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Evaluation of amoxicillin antibiotic removal by electrocoagulation process from aqueous solutions: optimization through response surface methodology

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ABSTRACT

In this research, electrocoagulation (EC) was studied to investigate the efficiency of amoxicillin (AMX) antibiotic removal using iron electrodes from aqueous solution. For this purpose, a central composite design (CCD) was employed to optimize the operating parameters including pH (2–12), current density (5–15 mA·cm^{-2}), AMX concentration (10–100 mg·L^{-1}), and electrode spacing (1–3 cm). Experiments were performed in batch mode at the constant time of 35 min. The residual concentration of AMX in samples was analyzed by measuring the AMX concentration through high-performance liquid chromatography (HPLC). Further, pollutant removal, sludge generation, and energy consumption were measured and discussed through response surface methodology (RSM). The results showed that the removal efficiency was achieved as 80.9% under optimized levels of parameters (pH: 7.87, current density: 10.17 mA·cm^{-2}, AMX concentration: 50 mg·L^{-1}, and electrode spacing: 1.5 cm), while sludge generation and energy consumption was 70.3 ml and 7.109 kWh·m^{-3}, respectively. The results revealed that at same conditions of all variables just one level reduction in current density has lead to the reduction to less than half of the energy consumption.

Keywords: Amoxicillin; Electrocoagulation; Response surface methodology; Optimization

1. Introduction

Antibiotics are one of the most widely used pharmaceuticals applied as instruments for killing of infectious diseases [1]. The World Health Organization has reported the production of antibiotics of about 7700 kg·d^{-1}on worldwide scale [2]. Antibiotics toxicity for bacteria and algae even at low concentrations has led to classifying them in a group of emerging pollutants. They are also known to cause bacterial resistance. The arrival of these compounds to aquatic biota can disrupt the vital activities including nitrification and denitrification [3], carcinogenic, mutagenic [4], and allergic effects, damage on DNA and lymphocytes [5] along with the low biodegradability are from the other controversial issues related to antibiotics wastes in the environment [6]. The extent of AMX usage in medicine, veterinary, and agricultural fields has led to its wide detection in domestic waste, healthcare facilities sewage, agricultural runoff,

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and pharmaceutical centers effluents [7]. Considering the possible discharge of effluent to the aquatic environment or reuse for irrigation, applying a suitable purification method is a prerequisite step before any decision-making for its final strategy treatment. Many researchers have suggested different processes for the removal of pharmaceutical compounds from water and wastewater. Biological treatment processes had been given priority because of their simple design and operation. But some drawbacks are attributed to biological techniques. Micro-pollutants are not fully eliminated in activated sludge process because some of them are trapped in the biological sludge [8]. The results of Zhou study are indicative for the ineffectiveness of the anaerobic process to remove two pharmaceutical compounds ampicillin and aureomycin [9]. Removal of antibiotics was also investigated through conventional treatment using coagulation and filtration [10], or in advanced treatment processes such as electro-Fenton [11], membrane technologies [12], and adsorption using activated carbon [13]. Each of the mentioned methods has its advantages and limitations. Electrocoagulation is another type of wastewater treatment which physical and chemical mechanisms are involved [14,15]. A literature review has made special attention to electrocoagulation technology for its evolvement during recent years [16]. Electrocoagulation is adopted as an efficient way for removing various types of pollutants from water and wastewater. Electro dissolution of sacrificial metals of iron, aluminum or any other electrode through a direct current between electrodes is the principal mechanism in EC process [17]. Mentioned metals are usually chosen as available and cost-effectiveness electrodes for running EC experiments [18,19]. At first step in situ formation of coagulant due to corrosion of anode material occurs. Fig. 1 shows the schematic of electrocoagulation process.

Water oxidation and iron electrode dissolution are electrolytic anodic reactions as follows [20]:

$$4Fe_{(s)} - 8e^{-} \rightarrow 4Fe_{eq}^{2+} \quad (1)$$

$$4Fe_{eq}^{2+} + 10H_2O_{(l)} + O_{2(g)} \rightarrow 4Fe(OH)_{3(s)} + 8H_{(aq)}^{+} \quad (2)$$

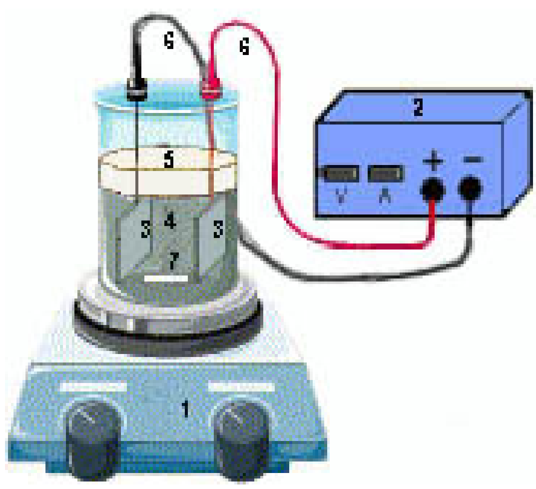

Fig. 1. Schematic of electrocoagulation process.

Alternative spontaneous mechanisms may oxide Fe on the electrode surface or in the solution. Water reduction at cathode develops evolution of hydrogen gas and hydroxide anions:

$$8H^{+}_{(aq)} + 8e^{-} \rightarrow 4H_{2(g)} \quad (3)$$

$$4Fe_{(s)} + 10H_2O_{(l)} + O_{2(g)} \rightarrow 4Fe(OH)_{3(s)} + 4H_{2(g)} \quad (4)$$

$$nFe(OH)_3 \rightarrow Fe_n(OH)_{3n(s)} \quad (5)$$

As a result flocs of ferric hydroxides form in pH ranges of 5–10 [6]. Strong affinity among metal hydroxide compounds and dissolved molecules or ions cleans polluted solution through coagulation or adsorption mechanisms [21]. At follow, flocs can be removed by subsequent sedimentation or flotation [6]. Although the production of sludge is inevitable in this process, a number of disposal solids reduces dramatically in comparison to conventional coagulation, as extra chemicals aren't added [22]. Other studies reported numerous benefits for EC process: ease of operation and maintenance, continuous, automatic, and low-cost operation, recycling and reuse of wastewater, and reducing the needed space for treatment plants because of the less number of units [4]. Response surface methodology was applied to evaluate the effects of main parameters, interaction and quadratic effect to achieve the optimal removal efficiency for the electrocoagulation process. Therefore, the main motivation behind this investigation is evaluating the EC process for removal of AMX from aqueous solution using iron electrodes and determine the influence of operating variables such as pH, current density, and inter electrode distance in the presence of different doses of AMX.

2. Methods

2.1. Chemicals and stock preparation

AMX antibiotic (≥ 85% purity) was supplied from the pharmaceutical DANA Company of Tabriz, (Iran). AMX stock solution was prepared by dissolving 1.176 g of it in 1000 mL of double distilled water (DDW). All the HPLC-grade reagents for conducting EC experiments and determining the remained concentration of AMX include (NaOH), (HCl), (KCl), (KH_2PO_4), and methanol was purchased from Merck Company, (Germany).

2.2. Reactor construction and feed

The electrocoagulation setup was made from Pyrex glass with effective volume of 250 mL. It was composed of rectangular Iron electrode with immersed dimensions of 110 × 30 × 2 mm. According to this,iron was preferred to aluminum metal due to its innocuity in leaving toxic effects with a comparison to Al electrode [4]. To increase the electrical conductivity of the solution, in each experiment, the cell was feed by 200 ml of a synthetic AMX solution in the presence of 0.3 g KCl as supporting electrolyte. The pH of the solution were adjusted between 2–12 using 0.1 N of NaOH or HCl. Then, the samples were stirrer by a magnetic stirrer (LABINCO) at 30 rpm for 35 min after washing Iron electrodes with HCl and polishing their surfaces by sandpaper. The electrocoagulation experiments were carried out in a mono polar batch reactor (0–5 A, 0–30 V) using two electrode as anode and cathode in parallel connections.

The test solution gently stirred (200 rpm) during run with the current density set at a given level using DC power supply [18]. When the reaction time was passed, pH of reactor content was determined and it was transferred to a cylinder 250 mL to observe the sludge volume after 30 min retention time. Afterward samples were taken from the supernatant over the cylinder and filtered through 0.45 µm paper filter and 0.22 µm cellulose acetate filter for injecting into the HPLC system and determining the residual concentration of AMX.

2.3. Method of analysis

A mixture of mobile phase consisted of 95% of phosphate buffer 0.025 M and 5% of methanol was injected into high-performance liquid chromatography (HPLC, KNAUER) equipped with a vortex column (C_{18}; 150 mm, 4.6 µm) and ultraviolet (UV) detector at the flow rate 0.5 mL·min^{-1} and wavelength 230 nm. Removal efficiency of AMX was calculated using Eq. (6).

$$\%removal = \frac{C_0 - C_t}{C_0} \times 100 \quad (6)$$

Besides, the electrical energy consumption during EC process was calculated as follows:

$$EEC = \left(\frac{UIt}{V}\right) \quad (7)$$

where U shows the cell voltage (V), I is the current density (A), t is the time of electrolysis (h) and V is the solution volume (m^3) [6,21].

2.4. Design of experiments

Design expert software was used to determine the optimum conditions and analysis the results. For this purpose, response surface methodology (RSM) as a potent technique for modeling and optimization was selected. Central Composite Design (CCD) under RSM designed 30 experiments based on $2^K + 2K + n_c$ (k: number of parameters, n_c: number of replicates) consisting of sixteen experiments in factorial points, eight in axial points and six replicates at the center point [23,24]. The operational factors in actual and coded levels are given in Table 1. Antibiotic removal percentage, volume of sludge generation and energy consumption were considered as the response. To analyze the obtained data for any response there must be an approximating function between the response and operating factors. This function is usually a polynomial of the independent variables:

$$y = \beta_0 + \sum_{i=1}^{k}\beta_i x_i + \sum_{i=1}^{k}\beta_{ii} x_i^2 + \sum_{i<j}^{k}\beta_{ij} x_i x_j + \in \quad (8)$$

where Y and X (i,j) are the response and variables; β_0 is coded value of response when other parameters are constant at central points, β_i, β_{ii}, β_{ij}, are the regression coefficients for linear, quadratic, and interaction effects, respectively and $\in$: is error [11,25].

Table 1
Variables in coded and actual levels

Symbol	Variables (Factor)	Experimental field				
		α–	–1	0	+1	α+
$A: x_1$	pH	2	4.5	7	9.5	12
$B: x_2$	Current density (mA·cm^{-2})	5	7.5	10	12.5	15
$C: x_3$	AMX concentration (mg·L^{-1})	10	32.5	55	77.5	100
$D: x_4$	Inter electrode distance (cm)	1	1.5	2	2.5	3

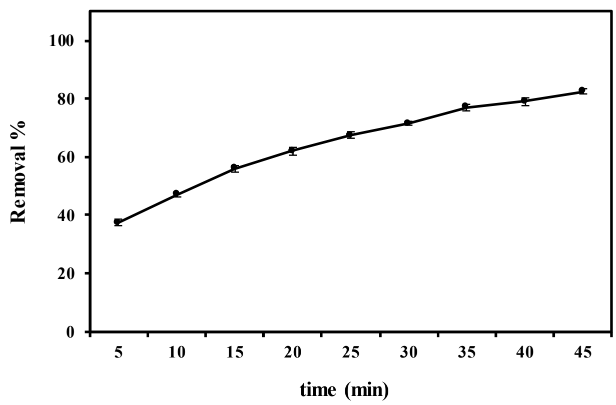

Fig. 2. AMX removal as a function of reaction time.

3. Results and discussion

3.1. Optimum reaction time

To achieve the optimum time AMX removal in the EC reactor was evaluated as a function of contact time. For this aim, the range of reaction time was taken 5–45 min at constant values of other parameters as current density 10.17 mA·cm^{-2}, pH 7.18, antibiotic concentration 50 mg·L^{-1} and electrode gap 1.5 cm. As presented in Fig. 2, more reaction time led to the better removal and a sharp removal trend with value of 73.42% was achieved during 35 min of contact time. Because of more energy consumption in higher reaction time, the reaction was stopped at 35 min. So, the maximum removal was observed under the optimum duration of 35 min and further time showed small influence on the degree of AMX removal. Hence 35 min was selected to continue other experiments. It is suggested that a number of iron cations increases with increasing the duration of EC process and reaches to a sufficient concentration for binding the target ions. These results are in agreement with the results reported by other studies on optimal condition of reaction time for running EC assays. Although exceeding the duration from optimal condition may lead to more efficiency, but it may not comply the economic concerns [26]. But what happens at high retention times can be attributed to the effect of temperature. Actually, with prolonging the reaction time of EC, the solution is warmed consequence in turbulence preventing agglomeration of coagulant particles [27].

3.2. Analysis of results with design expert

Table 2 shows predicted and experimental values of responses besides the experimental matrix. It explains the technical efficiency of EC process for samples depletion from antibiotic concentration. Based on Table 2 the most removal efficiency of 86.92% was achieved under conditions of 32.5 mg·L^{-1} of initial concentration of AMX, solution pH of 9.5, applied a current density of 12.5 mA·cm^{-2} and an inter electrode distance of 1.5 cm. Also, the settled solids were in the range of 10–95 mL. In addition, broad variations in energy consumption were observed. The maximum level of electrical energy consumption 19.73 kWh·m^{-3} was observed under central values of pH, initial concentration of AMX, and inter electrode distance, while a current density was applied to its highest value (run 9). In these conditions, the removal efficiency was yielded 79.08% while at run 2 and at same values of parameters except the current density which was applied at one smaller level comparing to run 9, almost an analogous removal rate 77.85% was obtained. In run 2 the amount of energy consumption 9.6 kWh·m^{-3} was below the half of run 9. Table 3 justifies the accuracy of the model predictability in confidence level of 95% for each response. The quadratic model was used to make relationship among variables and responses through Analysis of Variance (ANOVA). The coefficient of determination was selected in order to express the fit or lack of fit of polynomials model for results. High R-squared values of 0.988, 0.973, and 0.996 for responses of AMX removal efficiency, sludge volume, and energy consumption respectively indicate a good association among measured and model predicted values. The low difference between predicted R^2 and adjusted R^2 also declares the model's significance. F-value and P-value were

Table 2
Experimental and predicted results corresponding to CCD along with designed experiments

Run order	Parameter				Pollutant removal %		Sludge generation mL		Energy consumption kWh·m^{-3}	
	X_1	X_2	X_3	X_4	Observed	Predicted	Observed	Predicted	Observed	Predicted
1	4.5	12.5	77.5	1.5	39.27	40.44	72	70.95	10.05	10.02
2	7	10	55	2	77.85	71.86	65	66.33	9.6	9.6
3	7	10	55	2	66.06	71.86	68	66.33	9.6	9.6
4	7	10	10	2	84.05	83.41	42	39.08	9.3	9.26
5	9.5	12.5	77.5	2.5	41.27	42.25	85	87.95	16.96	17.17
6	7	10	55	2	73.98	71.86	70	66.33	9.5	9.6
7	4.5	12.5	77.5	2.5	31.39	32.43	65	63.29	16.18	16.22
8	4.5	7.5	32.5	1.5	52.52	52.30	18	17.45	4.54	4.4
9	7	15	55	2	79.08	77.16	85	84.08	19.73	19.25
10	4.5	7.5	32.5	2.5	40.50	41.64	12	11.79	6.81	6.5
11	2	10	55	2	27.61	24.95	10	16.91	7.83	8.21
12	4.5	7.5	77.5	1.5	14.83	16.45	28	27.45	4.15	4.2
13	7	10	55	3	42.05	42.60	40	37.41	13.49	13.75
14	4.5	7.5	77.5	2.5	11.10	8.54	20	18.29	6.57	6.28
15	9.5	12.5	32.5	1.5	86.92	90.22	63	67.12	10.7	11.06
16	9.5	7.5	32.5	1.5	71.12	68.59	40	44.12	4.85	4.91
17	9.5	12.5	32.5	2.5	83.94	80.82	58	60.95	17.35	17.4
18	9.5	7.5	32.5	2.5	59.70	59.28	33	36.45	7.05	7.14
19	7	10	55	1	59.73	59.92	55	52.75	5.74	5.31
20	7	10	55	2	73.06	71.86	65	66.33	9.7	9.6
21	7	5	55	2	28.96	31.63	20	16.08	2.87	3.18
22	9.5	12.5	77.5	1.5	51.54	48.90	95	97.62	10.44	10.84
23	4.5	12.5	32.5	2.5	60.01	62.49	38	37.29	16.65	16.57
24	7	10	55	2	72.75	71.86	60	66.33	9.4	9.6
25	9.5	7.5	77.5	2.5	19.06	17.67	39	43.95	7.12	7.05
26	12	10	55	2	47.66	51.06	80	68.25	10.23	9.68
27	7	10	55	2	67.49	71.86	70	66.33	9.81	9.6
28	7	10	100	2	7.62	9.00	78	76.08	8.97	8.84
29	9.5	7.5	77.5	1.5	25.96	24.23	52	55.12	4.7	4.84
30	4.5	12.5	32.5	1.5	73.35	73.25	44	41.45	10.18	10.35

also considered for expressing the significance of the model terms. P-value more than 0.1 suggests an insignificant model or model term. Regarding P-values of fitted models in Table 3, all them can well navigate the design space. High P-value of lack of fit for AMX removal efficiency model and solid generation model also express the proper correlation among model predicted values and experimental data. With regards to Table 3 high values of fisher distribution test results highlight the model's goodness [24]. Checking the model precision plays an important role in analyzing the responses. Based on RSM an adequate precision greater than 4 is desirable. This parameter for AMX removal efficiency,sludge volume and energy consumption was calculated 32.74, 22.98, and 66.24, respectively. Experimental data from the CCD was analyzed and fitted to a second-order polynomial model expressed as follow:

$$y_1 : \text{AMX removal}(\%) = +71.87 + 6.53x_1 + 11.38x_2 \\ -18.60x_3 - 4.33x_4 - 2.13x_1x_3 + 0.76x_2x_3 - 0.025x_2x_4 \\ -8.46x_1^2 - 4.37x_2^2 - 6.41x_3^2 - 5.15x_4^2 \tag{9}$$

$$y_2 : \text{Sludge volume}(\text{ml}) = +66.33 + 12.83x_1 + 17x_2 + 9.25x_3 \\ -3.83x_4 + 0.25x_1x_3 + 4.87x_2x_3 + 0.37x_2x_4 \quad 5.94x_1^2 \\ -4.06x_2^2 \quad 2.19x_3^2 \quad 5.31x_4^2 \tag{10}$$

$$y_3 : Energy\ consumption\left(\frac{kwh}{m^3}\right) = +9.61 + 0.37x_1 + 4.02x_2 \\ -0.11x_3 + 2.11x_4 + 0.031x_1x_3 \quad 0.034x_2x_3 + 1.03x_2x_4 \\ 0.16x_1^2 + 0.40x_2^2 \quad 0.14x_3^2 - 0.018x_4^2 \tag{11}$$

In the above equations, x_1, x_2, x_3 and $x_4$are operational variables of pH, applied potential, antibiotic concentration and electrode distance, respectively. The first equation remarks that EC process efficiency for the removal of AMX is averagely 71.87% which would experience variation depend on the various values of parameters. Table 3 verifies the considerable influence of all main and second-order effects on the response, while interaction terms have the least impact on pollutant removal percentage except the concurrent effect of pH and AMX concentration. According to first response function, current density has the most positive effect on response with a coefficient of +11.38 while AMX concentration shows the maximum prohibiting impact on the AMX removal efficiency with a negative coefficient of 18.60. But all variables exhibit almost a same behavior in terms of second-order effects which can be better understood viewing the perturbation plot of all main effects in Fig. 3. Upward direction of all graphs confirms the curve line relationship among factors and removal efficiency of antibiotic in which the most important squared effect is assigned to pH variable. Based on the curve of coded factor A, more removal percent was achieved under neutral to little alkaline pH values. In pH value of 4.5, 56.87% of the AMX was removed, while removal efficiency reached to 72% in pH 7 and it confronted a subsequent reduction to 69.93% at pH 9.5. Factor B implies on the growing trend of AMX removal percent in more current density. When applied current increased from level –1 to level +1 removal efficiency was observed about 22.77%. Increasing the AMX concentration in the effluent from 32.5 to 77.5 mg·L^{-1} decreased its removal percent from 84% to 46.85%. Removal efficiency showed a slight growth when inter electrode distance was raised from 1.5 to 2 cm, but it reduced 10% by increasing the inter electrode distance

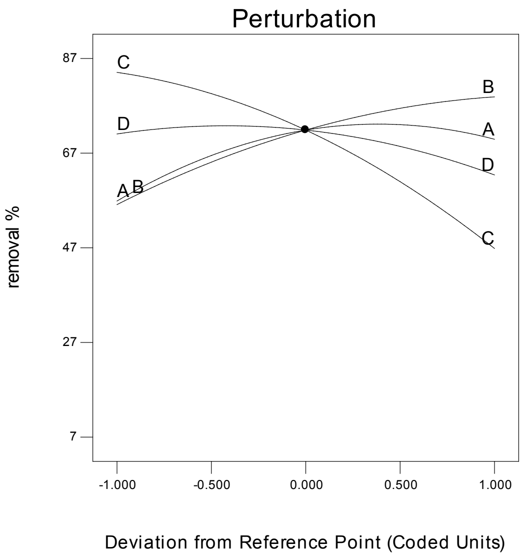

Fig. 3. The plot of the main effects on the AMX removal efficiency.

Table 3
Analysis of variance (ANOVA) for the selected quadratic models

Source	Sum of Squares			Degree of freedom (df)			Mean square			F-value			Probability P-value > F		
	Y_1	Y_2	Y_3	Y_1	Y_2	Y_3	Y_1	Y_2	Y_3	Y_1	Y_2	Y_3	Y_1	Y_2	Y_3
Model	16142.21	15428.08	521.43	14	14	8	1153	1102.01	65.18	92.64	39.49	719.33	< 0.0001	< 0.0001	< 0.0001
Residual	186.69	418.58	1.9	15	15	21	12.4	27.91	0.091	–	–	–	–	–	–
Lack of fit	91.44	345.25	1.75	10	10	16	9.1	34.53	0.11	0.48	2.35	3.56	0.8487	0.1785	0.0832
Pure error	95.25	73.33	0.15	5	5	5	19.0	14.67	0.031	–	–	–	–	–	–
Core total	16328.89	15846.67	523.33	29	29	29	–	–	–	–	–	–	–	–	–

Y_1: R-Squared = 0.9886, Adeq Precision = 32.743
Y_2: R-Squared = 0.9736, Adeq Precision = 22.979
Y_3: R-Squared = 0.9964, Adeq Precision = 97.497

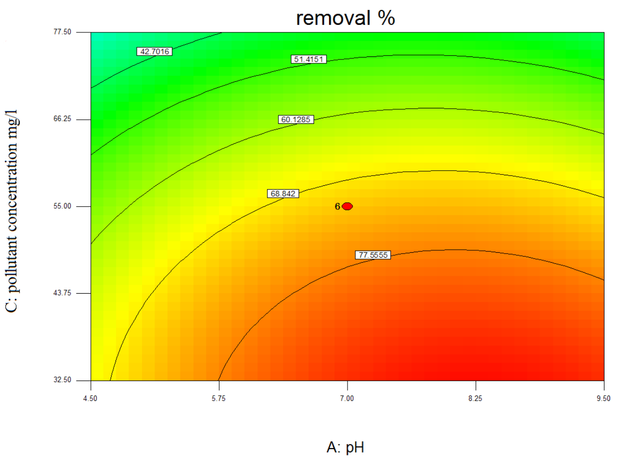

Fig. 4. The contour plot for simultaneous effect of pH and AMX concentration on the removal efficiency.

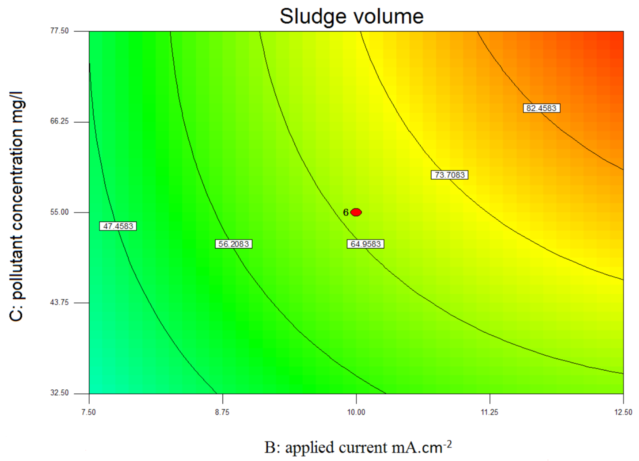

Fig. 5. Contour plot for simultaneous effect of current density and AMX concentration on sludge generation.

from 2 to 2.5 cm. Fig. 4 shows the interaction effect of pH and AMX concentration. It implies on more removal efficiency at higher levels of pH for various concentrations of AMX. It is clear from the constant part of the second equation that EC process has produced averagely 66.33 mL solids during the treatment of 200 mL of wastewater containing AMX. Sludge production which was a sign of AMX removal had a direct relationship with all parameters except the inter electrode distance. The most effective factor on sludge generation was the current density. Simultaneous effect of applied current with the AMX concentration was the highest in terms of interaction effects which is presented in Fig. 5.

Eq. (11) shows a variation of AMX concentration which had a negligible effect on the energy consumption, while current density possessed AMX impact on this response with a positive effect of +4.02. Energy consumption was also proportional to the inter electrode distance and pH of the solution. Synergic effect of factors x_2 and x_4 on energy response is shown in Fig. 6.

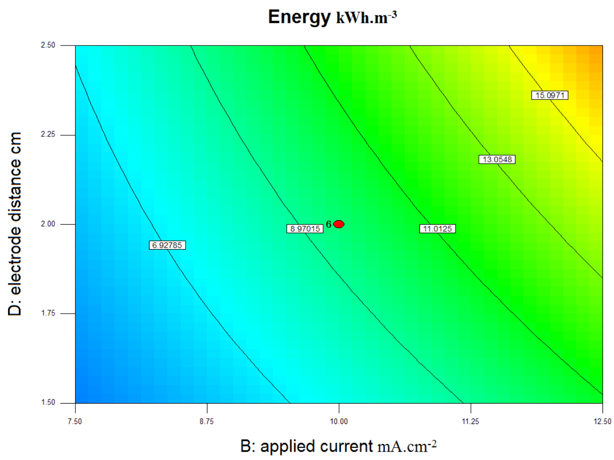

Fig. 6. Contour plot for simultaneous effect of current density and electrode distance on energy consumption.

3.3. *Effect of pH*

Solution pH is one of the main influential factors on the electrochemical process performance [28]. The range of pH determines the formation of monomeric and polymeric hydroxide complexes after hydrolysis of ferrous ions. New cationic polymers form flocs by means of destabilizing and aggregation of colloidal particles [29]. In Fig. 4, the effect of pH on removal efficiency demonstrated the ranges of 4.5–9.5 generally shows a positive impact on response, but the maximum removal efficiency of AMX was achieved at electrolyte pH of 7–8. Removal efficiency of AMX decreased at pH values above 8. It can be explained by the predominance of different species of Fe under different pH values. In fact, under acidic to low alkaline condition Fe (III) ions may create hydrated compounds of $Fe(OH)^{2+}$, $Fe(OH)_2^+$ and $Fe(OH)_3$. The better removal in pH values of 7–8 compared to lower solution pH is the result of more severe reaction between hydroxide and iron ions under the presence of alkalinity. In alkaline pH values higher than 8, the solubility of $Fe(OH)_3$ increases resulting in the formation of $Fe(OH)_6^-$ and $Fe(OH)_4^-$ [30] which don't participate in AMX reduction [6,21]. Furthermore the negative charge of them has converse effect on process performance [30]. In the research of Merzouk on the turbidity removal by EC process the role of pH was investigated in values of 4–10. Maximum removal efficiency was yielded at pH 8 and increasing the solution pH didn't improved the treatment process [31]. Farhadi studied the efficiency of EC process using iron electrodes on the pharmaceutical industry wastewater for the removal of COD. They reported that the best results was obtained at pH of 7 [32]. With respect to formula devoted to volume of sludge discussing on the effect of pH seems important as it shows considerable main and second order effects on the formed solids. The positive sign of pH implies on its direct effect on response. Really when solution is saturated of metal hydroxides, releasing more iron ions to water develops the formation of $Fe(OH)_3$ precipitates which ends to sweep-floc coagulation [21]. It can be better understood by reminding the soluble forms of $Fe(OH)_6^-$ and $Fe(OH)_4^-$ under more pH values that causing sooner saturation of aquatic media. Nearly 25 mL of more sludge quantity was collected under pH range of 4.5–9.5, where 10 mA·cm^{-2} of current was applied between two electrodes at distance of 2 cm in a solution of 55 mg·L^{-1} AMX antibiotics. The role of pH variation on energy consumption was negligible.

3.4. Effect of current density

In perturbation plot, the increase of current density from 7.5 to12.5 mA·cm^{-2} promoted the removal efficiency of AMX from 56.12% to 78.88%. However, the sharp trend of the curve has been ended at applied current of 12.5 mA·cm^{-2}. In fact at a higher rate of current densities evolution of more hydrogen bubbles at lower sizes intensify the removal of AMX through floating them [27]. Smaller size bubbles comparing to large ones have greater effective surface and more retention time which enhances the process efficiency. In addition at more current densities, more amounts of iron electrode which is responsible for coagulation of AMX molecules are oxidized and improve the floc formation [27]. Although EC process performance enhances by applying more values of current density, it must be noticed that increasing the reactor voltage, can't be admitted in terms of economic feasibility [6]. Herein, one-factor plot of current density effect on the consuming energy (not shown) declared 5.99 kWh·m^{-3} of energy consumption at 7.5 mA·cm^{-2} of applied current and it grew to14 kWh.m^{-3} at electrical current of 12.5 mA·cm^{-2}.

3.5. Effect of AMX concentration

Coded value C in Fig. 3 exhibits the effect of AMX concentration on its removal efficiency. Removal efficiency of AMX was reported to 46.85% and 84% at initial AMX concentration 77.5 and 32.5 mg·L^{-1}, respectively. This decrease is due to the fact that the rate of metal hydroxides generation and produced flocs in the solution is a constant quantity when values of other operational factors include electrical current, pH and inter electrode distance are constant. Consequently, at high AMX concentrations, the amounts of produced flocs weren't enough for the adsorption of AMX molecules [33].

3.6. Effect of inter electrode distance

As can be read from curve D in Fig. 2, effect of increasing the inter electrode distance from 1.5 to 2 cm on process efficiency was insignificant. However, large inter electrode distance decreased, 9% less removal was obtained with a 0.5 cm more gap from 2 cm between anode and cathode. This is due to the lower electrical currents which slow down the production rate of cations at the anode. Also, in more inter electrode distance; the possibility of interaction of hydroxide polymers and ions reduces as a result of weakened electrostatic attraction. So less concentration of flocculating material along with the reduced number of connections affects the performance of process negatively [34].

3.7. Interaction effects

As depicted in Fig. 3 when the initial concentration of AMX increased from 32.5 to 77.5 mg·L^{-1}, in pH value of 4.5, the removal efficiency decrease from 67% to 34%, and in alkaline pH value of 9.5, an efficiency reduction from 84% to 43% was observed. These variations influence on removal percent more than changes in pH values at constant concentrations of AMX. It confirms that however pH rate has a strong effect on removal efficiency, but its performance reduces significantly when higher levels of AMX must be removed. Fig. 4 displays the considerable interaction effect between current density and AMX dose at levels of –1 to +1 on the sludge volume. Since the plot sludge generation is directly related to both current density and AMX concentration, 38.84 mL of sludge was measured at level –1 for both variables, while at level +1 of them it increased markedly and reached to 90.8 mL. In this condition, Faraday's law describes:

$$C = \frac{ItM}{Zfw} \tag{12}$$

where C applies for the concentration of released coagulant to the electrolyte, t is the operating time, the applied current is in the format of I, M is the molecular weight of iron, Z shows the chemical equivalence, f exhibits the constant of Faraday and w is the volume of EC reactor. From this equation, the proportional effect of iron concentration and the current density is clear. Actually, at higher currents, the rate of iron ions liberation to the solution is a function of Faraday's law in which more amounts of generated coagulant will trap the pollutant molecules at a better rate consequence in more deposits [35]. Fig. 5 presents the simultaneous significant effect of inter-electrode spacing and current density on the energy consumption. The lowest value of energy consumption was occurred at level –1 (1.5 cm and 7.5 mA·cm^{-2}) for both parameters about 4.95 kWh·m^{-3}, while at the same coded value of current density, increasing the inter electrode distance up to 2.5 cm, led to the greater energy consumption almost 7 kWh·m^{-3}. Analogously, at applied current of 12.5 mA·cm^{-2}, 10.85 kWh·m^{-3} of electrical energy was used at the 1.5 cm inter electrode distance and up to 2.5 cm it reached to17 kWh·m^{-3}. Researchers have referred to the inter electrode distance as an important parameter on energy consumption in an electrolysis reactor. At larger spacing applying more current densities seems necessary to compensate for the restricted motion as a result of more resistance in the sample [34]. With respect to the proportional relationship between consumed energy and applied current, this consequence is unavoidable.

3.8. Optimization

The quadratic models previously provided by design expert were used for the optimization of operational conditions. In the optimization section of the software, the conditions which are favorable for each of the dependent and independent factors can be defined by selecting one of the "maximize", "minimize", "target", or "in range" goals that are named as the desired goals in the software. After determining the desired goal for each factor, several solutions were proposed by RSM that are given in Table 4. Then, the solution number 1 was chosen for conducting the confirmatory test. Accordingly, the selected solution was

Table 4
Optimum EC conditions for the removal of AMX

NO	Proposed values for independent factors				Predicted responses		
	X_1	X_2 mA·cm^{-2}	X_3 mg·L^{-1}	X_4 cm	Y_1%	Y_2 mL	Y_3 kWh·m^{-3}
1	7.87	10.17	50	1.5	77.06	67.44	7.8
2	7.9	10.2	50	1.5	77.19	67.71	7.83
3	7.92	10.19	50	1.5	77.16	67.74	7.82
4	7.37	10.52	50	1.5	77.97	67.39	8.18

Table 5
The actual values of responses resulted from validation test conducted under conditions determined by solution number 1

Parameter	Predicted value	PI low	Actual value	PI high
Removal efficiency (%)	77.06	68.93	80.2	85.19
	77.06	68.93	81.6	85.19
	77.06	68.93	80.9	85.19
Sludge volume (ml)	67.44	55.27	71.7	79.61
	67.44	55.27	69.2	79.61
	67.44	55.27	70	79.61
Energy consumption (kWh·m^{-3})	7797.79	7007.3	7121.3	8588.2
	7797.79	7007.3	7095.7	8588.2
	7797.79	7007.3	7110.1	8588.2

experimented 3 times to ensure regarding the accuracy and precision of the results in the validation test. Table 5 provides the results of the validation test for each of the responses. As Table 5 shows, the AMX removal obtained under optimized levels of parameters was in the prediction interval (PI) with a confidence level (CI) of 95% and was also close to the high PI.

4. Conclusions

Amoxicillin is a widely used antibiotic entering into the aquatic environments mostly via discharge of domestic and healthcare facilities effluents. Its harmful effects on aquatic organisms have caused trying various treatment methods which have not resulted in satisfactory removal efficiency. In this current work, the removal of AMX at different operational conditions and constant treatment time was performed in a simple electrocoagulation cell using iron electrodes. It was found that the removal efficiency was on average 80.9% in a solution containing 50 mg·L^{-1} of AMX atoptimum condition of parameters including pH 7.87, inter electrode distance 1.5 cm, and current density 10.17 mA·cm^{-2}. It was shown that current density was the most determining factor among all factors. Data of sludge generation exhibited more volumes at experiments performed under Faradic currents. With respect to the energy consumption as a drawback for a treatment method, precision in selecting the levels of operating parameters can reduce the expenses dramatically as findings of present study support.

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