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Application of photoelectro-fenton process modified with porous cathode electrode in removing resistant organic compounds from aquatic solutions: modeling, toxicity and kinetics

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Abstract−The presence of antibiotics in the environment as persistent micropollutants, due to their widespread consumption, has increased the concerns about the harmful effects of these compounds on human and animal health. Advanced oxidation processes are one of the most effective methods to remove these types of organic pollutants. In this study, amoxicillin (AMX) removal in a modified photoelectro-Fenton (PEF) reactor in which porous stainless steel was used as a cathode electrode, and the ability of air injection into its center to produce H_2O_2 was investigated. A graphite anode electrode equipped with iron rings was used to increase the electrochemical reaction surface and produce iron ions. The effect of current density, time, and electrolyte concentration on AMX removal efficiency was evaluated by Box-Behnken design method. Subsequently, the effect of AMX concentration variable and pH on removal efficiency was investigated. Finally, the chemical oxygen demand (COD) removal efficiency, toxicity, and effluent activity from the PEF reactor were investigated. The results showed that the modified photoelectro-Fenton process could have efficiency of 99% to remove AMX, in 20 min using current density of 36 mA/cm^2 and 16 mM/L electrolyte concentration. Reducing pH and AMX concentration increased the removal efficiency. The PEF process can completely remove the COD in 58 min. Also, toxicity studies indicated an effective reduction in the effluent. This modified reactor improves the efficiency of the PEF process, which, in addition to the 99% removal of AMX, provides a proper function for COD removal, reducing the toxicity properties of the effluent.

Keywords: Box Behnken Design, Photoelectro-Fenton Process, Modeling, Porous Electrode, Toxicity

INTRODUCTION

Since the Second World War, consuming antibiotics to prevent contagious diseases has dramatically increased [1]. The presence of antibiotics in the aquatic environment, in addition to causing environmental pollutants due to bioaccumulation, promotes the development of antibiotic resistant bacteria. Other characteristics of antibiotics such as high COD, poor bio-degradation and high toxicity have raised concerns about the presence of this pollutant remaining in the environment. Amoxicillin (AMX) is a semi-synthetic antibiotic that has a β-lactam ring and can enter the environment through pharmaceutical industries wastewater, hospitals, as well as the amount of AMX remaining in human swages. Only 10-20% of the AMX consumed in the body is absorbed and the rest is excreted [2-5]. Biological methods of wastewater treatment are not suitable for treating wastewater containing these materials due to their susceptibility to toxic substances and emergent organic contaminants (ECs) [6,7].

Recently, advanced oxidation processes (AOPs) have been widely used as a suitable and effective way to degrade toxic and biodegrad-

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able pollutants [8,9]. AOP has been mostly used as pretreatment for the degradation of resistant organic compounds and their conversion to biodegradable and non-toxic products [10,11]. Among the AOPs, Fenton-based processes, due to high efficiency, ease of use and low cost, are among the most widely used [5,12]. The Fenton process is one of the AOPs that can efficiently degrade persistent aromatic compounds through producing high-power free radicals. The Fenton process is performed by the reaction between bivalent iron and hydrogen peroxide according to Eqs. (1) and (2) [13].

$$\mathrm{Fe(II)+H_2O_2 \rightarrow Fe(III)+OH^- + {}^{\circ}OH} \qquad (1)$$

$$\mathrm{Fe(II)+{}^{\circ}OH \rightarrow Fe(III)+OH^-} \qquad (2)$$

Due to the high potential (2.8 V) of hydroxyl radicals resulting from the Fenton reaction, this reaction is used to degrade organic compounds resistant to biological degradation [14]. The efficiency of this process depends on variables such as temperature, pH, hydrogen peroxide concentration, and bivalent iron [1]. Various studies have been carried out on the removal of organic compounds resistant to biological degradation using the Fenton process. For example, Ben et al. examined the efficacy of removing six antibiotics using the Fenton process, and observed that effective removal of antibiotics in optimal conditions $[H_2O_2]/[Fe(II)]=1.5/1$ was achieved [15]. It was also observed in another study on AMX, ampicillin, and cloxacillin antibiotics that the Fenton process was able to completely degrade these antibiotics in molar ratio $COD/H_2O_2/Fe(II)$ 1/3/0.30 and pH 3 [16]. In another study, the photo-Fenton oxidation process was used to degrade the paracetamol (PCT), bezafibrate (BZF), and AMX, and it was observed that the photo-Fenton process could effectively remove these three drugs in the effluent from the reactor in pH 3 [17]. Arslan-Alaton and Dogruel conducted a study on the treatment of sewage containing AMX and potassium clavulanate using the AOP process. The maximum amount of antibiotic in the sewage was 400 mg/l with COD of 1,395 mg/l, and the considered process was AOP, including ozonation, H_2O_2/UV, Fenton and photo-Fenton. To investigate the process efficiency, COD and TOC removal experiments were used and it was observed that the maximum removal rate of COD was achieved by the processes of ozonation and photo-Fenton in 60 min [18]. The main objective of the present work was to investigate the removal efficiency of AMX from aquatic solutions using photoelectro-Fenton process. The effective variables, such as electrolyte concentration, current density, retention time, antibiotic concentration, and pH, were examined and optimized. The second objective was to determine the COD removal efficiency. Finally, the amount of toxicity of the effluent from the designed reactor was also evaluated using *Staphylococcus aureus*.

In the present study, a new photoelectro-Fenton reactor will be used based on a porous stainless steel cathode electrode for producing H_2O_2 and a graphite anode electrode containing iron rings to produce iron ion, and irradiation was simultaneously done by UVC lamp. Unlike existing studies, the reactor will not require the addition of H_2O_2 and iron ions, and these compounds were produced by the photoelectro-oxidation process and ultimately produced the final radical hydroxyl product resulting in the degradation of organic pollutants.

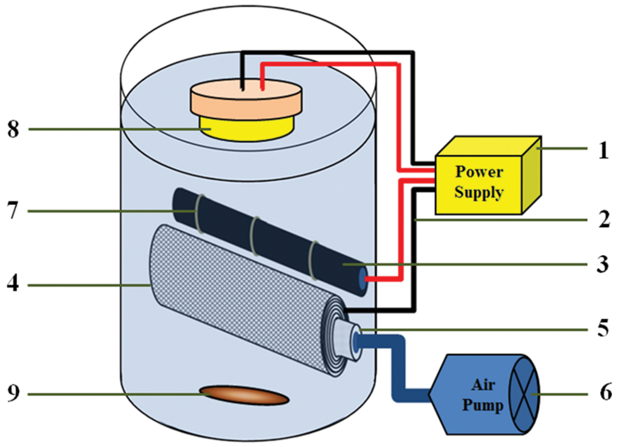

Fig. 1. Schematic of the batch reactor used in this study.
1. Power supply
2. Connecting cable
3. Graphite electrode (Anode)
4. Stainless steel electrode (Cathode)
5. Air inlet tube to the center of cathode electrode
6. Air pump
7. Iron rings
8. UV lamp
9. Magnet mixer

MATERIALS AND METHODS

1. The Reactor

The reactor used in this study was a batch reactor with 500 ml volume. Located in this reactor was a 5-watt 45-volt UVC lamp with a wavelength of 254 nm, 10 cm length, a graphite rod electrode with a length of 15 cm and an 8 cm diameter as an anode electrode accompanied with a porous stainless steel cathode electrode, inside of which a porous pipe was placed for air injection. The reactor influent was controlled by an electricity current power supply, DAZHENGPS-305D. Mixing was done by magnet with a constant rate of 150 rpm. A diffuser was used to inject the air into the porous stainless steel electrode. A schematic of the reactor is shown in Fig. 1.

2. Chemicals and Reagents

AMX from Sigma Aldrich (St. Louis, MO, USA) was used with a purity of 97% for constructing synthetic wastewater. All of HPLC solvents were purchased from Sigma Aldrich. The NaCl from Merck (Germany) was used as an electrolyte. The solution pH was adjusted using HCl (1 N) and NaOH (0.1 M). The toxicity was evaluated by the *Staphylococcus aureus* PTCC1112 bacteria, prepared from the collection center of industrial microorganisms in Iran.

3. HPLC-UV Analysis

An HPLC (YL9100-Technolab system©, South Korea) equipped with a pump (YL9110Quaternary model) and a detector (YL9160PDA) was used to measure the AMX concentration. The flow rate injected into the HPLC was 1 ml/min, and AMX amount was determined at wavelength of 235 nm. The methanol and distilled water with a ratio of 75 to 25 were used as the mobile phase. The column used in the HPLC was Brisa LC2 C18 Analytical Column, 4.6× 250 mm, 5 µm (© TeknokromaAnlítica, SA).

4. Design of Experiments

In the first stage of this study, the number of experiments and optimal conditions were determined for three variables, including retention time, electrolyte concentration and current density by

Table 1. Variables and levels intended to Box-Behnken design

Variable	Level		
	Lower	Central	Upper
Electrolyte concentration (mM/L)	10	15	20
Current (mA/cm^2)	10	30	50
Retention time (min)	10	20	30

Box-Behnken design using Design Expert software (version 10). The range for each of the variables was determined at three levels and its average was reported (Table 1). The pH and AMX concentration variables were fixed at this stage and were 7 and 50 mg/l, respectively. To analyze the experimental results, the response surface regression was used and optimal conditions for AMX removal by the polynomial second-order model were presented based on Eq. (3) [19].

$$Y=\beta_0+\Sigma_{i=1}^{k}\beta_i X_i+\Sigma_{i=1}^{k}\beta_{ii}X_i^2+\Sigma_{i=1}^{k}\Sigma_{j=1}^{k}\beta_{ii}X_iX_j+\varepsilon \tag{3}$$

where Y is the AMX removal efficiency (%), X_i and X_j are the coded variables, β_0 is the constant coefficient of the model; β_i, β_{ii}, and β_{ij}, respectively, are linear, quadratic, and interaction coefficients.

In the second stage, the effect of AMX concentration and pH was evaluated on AMX removal efficiency at optimal conditions for three variables, including current density, electrolyte concentration, and reaction time. In the first step, the experiments were conducted while concentration of AMX was kept constant (50 mg/L) and pH were regulated in the range of 4, 8, and 12 (in triplicates). In the next stage, at pH of 7 and 4, AMX concentration was adjusted in the ranges of 10, 30, 70, and 100 mg/L. Considering the above-mentioned conditions, the efficiency removal of the AMX was determined.

5. COD Measurement

For COD measurement, Closed Reflux, Colorimetric method was used according to standard method number 5220D [20].

The COD removal efficiency was evaluated under optimal conditions for electrolyte concentration and current density at neutral pH until complete removal of the remaining organic compounds and was compared with AMX removal efficiency. The COD removal percentage was calculated by means of Eq. (4).

$$n=[(COD_0-COD)/COD_0]\times 100\% \tag{4}$$

where n is removal percentage of COD, COD_0 and COD are the chemical oxygen demand, before and after the reaction in mg/l, respectively.

6. Evaluating Antimicrobial and Toxicity Properties

The inhibition zone method [21] and *Staphylococcus aureus* PTCC1112 [22] were used to evaluate the toxicity of the final effluent.

RESULTS AND DISCUSSION

1. Modified Photoelectro-Fenton Process

In the current work, a modified photoelectro-Fenton reactor was utilized to help AMX removal. The reactor increased the removal efficiency of AMX, and also reduced the reaction time without adding H_2O_2 and iron ions. In this regard, the Fenton process has the potential to produce hydroxyl radicals through reaction of bivalent iron ions and hydrogen peroxide. In other studies, H_2O_2 and iron ions were added to the reaction environment as Fenton reaction agents; however, in the reactor used here, these agents were produced by the electrodes in the reaction environment. H_2O_2 can be produced by reducing two electrons from oxygen (either pure or by air injection into the solution) at the cathode surface under acidic or normal conditions according to Eq. (5) (E^o=0.68 V/SHE) [23].

$$O_{2(g)}+2H^++2e^-\rightarrow H_2O_2 \tag{5}$$

This equation is easier than reducing four electrons from water oxygen with E^o=1.23 V/SHE. Electrochemical generation of H_2O_2 is recognized as electroperoxidation [24]. The advanced oxidation process conducted via the oxidants produced in the electrochemical process is termed anodic oxidation with electrogenerated H_2O_2 [25]. To keep the effectiveness of H_2O_2 generated via the electrochemical procedure, oxygen, cathode, and water contact should be kept at its maximum level. Accordingly, applying porous cathodes having a high level of surface is favored to generate high quantity of H_2O_2 [26]. In this study, porous stainless steel was applied as a cathode electrode. Porosity enhances the contact surface between the electrode and the water. The aeration procedure was also applied to raise the oxygen contact with water and the electrode by injecting air into the cathode electrode center. By applying porous electrode and air injection into the electrode center the oxygen, cathode and water contact will be improved at their maximum values, which leads to increased H_2O_2 generation.

In electrochemical processes which are along with H_2O_2 production, it is desirable that the process is performed in the presence of Fe^{2+} ions as the Fenton reaction agents. The concurrent application of a porous cathode intended for H_2O_2 generation (based on Eq. (5)) and an iron anode, which causes the release of Fe^{2+} (based on Eq. (6)), makes the contaminants oxidized in exposure of OH^o. Moreover, producing iron hydroxide as a coagulant removes contaminants [27].

$$Fe\rightarrow Fe^{2+}+2e^- \tag{6}$$

In the modified reactor, a graphite electrode comprising iron rings was utilized as an anode electrode. The high surface of the anode electrode raises the current density and, hence, increases the effective oxidation of organic chemicals. By using iron electrodes, the quantity of sludge production increases sharply; therefore, a graphite electrode was applied to keep the electrode surface and reduce the amount of sludge generated by iron oxidation. On the other hand, to generate iron ions, the iron compound should be available in the anode electrode; hence, iron rings were utilized to generate and release iron ions on the graphite electrode.

If the Fenton electrochemical process is carried out in the presence of UV light or sunlight, the degradation of organic chemicals will be worsened by the photo-reduction of Fe(III) hydroxyl complexes, such as photoactivation of $FeOH^{2+}$ at pH levels near to 3 based on Eq. (7) [28].

$$FeOH^{2+}+hv\rightarrow Fe^{2+}+{}^oOH \tag{7}$$

Applying UV-C in the presence of H_2O_2 can produce a higher value of OH^o through the hemolytic cleavage of peroxide based on Eq.

(8) [29]. High removal effectiveness of organic chemicals in the presence of UV radiation is attributed to the generation of free radicals through the effect of UV radiation on the electro-oxidation process products [30], which can act as an indirect oxidizing factor and degrades organic chemicals [31]. Eqs. (8) to (10) indicate the majority of UV-affected products [32].

$$H_2O_2 \xrightarrow{hv} 2^{o}OH \tag{8}$$

$$H_2O_2 + O_3 \xrightarrow{hv} 2^{o}OH + \frac{3}{2}O_2 \tag{9}$$

$$ClO^- \xrightarrow{hv} (Cl)^o + (O^-)^o \tag{10}$$

In this work, UVC lamp was used to enhance the efficiency of hydroxyl radical production in the modified photoelectro-Fenton reactor.

2. Effect of Current Density, Time, and Electrolyte Concentration

At first, the effect of three variables, including current density, electrolyte concentration, and time on the removal efficiency of AMX in the photoelectro-Fenton reactor was investigated. Table 2 presents the AMX removal efficiency for the three variables based on Box-Behnken design using Design Expert software. Figs. 2-4 show the removal efficiency based on current density and time (Fig. 2), current density and electrolyte concentration (Fig. 3), and time and electrolyte concentration (Fig. 4).

According to the results, at the optimum current density (36 mA/cm^2) the maximum AMX removal efficiency was obtained. The role of the current density in the oxidation process of organic compounds is to determine the oxidizing factors in the process flow. The direct oxidation agent (M (OH^o) in Eq. (1)) and the active chlo-

Table 2. Removal efficiency based on Box Behnken design for three variables, including current density, time, and electrolyte concentration

Run number	Electrolyte concentration (mM/L)	Current density (mA/cm^2)	Time (min)	Removal (%)
1	20	50	20	98
2	10	30	30	85
3	15	30	20	95
4	15	10	30	77
5	15	30	20	98
6	20	10	20	72
7	10	30	10	68
8	15	30	20	97
9	15	50	30	99
10	10	50	20	81
11	10	10	20	58
12	15	10	10	47
13	15	30	20	96
14	15	30	20	94.5
15	20	30	10	74
16	20	30	30	99
17	15	50	10	87

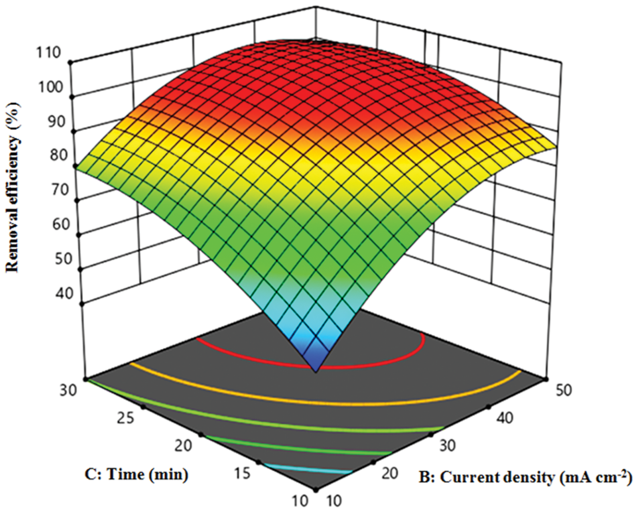

Fig. 2. Removal efficiency based on current density and time.

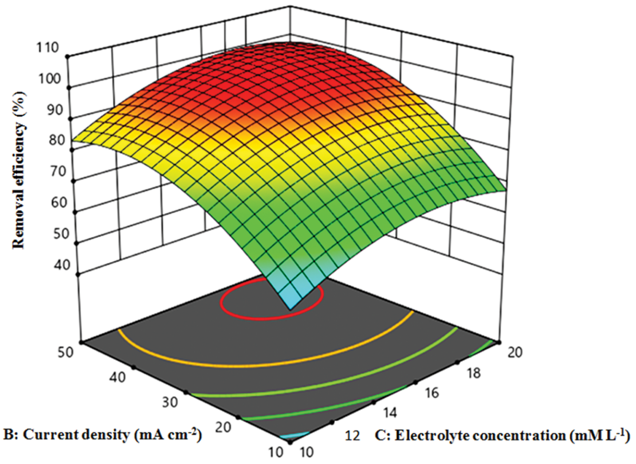

Fig. 3. Removal efficiency based on current density and electrolyte concentration.

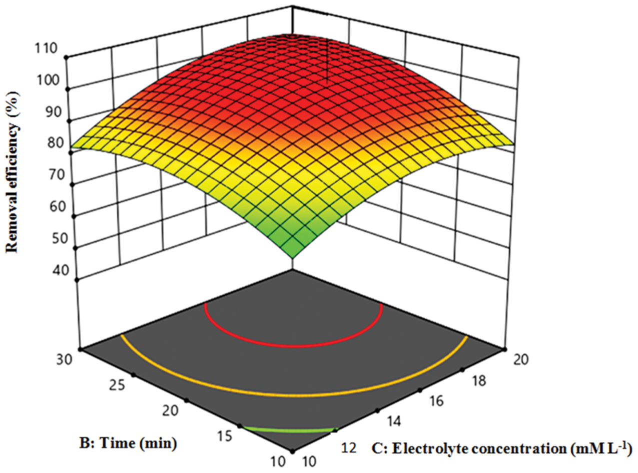

Fig. 4. Removal efficiency based on time and electrolyte concentration.

rine species that are indirectly oxidation agents are determined by the current density according to Eqs. (11) and (12) [33]. By increasing the current density, the production of direct and indirect oxidants increases and so the removal efficiency of the organic compound would be increased [34]. HCLO can react with Fe^{2+} in a Fenton-type reaction and produce large amounts of radical hydroxyl [35].

$$2Cl^{-}\rightarrow Cl_2+2e^{-} \tag{11}$$

$$Cl_2+H_2O\leftrightarrow HCLO+Cl^{-}+H^{+} \tag{12}$$

Electrolyte concentration is another factor which affects the electrolysis process. Electrochemical processes are not carried out in the absence of electrolyte. In previous studies, electrolytes such as NaCl and Na_2SO_4 were frequently used [8]. Using NaCl is more preferred, since its mineralization process of organic compounds is faster than Na_2SO_4. Moreover, in the presence of NaCl, oxidizing active chlorine species are produced, which are indirect oxidation factors and increase the oxidation rate [36]. Increasing the hydroxyl radicals degradation in the presence of sulfate produced from Na_2SO_4 is another reason to use NaCl instead of Na_2SO_4 [37]. Based on the results provided in Table 4, the optimum amount of electrolyte to achieve the maximum AMX removal efficiency was 16 mM/L. Table 3 indicates ANOVA test for statistical analysis of the data extracted from the experiments. In Eq. (13) (uncoded equation), the removal efficiency and regression coefficients are presented.

$$\begin{aligned}\text{Removal (\%)}=&-84.19+9.16A+2.745B+3.995C-0.022BC\\&-0.297A^2-0.0285B^2-0.0717C^2\end{aligned} \tag{13}$$

Based on Eq. (13), coefficients of electrolyte concentration (A), current density (B), and time (C) are positive, indicating a direct relationship between these variables and AMX removal efficiency. Based on ANOVA results, among the three investigated variables, the electrolyte concentration variable has the greatest effect on AMX removal efficiency due to the production of active chlorine species involved in indirect anodic oxidation of organic compounds [38]. According to Eq. (11) in anode electrode, chloride ions are produced by direct oxidation, and then, according to Eq. (12), they produce hydrochloric acid (HClO) [39]. Furthermore, the irradiation of solutions containing ClO^{-} can lead to the production of radicals Cl^{o} and OH^{o} in accordance with Eqs. (14) and (15) [40].

$$ClO^{-}+hv\rightarrow O^{o-}+Cl^{o} \tag{14}$$

$$O^{o-}+H_2O\rightarrow OH^{-}+{}^{o}OH \tag{15}$$

H_2O_2 is also produced by cathode reduction process, which has a direct correlation with electrolyte concentration [33].

The expected removal efficiency of the model and actual AMX, as well as the optimal predicted conditions (Table 4, Fig. 5) shows the actual and predicted AMX removal chart.

3. The Effect of Antibiotic Concentration

The removal efficiency in the concentration range of 10 to 100 mg/L of AMX was investigated to evaluate the effect of antibiotic concentration, as shown in Fig. 6.

Although increasing the concentration of contaminants increases the amount of removal per unit of time, the removal efficiency decreases; this is due to the increase in organic loading per unit area

Table 3. ANOVA for response surface reduced quadratic model

Source	Sum of squares	df	Mean square	F value	p-Value
Quadratic model	3954.43	9	439.38	69.19	<0.0001
A-Electrolyte conc	325.13	1	325.13	51.20	0.0002
B-Current density	1540.13	1	1540.13	242.54	<0.0001
C-Time	882.00	1	882.00	138.90	<0.0001
AB	2.25	1	2.25	0.3543	0.5704
AC	16.00	1	16.00	2.52	0.1565
BC	81.00	1	81.00	12.76	0.0091
A^2	232.13	1	232.13	36.56	0.0005
B^2	549.60	1	549.60	86.55	<0.0001
C^2	216.76	1	216.76	34.14	0.0006
Residual	44.45	7	6.35		
Lack of fit	36.25	3	12.08	5.89	0.0597
Pure error	8.20	4	2.05		
Cor total	3998.88	16			
		R-squared	0.9848		
		Adj R-squared	0.9695		

Table 4. Optimal conditions for three variables, including current density, time, and electrolyte concentration

Parameter	Current density (mA/cm^2)	Time (min)	Electrolyte concentration (mM/L)	Removal (%)	
				Predicted	Experimental
Optimum condition	36	20	16	100	99

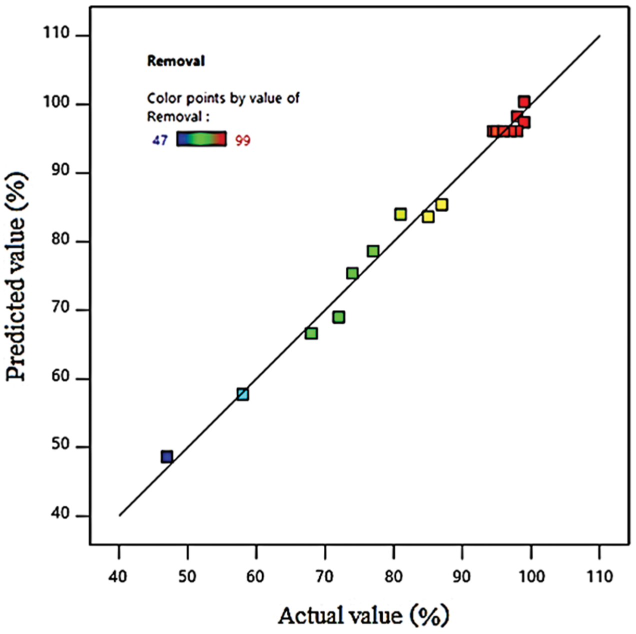

Fig. 5. Actual and predicted AMX removal chart.

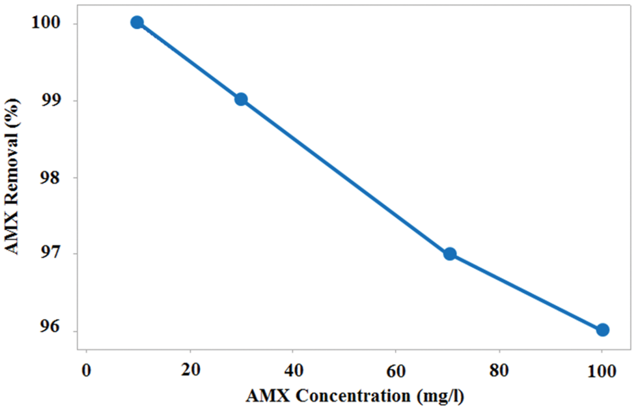

Fig. 6. Removal efficiency at various concentrations of AMX (current density 36 mA/cm^2, time 20 min, electrolyte concentration 16 mM/L, and pH 7).

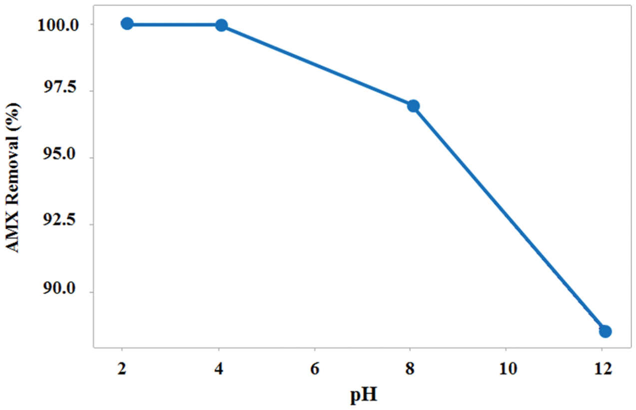

Fig. 7. AMX removal efficiency at different pH (current density 36 mA/cm^2, time 20 min, electrolyte concentration 16 mM/L and AMX concentration 50 mg/l).

of the electrode. This finding is similar to the result of previous studies conducted in the fields of advanced electrooxidation processes [41]. However, due to the wide range of electrode levels in this study and the role of products produced in indirect oxidation, the reduction in efficiency is less than the previous studies carried out by the electrooxidation process [42].

4. pH Effect

pH plays a crucial role in the removal efficiency of organic compounds by electrooxidation processes, since it can affect the amount of active species in indirect oxidation of organic compounds in electro-oxidation processes. AMX removal efficiency under optimal conditions obtained at the previous stages and the concentration of 50 mg/l of AMX in this study was investigated within the pH range of 2 to 12 (Fig. 7). The results showed that increasing pH had a reverse effect on AMX removal efficiency, so that the maximum removal rate was at pH less than 3.

Organic compounds oxidation in acidic conditions is faster due to the higher redox potential of products. Chlorine is one of the products of the electrooxidation process affecting indirect oxidation. At pH 3 and lower, the dominant species of chlorine (E^o= 1.36 V/SHE) is Cl_2; between the neutral pH and 3, the dominant species is HClO (E^o=1.49 V/SHE); and at the pH above 8 is ClO^- (E^o=0.89 V/SHE) [43]. Similar results have been reported in studies on the removal of organic compounds using AO and AO-H_2O_2 processes [44]. Other reasons for reducing the removal efficiency of organic compounds in alkaline pH are the increased degradation of hydroxyl radicals in the presence of carbonate and bicarbonate species at high pH [45]. H_2O_2 alone acts as a potent oxidant, especially in acidic conditions [46], and can reduce the inorganic compounds with sulfur and cyanide moiety as well as organic compounds, such as aldehydes, formic acid, nitrogenous organic compounds, and sulfo-organic compounds [47]. Increasing spontaneous H_2O_2 degradation at pH 5 is another reason for reducing the removal efficiency of organic compounds by increasing pH [48]. In alkaline conditions, oxygen reduces in hydro peroxide ions (HO_2^-), which has a reverse effect on the hydrogen peroxide production efficiency [49]. Fenton reactions can be efficiently performed in acidic conditions with a pH of 2.8-3.0. For high levels of H_2O_2, according to Eqs. (16) and (17), Fe^{3+} can be reduced to Fe^{2+}. Eqs. (16) and (17) are much slower than the Fenton reaction.

$$Fe^{3+}+H_2O_2\rightarrow Fe^{2+}+HO_2^{o}+H^+ \qquad (16)$$

$$Fe^{3+}+HO_2^{o}\rightarrow Fe^{2+}+O_2+H^+ \qquad (17)$$

5. Comparison of COD Removal Efficiency

To investigate the efficiency of the modified PEF reactor in removing organic compounds, the removal efficiency of COD in this reactor was examined and compared with AMX removal efficiency at different times. Therefore, the PEF process continued until complete removal of organic compounds. Fig. 8 shows AMX and COD removal efficiency at different times.

The results showed that although AMX is removed by the PEF process in 20 min, removal of the products resulting from its deg-

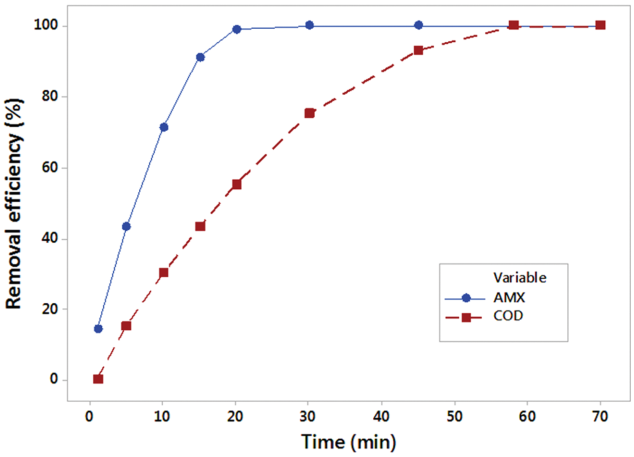

Fig. 8. AMX and COD removal efficiency in PEF reactor at different times (36 mA/cm^2 current density, 16 mM/L electrolyte concentration, 50 mg/l AMX concentration, and pH=7).

radation requires 58 min. Producing hydroxyl radicals by the Fenton process in the presence of UV rays that is effective in degradation of organic compounds as well as producing iron oxide acting as a coagulant in this process have a role in removing AMX and COD. It enables this process to remove organic compounds in shorter time compared to previous studies.

6. Kinetic Studies

Kinetic studies were carried out to determine the hydraulic retention time in different treatment processes [10]. In kinetic studies, the reaction rates indicate the change in reactants concentration per unit time. It is essential to know the reaction rates for designing wastewater treatment units. The kinetic study of AMX removal in PEF process showed that the removal process follows a first-order kinetic with a correlation coefficient >0.95 following the Eqs. (18) (Fig. 9(a)) and (19) (Fig. 9(b)).

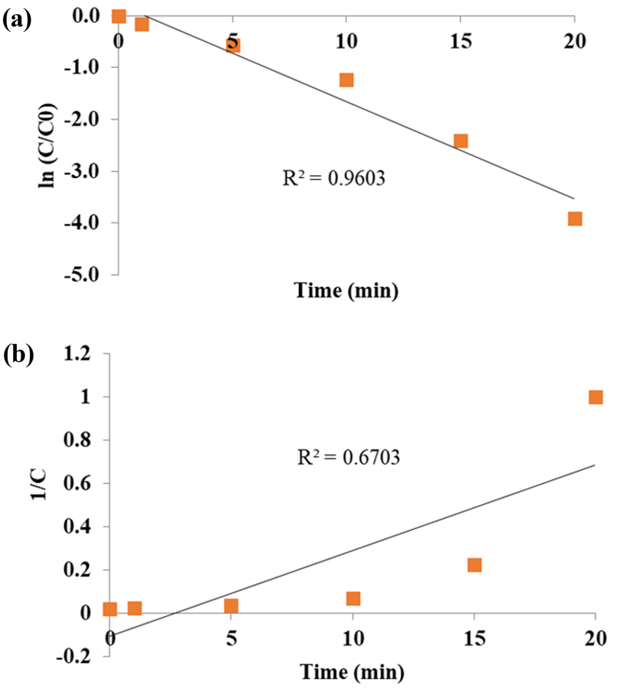

Fig. 9. The chart of (a) first order kinetic (b) second order kinetic.

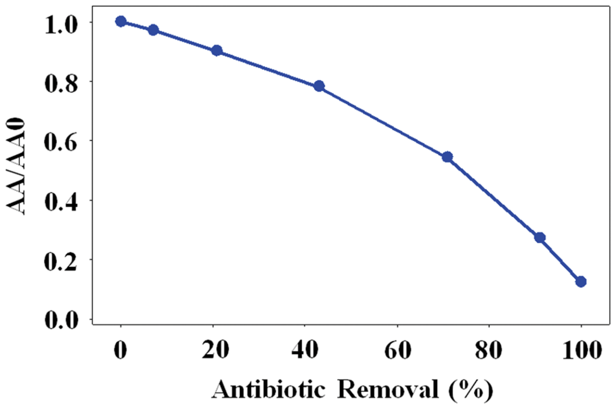

Fig. 10. The toxicity test by *S. aureus* on PEF process effluent (current density 36 mA/cm^2, electrolyte concentration 16 mM/L, AMX concentration, 50 mg/l, and pH=7).

$$C=C_0e^{-kt} \tag{18}$$

$$\frac{1}{C}-\frac{1}{C_0}=kt \tag{19}$$

In this equation, C_0 is AMX concentration before the reaction (mg/l), C is AMX concentration (mg/l) after the reaction, t is the reaction time (min), and k is the reaction rate constant (min^{-1}). Fig. 9 shows the first- and second-order kinetic chart, respectively. The obtained results from kinetic study revealed that there is a direct relationship between the concentration of pollutant and the rate of reaction.

7. Antimicrobial and Toxicity Test Results

The amount of toxicity of the effluent from the PEF reactor was evaluated using *Staphylococcus aureus* (inhibition zone method) [50]. The results of the toxicity test of the final effluent are presented in Fig. 10.

To investigate the toxicity of the effluent from the reactor, the diameter ratio of *S. aureus* bacteria inhibition zone between 0-100% AMX removal to the diameter of the inhibition zone of the bacteria in contact with 50 mg/l solution containing AMX was determined, results of which are presented in Fig. 10. The results of activity investigation showed that by increasing AMX removal percentage, the AA/AA$_0$ ratio decreases and causes a significant reduction in the antibacterial property or final effluent activity.

CONCLUSION

The effect of photoelectro-Fenton process in a new modified reactor with the ability of H_2O_2 and iron ion production in AMX removal was evaluated. By selecting a porous stainless steel cathode electrode and injecting air into the electrode center in the photoelectro-Fenton reactor, the contact surfaces between the electrode, air, and sewage were kept at their maximum level; therefore, H_2O_2 was produced in the solution. Selecting graphite anode electrode with iron rings led to the reduction of sludge production in addition to increasing the electrode surface to improve electron transfer and performing the electrochemical process. The results of this study show that at optimal conditions: the current density 36 mA/cm^2, electrolyte concentration 16 mM/L, time 20 min, and pH 7, the optimal value of AMX removal efficiency was 100%. Investigating the effect of pH on the removal efficiency showed that by decreasing the pH of the environment, the removal efficiency increased, due to the high degradation of chlorine species that cause indirect oxidation of AMX. Evaluating the effect of AMX concentration on AMX removal efficiency showed that increasing the concentration decreases the removal efficiency.

Based on the findings, it can be concluded that the modified PEF reactor, by increasing the contact surface of the porous electrode with air and sewage, can completely degrade AMX in the aquatic environment. The reactor is also able to remove 100% of COD in 58 min. Investigating toxicity showed that the effluent from the reactor had the least toxicity.

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