Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2020.25400

185 (2020) 185–195
May

Investigating the effect of photo-electro oxidation process modified with activated carbon bed as a porous electrode on amoxicillin removal from aqueous solutions

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Received 18 August 2019; Accepted 24 December 2019

ABSTRACT

In this study, the efficiency of photo-oxidation (P) and electro-oxidation (E) processes were examined, combined and separately, in amoxicillin (AMX) removal in a modified reactor in which a granular activated carbon bed was used as an electrode in the E process. Moreover, the effects of time, electrolyte concentration, and current density on AMX removal efficiency were investigated using Design-Expert software and Box–Behnken design to determine optimum conditions for removing the contaminant. Then, the effect of concentration and pH variables on the removal efficiency was investigated. After determining the optimal conditions for all variables, chemical oxygen demand (COD) removal efficiency and finally the toxicity of the effluent from the combined photoelectron oxidation reactor (PE) were also investigated. The results showed that in order to achieve the efficiency of about 98%, the optimum conditions for electrolyte concentration, time, and current density variables were 950 mg/L, 10 min, and 40 mA/cm^2, respectively. Furthermore, the removal efficiency of AMX increased by decreasing pH and contaminant concentration. The analysis of the effluent from the reactor in terms of toxicity showed that the toxicity reduced. Using granular activated carbon as a porous electrode increases the efficiency of the PE process, which, by removal of 98% AMX and 64% COD, provides good performance in reducing the toxicity properties of effluent.

Keywords: Amoxicillin removal; Box–Behnken design; Modeling; Photo electro oxidation; Porous electrode; Toxicity evaluation

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1. Introduction

Water pollution is one of the most important human concerns due to the development of industries, population growth, and expansion of cities. Therefore, many methods have been developed for wastewater treatment. Using electrochemical advanced oxidation processes (EAOPs) has been more paid attention due to their ability to remove contaminants resistant to biological and toxic decomposition [1,2]. Medications are among the emerging pollutants entered the environment through human resources [3]. Regarding the biological effects of medications, increasing their disposal in the environment increases the environmental and human health risks. Concerns about this group of micro-pollutants have increased due to the amount of disposal and the resulting risks [4]. Among medications, antibiotics have been more found in the environment, including rivers, lakes, underground waters, drinking water, coastal waters, urban sewage and treatment plants due to their wide usage in preventing human and animal diseases [5,6]. Many studies have reported the presence of antibiotics in the range of several ng/L to 100 mg/L in surface waters, groundwater, and wastewater treatment plants [7]. Despite the low level of antibiotics in the environment, antibiotics are known as "pseudo persistent" contaminants due to their environmental sustainability and their continuous release [8,9]. Amoxicillin (AMX) is among beta-lactam antibiotics which have a major contribution to medical science and disease prevention since the end of World War II [10]. AMX is one of the most commonly used antibiotics to prevent human and animal diseases worldwide. Eighty percent of consumed AMX is disposed of unchanged through urine and feces [11], and conventional treatment is not able to effectively remove this contaminant from wastewater [5]. Failure to remove AMX in the wastewater treatment process results in the presence of the substance in water and drinking water resources. AMX is an emerging pollutant which its effect on human health is not well defined [12]. The most concern is related to long-term exposure to this pollutant, which can cause chronic effects and resistant genes [13]. Many efforts have been made to develop new treatment processes that can overcome the sustainability of antibiotics against biological treatment [12,14,15]. Removing pollutants using electrochemical processes has many advantages, including low cost, high energy efficiency, easy and safe management through simple equipment, which has led them to be used in removing a wide range of pollutants [16–18]. Electrocoagulation (EC) process is one of the most widely used electro-oxidation (EO) processes in the treatment of wastewater containing resistant organic compounds. In the EC process, the metal oxide is formed using a non-resistive electrode, which is able to remove pollutants from the solution by coagulation and flocculation. Although the EC process is efficient in removing toxic and resistant organic compounds, the production of high volumes of sludge and electrode degradation which increases the cost is one of the main limitations of this process [19,20]. Currently, the electrochemical oxidation (EO) is a process widely used in wastewater treatment by producing free radicals that have the ability to mineralize organic compounds [21–23]. Electrolysis is one of the advanced oxidation processes with the ability to remove organic compounds, which has recently been widely considered [24,25]. The most important advantages of the EO are: (1) No sludge production. (2) Minimum need to add chemical additive compounds. (3) Ability to be used for removing different organic pollutants. (4) Easy management and the need for simple equipment. (5) The possibility of starting and ending the reaction by only disconnecting electrical current [26]. EO processes can decompose and remove organic compounds in two ways: direct oxidation on the anode surface, and indirect oxidation by the products on anode surface [27]. Anodic oxidation is one of EAOPs that has the potential for effective oxidation of organic compounds in aquatic environments. This process is performed by the hydroxyl radicals produced at the surface of the M anode and the water oxidation according to Eq. (1) [28,29]. Surface hydroxyl radicals M $(OH^{\bullet})$ are non-selective high-oxidizing agents that are capable to decompose and completely mineralize organic pollutants [30].

$$M + H_2O \rightarrow M\left({}^{\bullet}OH\right) + H^+ + e^- \tag{1}$$

Using porous electrodes in the role of anode electrode due to increased electrode contact with the solution has led to a significant increase in pollutants removal efficiency in recent studies. Meanwhile, using porous carbon electrodes, such as graphite and carbon felts [31], carbon sponge [32], activated carbon fibers [33] and carbon nanotubes [34] due to the proper current transferability, sustainability, and affordability have been more noticeable. The present study aimed to investigate the effectiveness of electrooxidation processes in a novel reactor with granular activated carbon porous electrode from and photodegradation of AMX antibiotic from aquatic environments in combination and separately. Moreover, the toxicity and bioavailability of the final products were investigated.

2. Materials and methods

2.1. Used reactor

In this study, the photo electro-oxidation (PE) reactor was used to remove AMX. The PE process is an electrode-resistant process in which organic compounds are oxidized by direct oxidation at the electrode surface or indirect oxidation using the resultant oxidants. In this reactor, sludge is not formed due to the use of a sludge-resistant electrode. Moreover, because of the use of the porous electrode, the surface is expanded and the oxidation process is performed more quickly and efficiently. The continuous reactor used in this study consisted of a three-chamber tank, in which the boxes are interconnected through the apertures in two lattices separating walls spaced two centimeters apart. Two chambers (primary and ending chambers) were filled by Jacobi Carbons Lanka (Pvt.) Ltd., Sri Lanka, JacobiCarbon, as a porous electrode. A 5-W 45-V UVC lamp with a wavelength of 254 nm and a length of 10 cm was placed in the space between the chambers (the box in the center between the two lattice walls). The current was controlled by a power supply (DAZHENG PS-305D, China). Due to continuous hydraulic flow, there was no need to use a stirrer. Fig. 1 shows the continuous flow reactor used in this study.

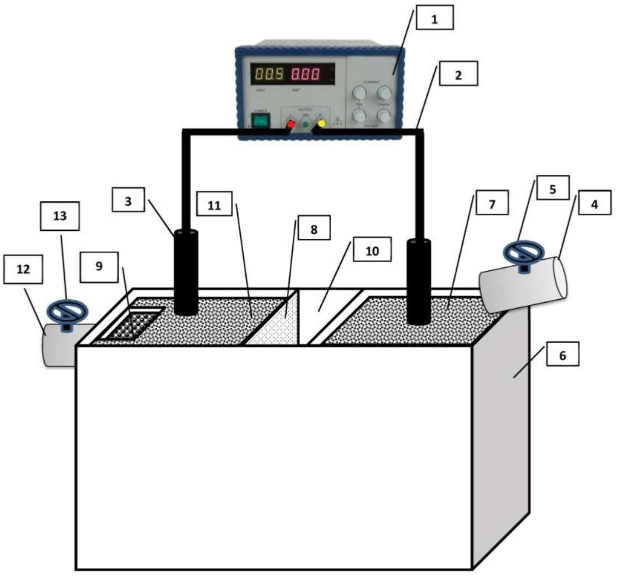

Fig. 1. Schematic of the continuous reactor used in the study (1. Power supply, 2. Cables and transducers of current transfer to the electrode, 3. Graphite electrode, 4. Wastewater inlet, 5. Inlet control valve, 6. Reactor chamber, 7. Granular activated carbon in the first chamber, 8. Lattice wall, 9. Small chamber filled with coarse sand, 10. Central chamber and location of UVC lamp, 11. Granular activated carbon in the third chamber, 12. Wastewater outlet, 13. Outlet control valve).

2.2. Chemicals and reagents

Synthetic wastewater was prepared using 97% purity AMX from Sigma-Aldrich Company (St. Louis, MO, USA). To supply the electrolyte, the NaCl of Merck Germany Company was used. Normal HCl and NaOH were used to adjust the synthetic wastewater pH during the process. The toxicity and bioavailability of the final effluent from the reactors were evaluated by the yeast *Saccharomyces cerevisiae* PTCC5052 and *Staphylococcus aureus* PTCC1112 bacteria, prepared from the collection center of industrial microorganisms in Iran.

2.3. Analytical methods

The concentration of AMX was measured by HPLC (YL9100-Technolab system©, South Korea). The model of the pump and detector used in the HPLC was YL9110 Quaternary and YL9160PDA, respectively. The concentration of AMX was determined at 235 nm and a flow rate of 1 mL/min. The mobile phase used to determine AMX concentration was methanol prepared from Merck Company and Sigma Aldrich HPLC distilled water, injected into the HPLC with a ratio of 75 to 25. The column used in the HPLC to determine AMX concentration in the solution was Brisa LC2 C18 Analytical Column, 4.6 × 250 mm, 5 um (© TeknokromaAnlítica, SA).

2.4. Experiments design

In this study, Box–Behnken design (Design-Expert software, version10) was used to determine the number of experiments and optimal conditions for the three variables, including retention time, electrolyte concentration, and current density. By specifying the range for each variable, three levels were considered, and a total of 17 runs with three repetitions were performed and the mean was reported (Table 1). At this stage, pH was in the neutral range and AMX concentration was fixed and equal to 50 mg/L. The response surface regression was used to analyze the experimental results and the optimal conditions for AMX removal by the polynomial second-order model were presented based on Eq. (2) [35].

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

In this equation, Y is removed AMX efficiency (%), β_0 is the model fixed coefficient, X_i and X_j are the coded variables, β_i, β_{ii}, and β_{ij} are linear, quadratic, and interaction coefficients, respectively. In the second stage, the effect of AMX and pH concentration variables on AMX removal efficiency was evaluated. Therefore, in the obtained optimal conditions for the three variables, including time, current density, and electrolyte concentration, first AMX at four concentrations, including 10, 30, 70, and 100 mg/L with fixed pH and 3 times repetitions were entered to the reactor and the other time, the current with AMX fixed concentration and four pH, including 2, 4, 8, and 12 were entered to the reactor with 3 times repetition.

2.5. Chemical oxygen demand (COD) measurement

The Closed Reflux Colorimetric method was used to measure the chemical oxygen demand (COD) value in a PE combined reactor according to the 5220D standard method [36]. The COD removal efficiency at optimal conditions for electrolyte concentration and current density at neutral pH and the time range of 0–15 min was investigated. Then, it was compared with the removal efficiency of AMX in the PE reactor as well as the P and E reactors, separately. The COD removal percentage was calculated using Eq. (3).

$$\eta=\left[\frac{\left(\mathrm{COD}_0-\mathrm{COD}\right)}{\mathrm{COD}_0}\right]\times 100 \tag{3}$$

In this equation, η equals to the removal percentage of COD; COD_0 and COD are chemical oxygen demand, respectively, before and after the reaction in mg/L.

2.6. Toxicity property

Toxicity or antimicrobial property evaluation was done using *Staphylococcus aureus* PTCC1112 bacteria [37] and the inhibition zone method [38].

2.7. Investigating energy consumption

To treat every cubic meter of wastewater, the consumed energy was calculated using Eq. (4).

$$E=\frac{(UIt)}{V} \tag{4}$$

Table 1
Variables and levels considered based on Box–Behnken design

Variable	Level		
	–1	0	1
Electrolyte concentration (mg/ L)	100	550	1,000
Current (mA/cm^2)	10	30	50
Retention time (min)	1	8	15

In this equation, E is the consumed electrical energy (kWh/m^3), U is the voltage (V), I is the current intensity (A), t is the reaction time (h) and V is the volume of solution (L).

3. Results and discussion

3.1. Effects of current density, time, and electrolyte concentration

In the first stage of the experiment, the effect of variables, including time, electrolyte concentration, and current density on AMX removal efficiency was investigated. Table 2 shows the results of AMX removal efficiency for the three variables based on Design-Expert software.

The amount of removal efficiency based on the current density and the detention time is shown in Fig. 2. The optimal current density calculated in this experiment is 40 mA/cm^2. Current density determines the oxidation factors of organic compounds in the process. Therefore, the value of M ($OH^•$) in Eq. (1), which is the direct oxidation factor and the active chlorine species which are the indirect oxidation factor of AMX according to Eqs. (5) and (6) in this process, are determined by current density [19]. Increased current density increases the direct and indirect oxidizing species, as well as the efficiency of removing pollutants [39].

$$2Cl^- \rightarrow Cl_2 + 2e^- \quad (5)$$

$$Cl_2 + H_2O \leftrightarrow HClO + Cl^- + H^+ \quad (6)$$

Another factor affecting AMX removal efficiency is the type and amount of electrolytes. In electrochemical processes, NaCl and Na_2SO_4 are usually used as electrolytes. According to the results of previous studies, such as the study by Thiam et al. [40] as well as the study by Orescanin et al., using NaCl causes the process of mineralization of organic compounds to be performed more quickly than using Na_2SO_4. Active chlorine oxidizing species are indirect oxidation factors produced in the presence of NaCl and increase the oxidation speed [41]. The other reason to select NaCl instead of Na_2SO_4

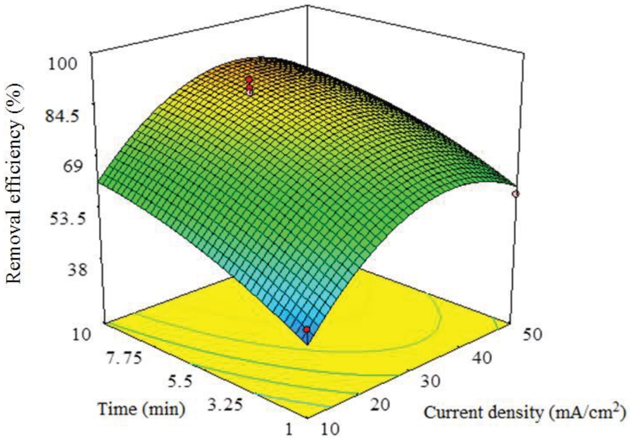

Fig. 2. Removal efficiency based on current density and time.

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

Run number	Current density (mA/cm^2)	Time (min)	Electrolyte concentration (mg/L)	Removal (%)
1	30	15	100	45.00
2	30	8	550	85.00
3	50	8	100	33.50
4	30	1	100	32.00
5	10	1	550	42.50
6	50	15	550	73.50
7	30	15	1,000	98.00
8	30	1	1,000	66.02
9	30	8	550	85.00
10	30	8	550	83.50
11	30	8	550	87.50
12	10	8	100	29.01
13	50	8	1,000	98.50
14	30	8	550	81.00
15	10	8	1,000	52.00
16	10	15	550	65.01
17	50	1	550	58.00

is increased destruction of hydroxyl radicals in the presence of sulfate [42]. The results of the experiments showed that the maximum removal efficiency of the NaCl electrolyte was 950 mg/L.

Table 3 shows the analysis of variance (ANOVA) test for statistical analysis of the data from the experiments. In Eq. (7), the removal efficiency and regression coefficients are presented.

$$\text{Removal}(\%) = +79.57 + 9.38 \times A + 10.72 \times B + 20.18 \times C + 10.50 \times A \times C + 3.05 \times B \times C - 15.83 \times A^2 - 3.65 \times B^2 - 15.32 \times C^2 \quad (7)$$

Due to the positive coefficients of current density (*A*), time (*B*) and electrolyte concentration (*C*), the effect of all three variables on AMX removal efficiency is positive. In the experiment, the *p*-value is significant for all three variables (Figs. 3 and 4). Among the studied variables, the electrolyte concentration has the greatest effect due to the products produced by the electrochemical process generated from the electrolysis of salt and is involved in AMX anodic indirect oxidation. The major products of the active species are chlorine and H_2O_2 [27]. By producing chlorine through anodic oxidation, H_2O_2 is produced by the reduction process in the cathode [43]. Chlorine (Cl_2) is produced in the direct oxidation of chloride ions in anode according to Eq. (5) and then, according to Eq. (6), produces hydrochloric acid (HClO) [44]. Table 4 shows the optimal predicted conditions by the model for AMX removal efficiency of 100% in the first stage. Table 4 also shows the actual removal efficiency in optimal conditions.

3.2. Effect of antibiotic concentration

The second stage of the study was to investigate the effect of AMX concentration on removal efficiency. At this stage, in the optimal conditions, the removal efficiency was investigated in the range of 10 to 100 mg/L of AMX, the result of which is shown in Fig. 5.

As shown in Fig. 5, increasing AMX concentration reduces the removal efficiency. In similar studies conducted to remove pollutants by EAOPs, consistent results have been found, and by increasing the pollutant concentration, the removal efficiency has decreased [45]. However, with increasing pollutant concentration, the amount of pollutant removal in a unit of time has increased [46,47].

3.3. pH effect

To investigate the pH effect, AMX removal efficiency in pH ranges of 2 to 12 were evaluated in optimal conditions for electrolyte concentration, time, current density, and concentration of 50 mg/L for AMX. The results showed that the removal efficiency increased by decreasing pH, and the highest removal value was obtained in acidic pH range and at pH less than 4 (Fig. 6).

Table 3
ANOVA for response surface reduced quadratic model

Source	Sum of squares	*df*	Mean square	*F* Value	*p*-value
Model	8,552.29	8	1,069.04	64.63	<0.0001
A-current density	703.12	1	703.12	42.51	0.0002
B-Time	1,129.99	1	1,129.99	68.32	<0.0001
C-electrolyte conc	2,595.33	1	2,595.33	156.91	<0.0001
AC	441.00	1	441.00	26.66	0.0009
BC	90.25	1	90.25	5.46	0.0477
A^2	1,054.44	1	1,054.44	63.75	<0.0001
B^2	327.92	1	327.92	19.83	0.0021
C^2	988.87	1	988.87	59.78	<0.0001
Residual	132.32	8	16.54		
Lack of fit	109.62	4	27.41	4.83	0.0782
Pure error	22.70	4	5.67		
Cor. total	8,684.62	16			
	R-Squared		0.9889		
	Adj *R*-Squared		0.9695		

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

Parameter	Current density (mA/cm^2)	Time (min)	Electrolyte concentration (mg/L)	Removal (%)	
				Predicted	Experimental
Optimum condition	40	10	950	100	98.2

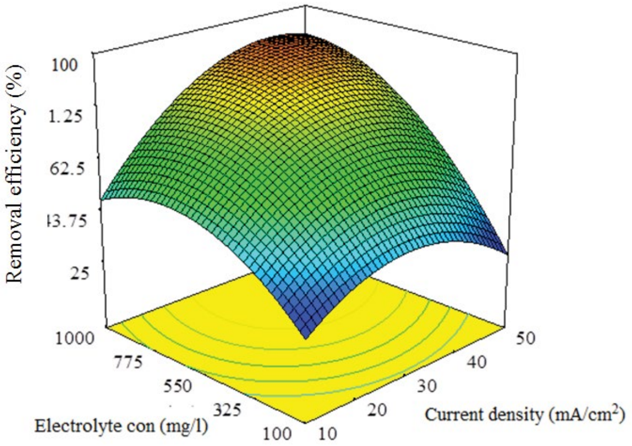

Fig. 3. Removal efficiency based on current density and electrolyte concentration.

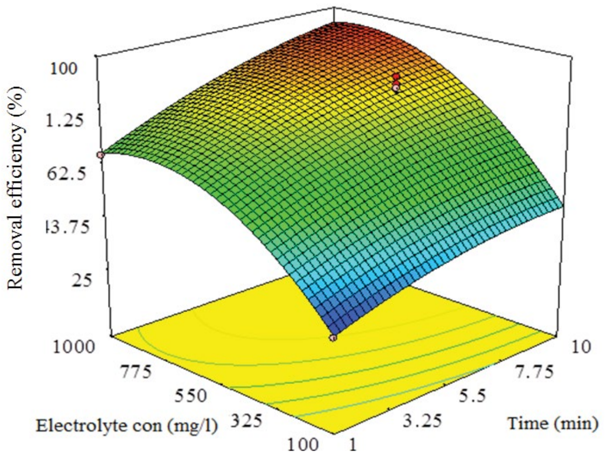

Fig. 4. Removal efficiency based on time and electrolyte concentration.

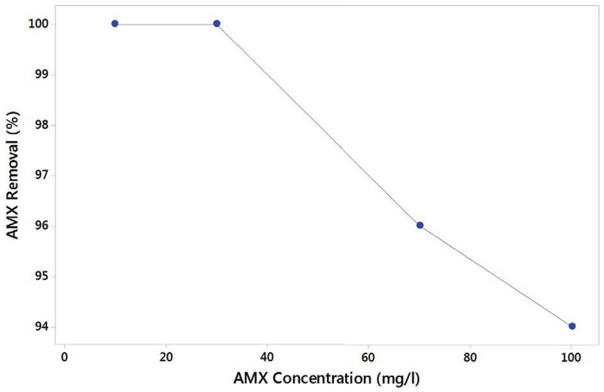

Fig. 5. AMX removal efficiency at different concentrations of AMX (current density 40 mA/cm^2, time 10 min, electrolyte concentration 950 mg/L, pH 7).

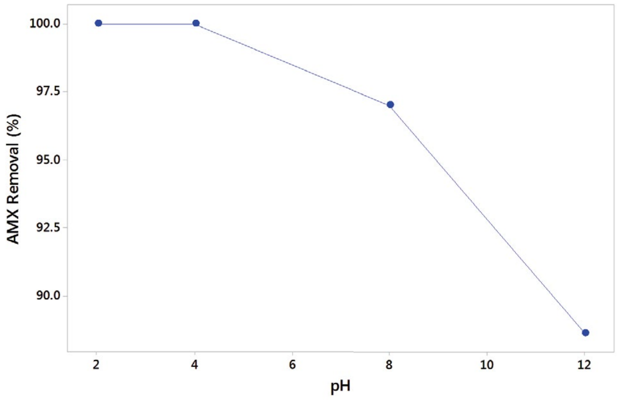

Fig. 6. AMX removal efficiency at different pH (current density 40 mA/cm^2, time 10 min, electrolyte concentration 950 mg/L, and AMX concentration of 50 mg/L).

pH affects indirect oxidation, which is the dominant chlorine species in the process, therefore, at pH 3 and below, chlorine species ($E°$ = 1.36 V/SHE) is Cl_2, between the neutral pH and 3, dominant species is HClO ($E°$ = 1.49 V/SHE), and at pH higher than 8, dominant species ($E°$ = 0.89 V/SHE) is ClO^-. Due to the higher redox potential of products produced at acidic pH, oxidation of organic compounds is performed more rapidly in acidic conditions [24]. Similar studies, such as the study by Abdessalem et al. [48] and Buxton et al., have reported the same results in increasing the efficiency of removing organic pollutants at pH below 3 in AO and AO-H_2O_2 processes. Reducing the process efficiency at high pH is due to the degradation effects of carbonate and bicarbonate species on radical hydroxyl [49]. Moreira et al. [43] have also reported that at a pH higher than 5, spontaneous H_2O_2 degradation occurs more rapidly. pH solution also affected the amount of voltage required to supply the current density of 40 mA/cm^2. The required voltage at neutral pH was about 23 V, while by decreasing and increasing pH, the voltage required to supply the current density decreased. The minimum voltage at pH = 2 was equal to 15 V and at pH = 12, equal to 7.5 V. Therefore, by changing the pH, the amount of energy required to supply the current density, and the AMX removal reduced.

3.4. *Effect of AMX adsorption on the activated carbon bed*

Given the fact that the granular activated carbon bed was used as an electrode in this study, and the possibility of removing AMX by adsorption on the granular activated carbon, a second similar reactor (without the PE process) containing the same amount of granular activated carbon was used to determine the amount of AMX adsorption on the activated carbon. Therefore, the solution containing 50 mg/L AMX was contacted with the granular activated carbon in the second reactor in 15 min. It was observed that a maximum of 8% of AMX in the solution at 15 min is absorbed on the granular activated carbon presented in the second reactor. Previous studies have reported that among antibiotics, including AMX, cefalexin, tetracycline, and penicillin, AMX has had the lowest removal rate by adsorption on the activated carbon [50]. The percentage of AMX removal by absorption on the granular activated carbon has been determined to be 26.31%

in a 24 h contact period. By increasing pH to 12, the removal efficiency decreases by less than 10% due to the absorption of AMX on the activated carbon [50]. As AMX concentration increases in the environment, the removal rate reduces by absorption on the activated carbon [51].

3.5. Performance evaluation of the used processes

In order to investigate and compare the efficiency of the processes used in the reactor, AMX removal efficiency in the PE combined reactor and separately in the reactor containing P and E processes were studied. The COD removal efficiency was also investigated in optimal conditions in the PE combined reactor (Fig. 7).

By examining AMX removal efficiency in these reactors, it is concluded that the best removal efficiency is related to the PE combined reactor and the lowest removal efficiency is related to the P process alone, with an average removal efficiency of 2%. By adding the P process with the E process, which alone has a removal efficiency of 92.58% in optimal conditions, the removal efficiency can be improved in the PE combined reactor by about 6% and increased to 98%. These results show the synergistic effect of the two processes combination in the combined process. Increasing AMX removal efficiency in the combined process of free radicals production is due to the effect of UVC radiation on the products from the electrooxidation process [52,53], which can act as an indirect oxidation agent and degrade organic compounds [10]. Eqs. (8)–(10) show the major products under UV exposure [54].

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

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

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

3.6. Kinetic studies

Kinetic studies for treatment processes play an important role in determining the hydraulic retention time in all systems to achieve the expected removal efficiency [55]. Knowing the reaction rates is essential to design wastewater treatment units. The reaction rate shows the rate of changes in the concentration of reactants per unit time. The results showed that AMX removal from first-order kinetic with a correlation coefficient > 0.98 follows Eq. (11).

$$\ln\frac{C}{C_0} = -kt \tag{11}$$

In this equation, C_0 is AMX concentration before the reaction (mg/L), C is AMX concentration after the reaction (mg/L), t is the reaction time (min), and k is the reaction rate constant (min^{-1}). The reaction rate constant was determined from the plot of ln C/C_0 against t (Fig. 8). According to Fig. 8, the reaction rate constant was 0.35 min^{-1}.

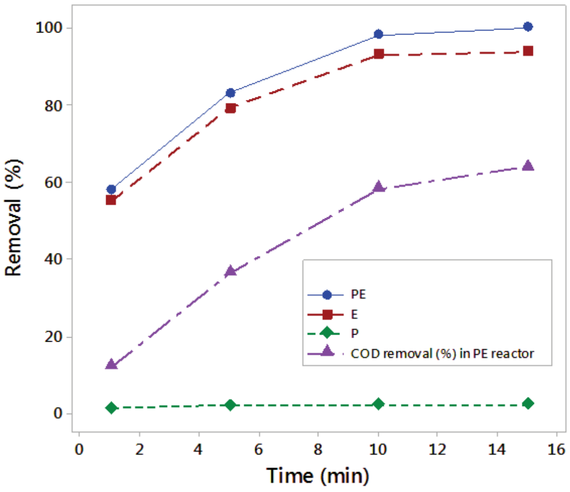

Fig. 7. AMX removal efficiency in the PE, E, and P reactors and COD removal efficiency in the PE reactor at different times (current density 40 mA/cm^2, electrolyte concentration 950 mg/L, AMX concentration 50 mg/L, and pH 7).

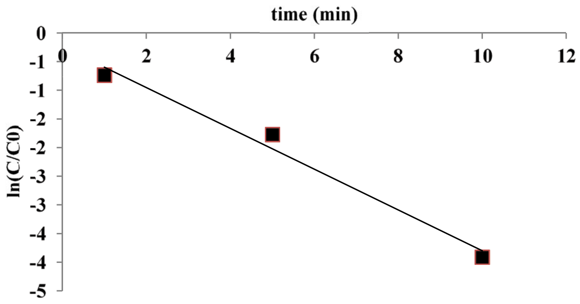

Fig. 8. First-order reaction chart.

3.7. Economic analysis

Operating costs during wastewater treatment processes include electricity, chemicals, sludge disposal, labor, maintenance, and equipment costs. In electrochemical processes, the most important parameters that can affect the operating costs are the cost of the used electrode and electrical energy [55]. The major cost in the reactor used in this study was electricity due to the stability of the electrode, which was calculated according to Eq. (4) in kWh/m^3. The average cost of electricity is 0.0847 US$ /kWh. The effect of current density on energy consumption is shown in Fig. 9. The results show that the cost of treating a cubic meter of wastewater containing AMX in optimal conditions with a current density of 40 mA/cm^2, is 0.0417 US$ to remove 98% of AMX in 10 min. However, in the maximum current density of 50 mA/cm^2 in similar conditions, it increases to 0.065 US$.

3.8. Toxicity evaluation

Microbiological tests are used to determine the amount of activity of the effluent from the reactor [56]. Therefore, *Staphylococcus aureus* bacteria and the inhibition zone test was used to determine the final effluent toxicity. Fig. 10

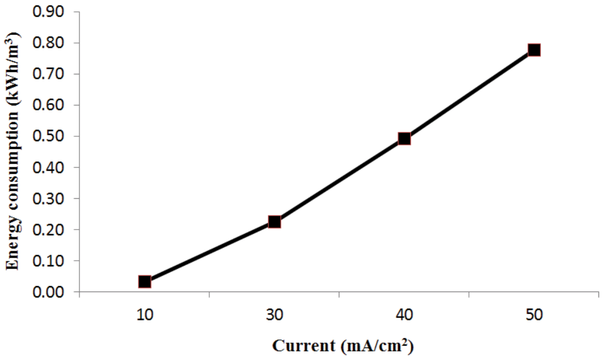

Fig. 9. Amount of energy consumed in different current densities.

shows the results of the toxicity test of the final effluent from the reactor. Fig. 10 shows the diameter ratio of the inhibition zone in different AMX removal percentages on the diameter ratio of the inhibition zone of *S.aureus* bacteria in contact with a solution containing AMX of 50 mg/L. Investigating toxicity showed that by increasing the AMX removal rate, the AA/AA0 ratio decreased, and also toxicity or antibacterial properties of the products in the effluent significantly reduced.

3.9. Comparison with other previous studies

The result of the current study was compared with other similar published works. Recently, various studies have been carried out on the use of EO and EC processes, some

Table 5
Comparison of the studies on the use of EO and EC processes in the removal of AMX from aqueous media

Pollutant	Process type	Results	References
Amoxicillin	Electro-catalytic oxidation using Ti/RuO_2	Optimum current density and initial pH were found to be 5.88 mA cm^{-2} and 7.0 which 60% AMX removal efficiency and 48% total organic carbon removal efficiency were achieved in 60 and 240 min of electrolysis.	[1]
Diclofenac, Carbamazepine, and amoxicillin	Electrocoagulation with aluminium and stainless steel as anode and cathode	Effects of current density (0.3, 0.5, 1.15 and 1.8 mA cm^{-2}), initial pharmaceutical concentration (0.01, 4 and 10 mg/L) and electrolysis duration (3, 6 and 19 h) in pharmaceutical removal efficiencies were evaluated. The high pharmaceutical abatement was recorded at an elevated current density and prolonged electrolysis duration due to additional electro-generated coagulant species in solution. High sludge production was observed in this process.	[57]
Amoxicillin	Photo-Electro oxidation process with graphite electrodes	Optimal conditions for variables, including current density, reaction time, and electrolyte concentration for removal efficiency of 62.4%, were 94 mA/cm^2, 95 min, and 997 mg/L, respectively. Investigating the amoxicillin and pH variables showed that by reducing the contaminant concentration and pH, the antibiotic removal efficiency increased.	[58]
Amoxicillin	Electrochemical degradation	Electro-oxidation of amoxicillin is achieved on a reticulated vitreous carbon anode applying a 1.25 V potential. The amoxicillin elimination amount was more than 80%.	[59]
Amoxicillin	Electro-Fenton with a boron-doped diamond (BDD) anode	AMX decay always followed pseudo-first-order kinetics using either Pt or BDD. The absolute rate constant between hydroxyl radical and AMX determined by the competition kinetics method using p-hydroxybenzoic acid as the reference compound was found to be $(2.02 \pm 0.01) \times 10^9$ M^{-1} s^{-1}.	[60]
Amoxicillin	Contact glow discharge electrolysis (CGDE)	Addition of Fe^{2+} or Fe^{3+} efficiently accelerated the degradation of AMX. Stainless steel wire was also used as the anode in CGDE to enhance the degradation of AMX. High sludge production was observed in this process. The energy efficiency increased with the increasing anode's diameter.	[61]
Amoxicillin	Photo-Electro oxidation process with granular activated carbon bed was used as an electrode	Results showed that in order to achieve an efficiency of about 98%, the optimum condition for electrolyte concentration, time, and current density variables was 950 mg/L, 10 min, and 40 mA/cm2, respectively. Furthermore, the removal efficiency of AMX increased by decreasing pH and contaminant concentration.	This work

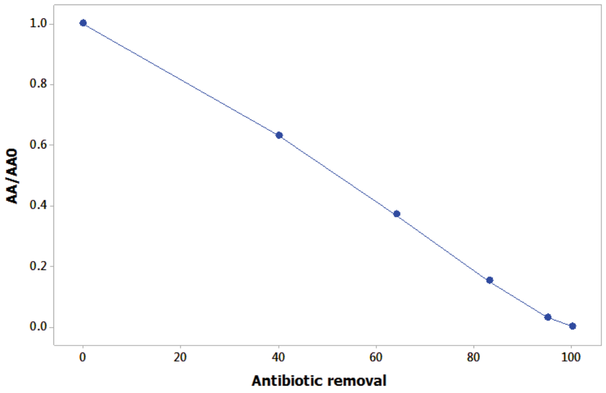

Fig. 10. Toxicity test by *S. aureus* bacteria on the effluent from the PE process (current density 40 mA/cm^2, electrolyte concentration 950 mg/L, AMX concentration 50 mg/L, and pH 7).

of which have been listed in Table 5. As shown in Table 5, most studies based on the EO process [1,57,58,59], where conventional resistive electrodes are used, have lower removal rate efficiency. Moreover, sludge production and also the increased cost due to corrosion of the electrode in studies based on EC process [60,61], limit the efficiency and also the application of the EC process. In the current work, the EO process, based on the porous electrode, was used. Based on the obtained findings, increasing the contact surface between water, pollutant and electrode surface increases the reaction rate and efficiency, and also no sludge is formed. Another study indicates that a combination of chemical coagulation and electrocoagulation process could have a better result [62].

4. Conclusion

In the present study, the effect of the PE process on AMX removal separately and combined in separate P and E reactors was investigated. In the E reactor, granular activated carbon was used as a porous electrode that increased the contact surface of the electrode with the pollutant in the aquatic environment. The results of this study showed that at the optimal current density of 40 mA/cm^2, electrolyte concentration of 950 mg/L, time of 10 min, and pH 7, the value of AMX removal efficiency was 98.2%. Increasing AMX concentration reduces the removal efficiency. Reducing pH and acidifying the environment increase the chlorine species in the environment, which by increasing indirect oxidation; increases the efficiency of AMX removal. The results of the comparison of the combined PE reactor and the reactor containing each of the P and E processes separately showed that the combined reactor had the maximum removal efficiency. Based on the findings, it can be concluded that the PE modified reactor with a granular activated carbon bed, which plays the role of a porous electrode, can completely degrade AMX in the aquatic environment by increasing the contact surface of the electrode with the pollutant. The reactor is also capable of removing COD by 64%. The final effluent has the least toxicity and antimicrobial properties and can be treated by biological processes to remove the remaining organic compounds.

Acknowledgements

We appreciate the Environmental Science and Technology research center at Shahid Sadoughi University of Medical Sciences in Yazd, Iran for the technical supports and funding (IR.SSU.SPH.REC.1397.058).

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