, activated sludge was produced. It provided a suitable environment for living bacteria and facilitated the process of biological decomposition of organic materials in the water sample.

3. RESULTS AND DISCUSSION

3.1. INFLUENCE OF CURRENT AND CATHODE TYPE ON OXIDATIVE DEGRADATION FOR PEF

The electrolytic cell (200 cm^3) of PEF (0.149 mM) with Fe^{2+} (0.2 mM) at pH = 3 was utilized to execute the oxidative degradation of PEF at the current density ranges from 80 to 500 mA/cm^2. for assessing the impact of cathode type on the efficiency of the electro-Fenton treatment.

The electro-Fenton process is based on in situ catalytic production of the Fenton reagent H_2O_2, thus avoiding the external input of large quantities of hydrogen peroxide. It consists of generating H_2O_2 by reduction of molecular oxygen. This first requires saturation of the solution to be treated with oxygen.

Hydrogen peroxide and ferrous ions are generated simultaneously at the working electrode at a potential of –0.5 V/ECS according to the electrochemical reactions:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2, \quad E° = 0.69 \text{ V/ERH} \tag{2}$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+}, \quad E° = 0.77 \text{ V/ERH} \tag{3}$$

The Fenton reagent ($H_2O_2 + Fe^{2+}$) produced in situ, leads to the formation of hydroxyl radicals (Eq. (1)).

Therefore, applying a current (2-electrode cell) or a low cathodic potential of –0.5 V/ECS (3-electrode cell) to the working electrode produces $OH^{\bullet}$ radicals. Dissolved dioxygen is reduced to superoxide ion ($O_2^{\bullet-}$) (Eq. (4)) which reacts rapidly with H^+ ions in an acidic medium, to generate peroxide radicals (Eq. (5)). These radicals are unstable and lead to the formation of hydrogen peroxide (Eq. (6)).

$$O_2 + e^- \rightarrow O_2^{\bullet-} \tag{4}$$

$$O_2^{\bullet-} + H^+ \rightarrow HO_2^{\bullet} \tag{5}$$

$$2HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \tag{6}$$

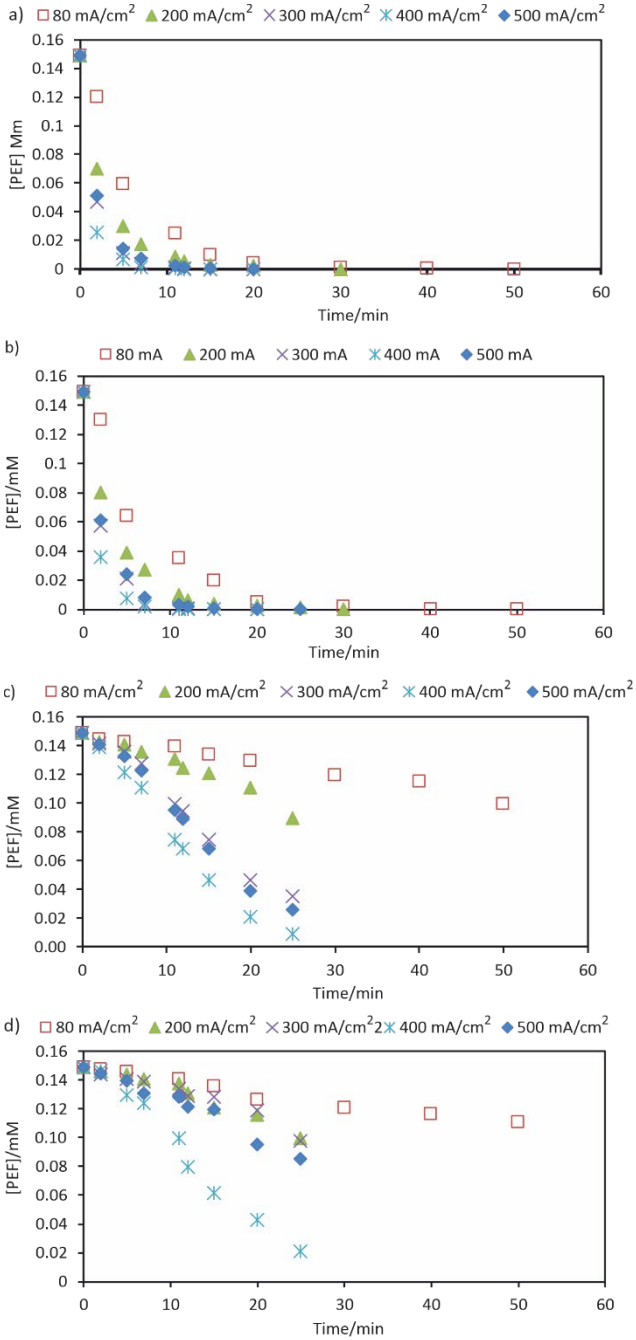


Fig. 1. Time dependences of PEF concentration during electro-Fenton oxidation using various electrodes: a) CF(l)/Pt, b) CF(s)/Pt, c) CG/Pt, d) SS/Pt; [PEF] = 0.149 mM, [Fe^{2+}] = 0.2 mM, [Na_2SO_4] = 50 mM, V = 200 cm^3, pH = 3

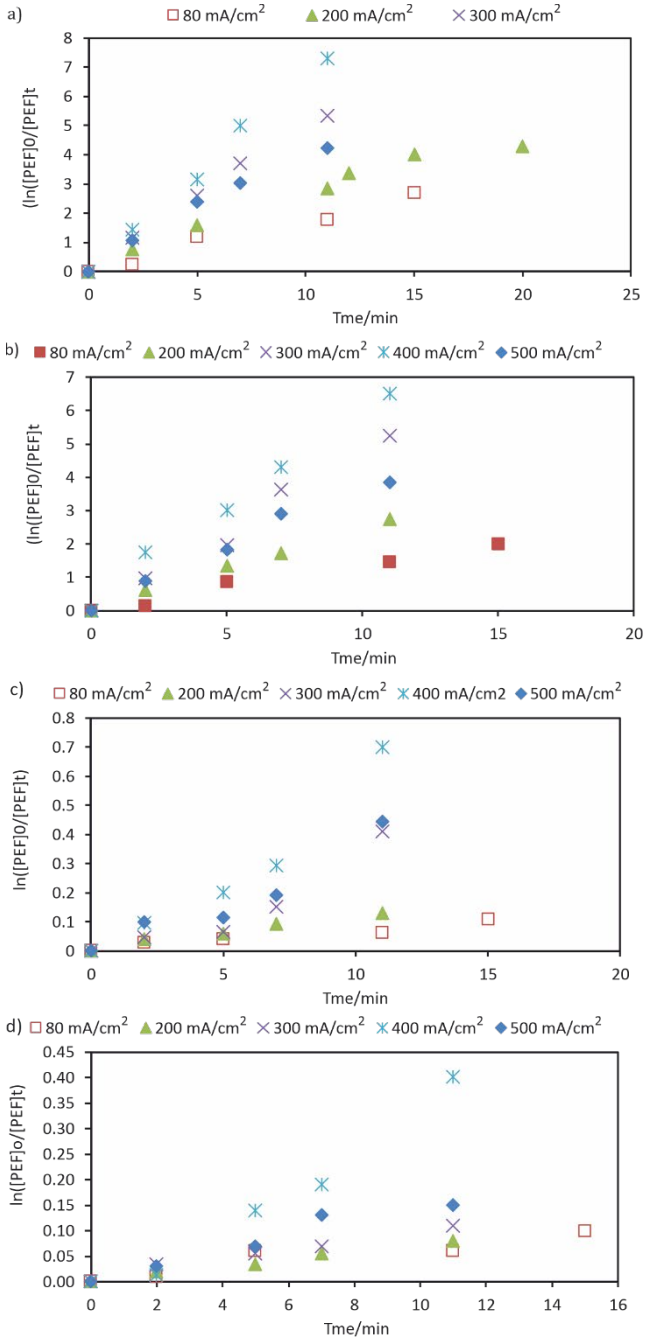


Fig. 2. Pseudo-first order kinetics for PEF degradation by electro-Fenton with various cathodes: a) CF(l)/Pt, b) CF(s)/Pt, c) CG/Pt d) SS/Pt, [PEF] = 0.149 mM, $[Fe^{2+}]$ = 0.2 mM, $[Na_2SO_4]$ = 50 mM, V = 200 cm^3, pH = 3

The result of the cathodic reaction is obtained by the sum of reactions

$$O_2 + 3H^+ + 3e^- \rightarrow H_2O + OH^\bullet \tag{7}$$

The anodic reaction is the oxidation of water to molecular oxygen, which is used for the production of hydrogen peroxide

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \tag{8}$$

The rate of degradation for PEF increases with the increase in the current as a result of the increased production of $Pt(OH^\bullet)$ radicals (Fig. 1). This is due to the increase of the rate of electrochemical reactions to generate and produce H_2O_2 and regenerate Fe^{2+} at the cathode

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{9}$$

and also rapid production of $OH^\bullet$ radicals at the anode

$$Pt + H_2O \rightarrow Pt(OH^\bullet) + H^+ + e^- \tag{10}$$

It is clear from the concentration decay curves that the decomposition of PEF at all cathodes used in this research is the pseudo-first order kinetics (Fig. 2). Actually, there was a strong connection ($R^2 > 0995$) between the decrease of PEF concentration and the pseudo-first order reaction, and the apparent rate constants increased steadily as current increased. The value of k_{app} is given by the slope of the straight lines that reflect the function $\ln([PEF]_0/[PEF]_t) = f(t)$.

CF(l) provided better results than CF(s), while the degradation kinetics of PEF at CG was slower compared to CF at all current density values. The degradation kinetics at the SS cathode was poor, due to the weakness in H_2O_2 generation (Fig. 1).

On the other hand, the rate of decomposition is enhanced by increasing current to produce $M(OH^\bullet)$ as it undergoes electrochemical processes:

$$M + H_2O \rightarrow M(OH^\bullet) + H^+ + e^- \tag{11}$$

The improvement, however, does not correspond to the current intensity, for example, curves for 400 and 500 mA/cm^2 are nearly identical. This fact can be explained by how side reactions, like O_2 evolution (Eq. (12)) at the anode, are boosted, as well as wasting reactions, like the oxidation for $(M/OH^\bullet)$ (Eq. (13)) at the anode (Eq. (14)). It is clear from the equation of recombination $OH^\bullet$, and by H_2O_2 scavenging of $OH^\bullet$ in the solution, as in Eq. (15), that high applied currents produce large quantities of $M(OH^\bullet)$.

$$H_2O \rightarrow 2H^+ + \frac{1}{2}O_2 + 2e^- \tag{12}$$

$$2(M/OH^\bullet) \rightarrow 2H^+ + 2M + O_2 + 2e^- \tag{13}$$

$$2OH^{\bullet} \rightarrow H_2O_2 \tag{14}$$

$$OH^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O \tag{15}$$

The apparent rate constants (k_{app}) for the degradation kinetics of PEF for the pseudo--first order reaction are listed in Table 1. The rate constants increase upon the increasing current to an ideal value. The optimal value of current, for the greatest rate constant, depending on the cathode material may be detected. Based on the results of this study, CF, which had excellent removal rates, was the optimum cathode for PEF removal.

Table 1

The apparent rate constants (k_{app}) for PEF degradation using various cathodes during the electro-Fenton process [min^{-1}]

Anode	Cathode	I [mA/cm^2]				
		80	200	300	400	500
Pt	CF(l)	0.176	0.224	0.49	0.67	0.38
	CF(s)	0.135	0.243	0.484	0.574	0.354
	CG	0.064	0.0114	0.04	0.061	0.037
	SS	0.0061	0.0071	0.01	0.04	0.015

All CF cathodes outperformed CG ones. In comparison to carbon-based cathodes, which have enormous surface areas (due to their 3D structure), stainless steel cathodes have inadequate capacity to oxidize PEF because they produce very few radicals of hydroxyl.

3.2. EFFICIENCY OF VARIOUS CATHODES FOR PEF SOLUTION MINERALIZATION

The oxidizing power for the electro-Fenton treatment with various cathodes was estimated through mineralization tests. Applying currents of 80–500 mA/cm^2, experiments were carried out under similar conditions. Figure 3 displays the outcomes in terms of the efficiency of COD removal for three cathodes. The efficiency of COD reduction has a similar pattern to oxidation experiments.

For a CF cathode and an optimal current of 400 mA/cm^2, the maximum COD elimination of 91.1% was accomplished. There is no improvement in mineralization efficiency for currents beyond 400 mA/cm^2 since the COD elimination curves produced at 500 mA/cm^2 and 400 mA/cm^2 are almost exact replicas of one another.

CG and SS cathodes produced decreased mineralization efficiency of PEF solution about the percentage elimination of COD (Table 2). At 400 mA/cm^2, the greatest COD abatement values for CF, CG and SS cathodes, were 90.1%, 75% and 66.1%, respectively.

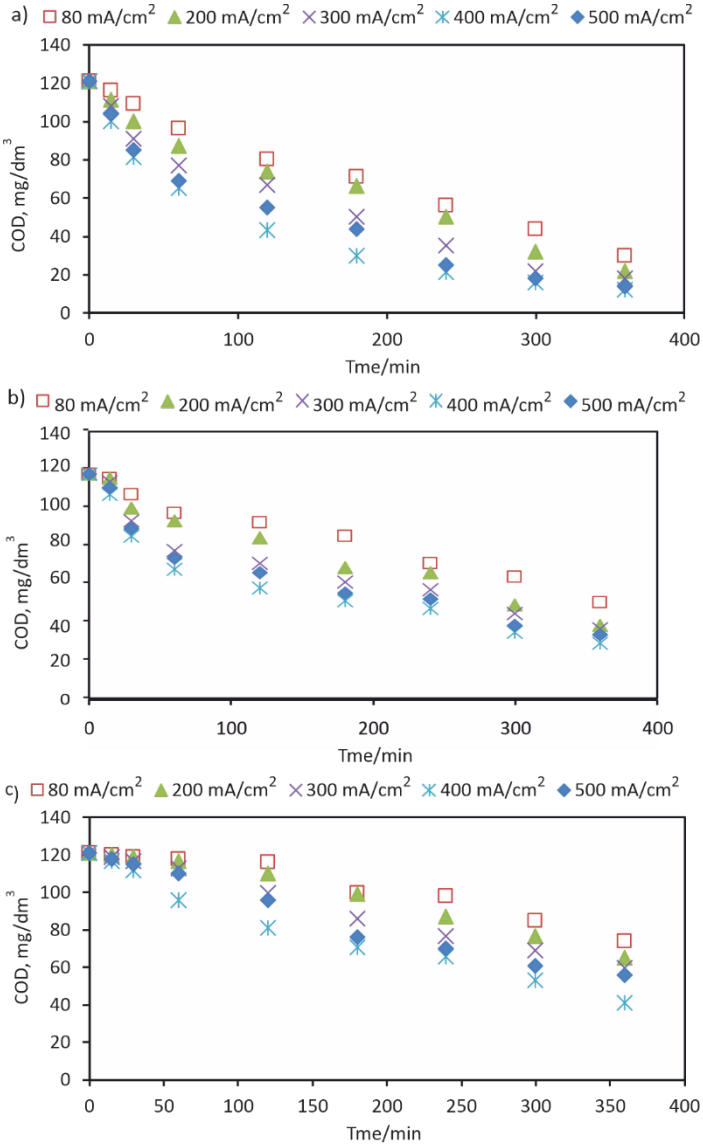


Fig. 3. Time dependences of COD during the mineralization of PEF depending on the current density at various cathodes: a) CF(l)/Pt, b) CG/Pt, c) SS/Pt;
[PEF] = 0.149 mM, [Fe^{2+}] = 0.2 mM, [Na_2SO_4] = 50 mM, V = 200 cm^3, pH = 3

The acceleration of the previously mentioned waste reactions (Eqs. (13) and (14)) prevents the increase in H_2O_2 generation at currents greater than 400 mA/cm^2. As the stainless steel cathodes reduced the ability to create H_2O_2, the level of mineralization was noticeably lower than that obtained with carbonaceous cathodes. It is important to

note that all CF cathodes significantly outperformed CG and stainless steel cathodes in terms of electro-Fenton process efficiency.

Table 2

The COD removal degree [%] after 6 h for various current densities during the electro-Fenton process with various cathodes

Anode	Cathode	I [mA/cm^2]				
		80	200	300	400	500
Pt	CF(l)	75	81.8	85	90.1	88
	CG	57	66.9	68.6	75	71.1
	SS	38.8	46.3	50.4	66.1	53.7

[PEF] = 0.149 mM, [Fe^{2+}] = 0.2 mM, [Na_2SO_4] = 50 mM, V = 200 cm^3, pH = 3.

The lowest COD reduction was achieved with the stainless steel cathode. Due to its tiny surface area and low H_2O_2 generation ability, it does not provide sufficient mineralization degrees. Using the following equation and the values of COD determined, the instantaneous current efficiency (*ICE*) for oxidizing the contaminant pefloxacin was calculated:

$$\mathrm{ICE} = \frac{\left(\mathrm{COD}_0 - \mathrm{COD}_t\right) FV}{8It} \tag{16}$$

where COD_0 and COD_t stand for COD, mg/dm^3, at the beginning and at time t, s, respectively, I is the current, A, F the Faraday constant (96 487 C/mol), V the volume of the solution, dm^3.

Figure 4 shows the ICE values for all cathodes applied. The findings shown in Fig. 4 were derived from the corresponding mineralization data of Fig. 3. At low current densities, the ICE values are rather high, while at higher current densities they decreased over time. The decrease in organic matter concentration resulted in a slower rate of reaction with hydroxyl radicals as electrolysis progresses, which in turn slows the rate of COD elimination.

On the one hand, decreasing ICE values for high current densities may account for the loss of energy from side processes including H_2O_2 breakdown on electrodes and oxygen and hydrogen advancement processes that occur at the anode (Eg. (14)) and cathode

$$H_2O_2 \rightarrow HO_2^{\bullet} + H^+ + e^- \tag{17}$$

These results indicate that CF electrodes are better than the remaining ones (Table 3). Stainless steel looks to be the least efficient cathode material with extremely low ICE

values at all applied current densities, due to its poor H_2O_2 generating ability and thus decreasing hydroxyl radicals of production. And in this instance, the mineralization primarily takes place at, Pt anode's surface, which has a low oxidation power.

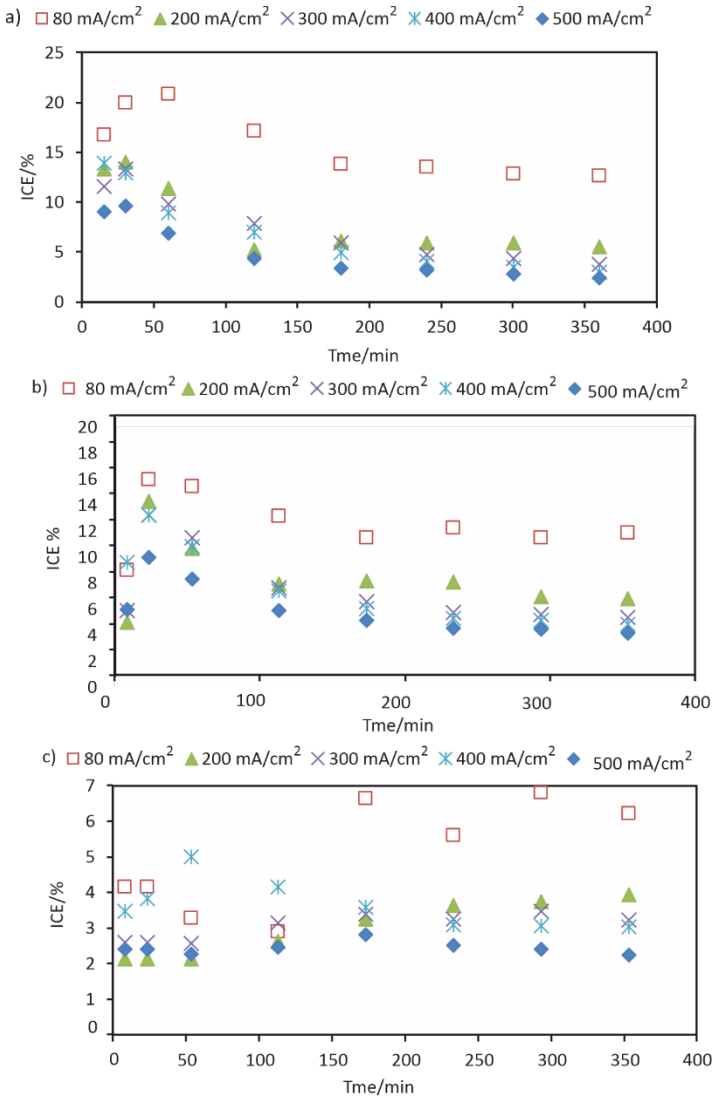


Fig. 4. Time dependences of ICE values at various cathodes: a) CF(l)/Pt, b)CG/Pt, c) SS/Pt; [PEF] = 0.149 mM, [Fe^{2+}] = 0.2 mM, [Na_2SO_4] = 50 mM, V = 200 cm^3, pH = 3

The CF leading the greatest ICE value for short electrolysis intervals is undoubtedly the highest of cathode efficiency for mineralizing (in terms of COD elimination) of PEF

solution. In the longer times of electrolysis, ICE declines, but these values always remain higher compared to the values of the other types of cathodes under investigation.

Table 3

Instantaneous current density efficiencies (ICE) [%] obtained during electro-Fenton process with various cathodes

Anode	Cathode	I [mA/cm^2]	Time [h]			
			0.5	2	4	6
Pt	CF(l)	80	20	17.2	13.6	12.7
		200	14.1	5.25	5.95	5.53
		300	13.4	7.93	4.8	3.83
		400	13	7	4.1	3.04
		500	9.7	4.42	3.2	2.48
	CG	80	18	10.9	10	9.6
		200	12	5.7	5.86	4.5
		300	11	5.36	3.5	3.1
		400	11	5.11	3	2.54
		500	7.7	3.6	2.24	1.9
	SS	80	3.35	2.1	4.8	6.6
		200	1.34	1.84	2.85	3.13
		300	1.79	2.35	2.46	2.42
		400	3.02	3.35	2.3	2.23
		500	1.61	1.68	1.71	1.45

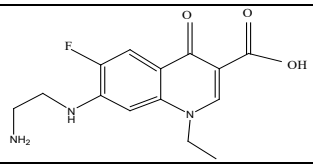
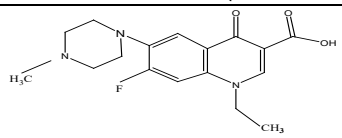
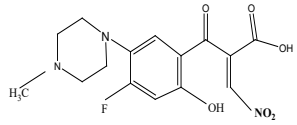
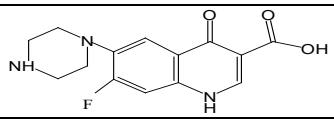
[PEF] = 0.149 mM, [Fe^{2+}] = 0.2 mM, [Na_2SO_4] = 50 mM, V = 200 cm^3, pH = 3.

As samples underwent electrolysis for the first 10 min. HPLC tests revealed that PEF gradually vanished and that other aromatic intermediates formed in its place. HPLC, LC-MS/MS, and direct MS/MS analyses were used to identify intermediates (four intermediates) (Table 4).

Before complete mineralization, carboxylic acids of low molecular weights are often described as organic final products. The last stage of mineralization is when they are oxidized to CO_2 and H_2O. When the original pollutant molecule contains heteroatoms, the mineralization of organics causes the creation of inorganic ions. Higher levels of oxidation result in the conversion of these heteroatoms to their inorganic ions. This was by the release of NH_4^+, NO_3^-, and F^- in the solution that was seen throughout the mineralization treatment (Fig. 5). The majority of the nitrogen atom in PEF was converted to NH_4^+ (0.334 mM). NH_4^+ and NO^-_3 together make up 0.413 mM or 89.6% of the original nitrogen quantity. Almost 0.1440 mM rather than 0.149 mM of fluoride was released. These results provide more proof that PEF was mineralized.

Table 4

Intermediates detected using HPLC and LC-MS/MS
in early stages of PEF degradation by electro-Fenton treatment

Intermediate	Chemical formula	*tr* [min]	*m/z*
A[1]		7.01	322
B[2]		–	319
C[2]		–	353
D[2]		–	291

Data for intermediate A obtained by HPLC and compared to genuine samples' retention times, those for B, C, D obtained by MS/MS are consistent with those in [20]. Figures representing HPLC and MS/MS data have not been published due to their poor quality.

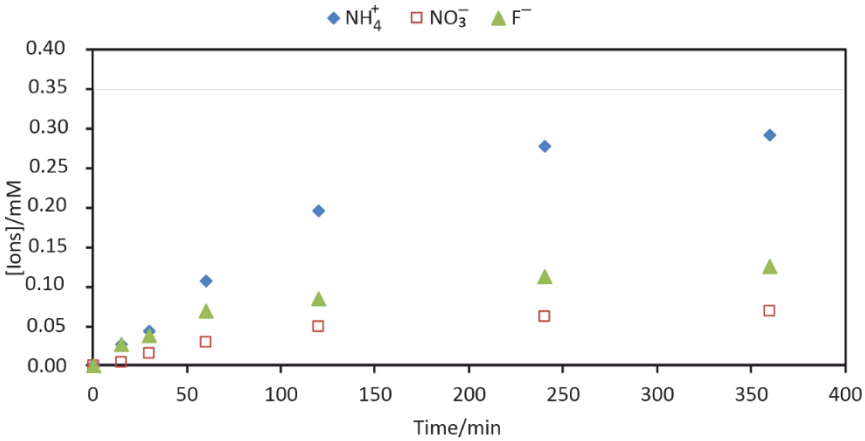


Fig. 5. The release of inorganic ions over time during electro-Fenton degradation of PEF by using CF/Pt; [PEF] = 0.149 mM, $[Fe^{2+}]$ = 0.2 mM, I = 400 mA/cm^2, $[Na_2SO_4]$ = 50 mM, V = 200 cm^3, pH = 3

3.3. BIODEGRADABILITY STUDY

Medications must undergo a lengthy electrolysis period which has a large energy consumption. Great interest has been paid to the concept of combined electro-Fenton treatment, which serves as a pretreatment step to degrade the undesired component, with a post-biological treatment, which may remove compounds in an extra price-effective manner [21–24]. Through a CF cathode and a platinum anode, aqueous solutions contaminated with PEF were electro-Fenton pretreated. Therefore, to monitor the progress of the PEF biodegradability, measurements of COD and BOD_5 were made. If the BOD_5/COD ratio is higher than 0.33, then the solution is considered easily biodegradable [25].

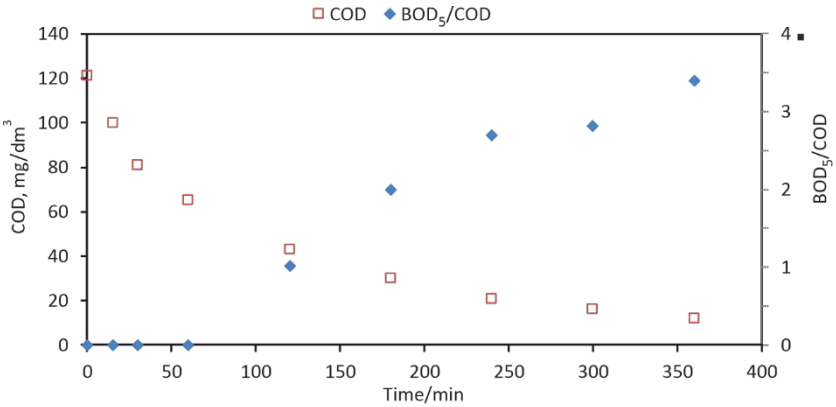


Fig. 6. COD and (BOD_5/COD ratio) during electro-Fenton degradation of PEF by using CF/Pt; [PEF] = 0.149 mM, $[Fe^{2+}]$ = 0.2 mM, I = 400 mA/cm^2, $[Na_2SO_4]$ = 50 mM, V = 200 cm^3, at pH = 3

The initial BOD_5/COD ratio was 1.02 (Fig. 6). This figure supports the molecule's limited biodegradability and shows the requirement for pre-treatment before biological treatment. This ratio reaches values of 1.02 to 2, 2.7, 2.81, and 3.4 after 2, 3, 4, 5 and 6 h of electrolysis, respectively. The by-products of electrolysis continue to react with $OH^{\bullet}$ radicals effectively forming short carbon chains that are less poisonous and more easily biodegradable.

4. CONCLUSIONS

The effectiveness of the three cathodes in the electro-Fenton process was evaluated during the oxidative breakdown of PEF and the mineralization in the solution. The efficiency is measured by the ability to generate H_2O_2, which regulates the rate of $OH^{\bullet}$ production in the solution. It turned out that CF electrodes yielded the best results. Stainless steel electrodes with a limited area, lower H_2O_2 generation, and lower concentration

for $OH^{\bullet}$ radicals contribute to poor oxidation/mineralization outcomes for the removal of PEF. The mineralization of PEF is discovered to be accomplished by numerous $OH^{\bullet}$ attacks with some intermediate products generated throughout the electro-Fenton process. At the end of mineralization, ions, carbon dioxide, and water are released. Finally, the potential was confirmed by combining biological therapy with electro-Fenton pretreatment to enhance the efficiency of the combined process.

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