Optimization of the electrocoagulation process for sulfate removal using response surface methodology

Hooshyar Hossini[1], Pouran Makhdoumi[2], Seyed Omid Rastegar[3], Fazel Mohammadi-Moghadam[4], Hamid Reza Ghaffari[5], Allahbakhsh Javid[6], <u>Nezam Mirzaei</u>[7,8*]

[1]*Department of Environmental Health Engineering, School of Public Health, Kermanshah University of Medical Sciences, Kermanshah, Iran.*
[2]*Department of pharmacodynamics and toxicology, School of pharmacy, Mashhad University of Medical Sciences, Mashhad, Iran.*
[3]*Chemical Engineering Department, Tarbiat Modares University, Tehran, Iran.*
[4]*Department of Environmental Health Engineering, School of Health, Shahrekord University of Medical Sciences, Shahrekord, Iran*
[5]*Social Determinants in Health Promotion Research Center, Hormozgan University of Medical Sciences, Bandar Abbas, Iran.*
[6]*School of Public Health, Shahroud University of Medical Sciences, Shahroud, Iran.*
[7]*Environmental Health Research Center, Kurdistan University of Medical Sciences, Sanandaj, Iran.*
[8]*Department of Environmental Health Engineering, School of Public Health, Tehran University of Medical Sciences, Tehran, Iran.*

Sulfate concentrations affected on the natural sulfur cycle in the anaerobic treatment, therefore pretreatment of wastewater containing sulfate must be considered. In this work electrocoagulation techniques have considered as an effective and environmentally friendly process for desulfurization from wastewater. Three factors including initial pH, initial sulfate concentration and current density were selected as the effective factors and were optimized using response surface methodology. An initial pH of 8, initial sulfate concentration of 80mg/l and current density of 12mA/cm^{2}were determined to be optimum values by the statistical models. The maximum sulfate removal and minimum sludge generation under optimal conditions were 68.5% and 0.075g, respectively. The kinetics of sulfate removal study investigated the pseudo-first models were better described experimental data and was selected as overall kinetic removal of sulfate.

Keywords: Sulfate removal; Electrocoagulation; Response surface methodology; Kinetics; Optimization

INTRODUCTION

High sulfate concentration in the wastewater faces important restrictions to anaerobic treatment due to several factors, including competition between sulfate reducing bacteria (SRB) and methanogenic microorganisms, non-competitive inhibition of methanogenesis due to SRB-generated sulfide, and finally the corrosive, dangerous and malodorous characteristics of sulfide. However, pretreatment of sulfate wastewater using the physical and chemical processes must be considered as an alternative [1]. Normally pulp and paper, petrochemical, edible oil, sugar-cane and solvent plants are industries that produce large amounts of wastewater containing high sulfate concentration [2]. To remove the sulfate several 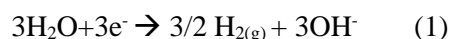processes can be applied encompassing (i) Membrane (such as reverse osmosis, electrical dialysis and filtration), (ii) Chemical precipitation(gypsum, limestone/lime, barite, barium salts or ettringite, $Ca_6Al_2(SO_4)_3(OH)_{12}.26H_2O$, (iii) ion-exchange technologies and (iv) biological treatment using sulfate-reducing microorganisms[3]. When sulfate is present in the wastewater, sulfate-reducing bacteria (SRB) are able to couple the oxidation of organic compounds and hydrogen to sulfate reduction [4].

In latest decade, electrocoagulation techniques have considered as an effective and environmentally friendly process for wastewater treatment. Due to several advantages of electrocoagulation techniques, treatment of various pollutants and contaminants such as heavy metals (Cr, Zn, Ni, and Cu), chemical oxygen demand, total organic carbon, total dissolved solids, oil and
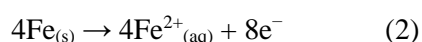
grease, phosphate, fluoride, chloride and etc. have been done [5-8]. These benefits are due to no chemical requirements, little sludge generation, strong oxidation ability, fast reaction rate and lower need space [9].

Based on electrochemical process, the electrodes (such as iron or aluminum) are generally better than other reported electrode materials. When iron is used as electrode materials, following reactions are occurred [10].
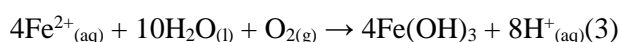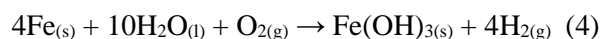
At the cathode:

$$3H_2O + 3e^- \rightarrow 3/2\ H_{2(g)} + 3OH^- \qquad (1)$$

At the anode:

$$4Fe_{(s)} \rightarrow 4Fe^{2+}_{(aq)} + 8e^- \qquad (2)$$

and with dissolved oxygen in solution:

$$4Fe^{2+}_{(aq)} + 10H_2O_{(l)} + O_{2(g)} \rightarrow 4Fe(OH)_3 + 8H^+_{(aq)} (3)$$

overall reaction:

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

During electrocoagulation with iron various species are formed such as: $Fe(OH)_4^-$, $Fe(H_2O)_3(OH)_3^0$, $Fe(H_2O)_6^{3+}$, $Fe(H_2O)_5(OH)^{2+}$, $Fe(H_2O)_4(OH)^{2+}$, $Fe_2(H_2O)_8(OH)_2^{4+}$, and $Fe(H_2O)_6(OH)_4^{4+}$ [11, 12]. In addition, depending on pH, Fe^{3+} and/or Fe^{2+} ions form various monomeric and/or polymeric metal hydroxides complexes. The most common complex is the hydrated ion $[Fe(H_2O)_6]^{3+}$. In acidic pH (pH 4–5) the hydroxo complexes reorient to a bi-nuclear iron complex species having a high surface charge, and the bi-nuclear ions have sufficient stability to exist in appreciable concentrations in solutions. In pH > 4, the octahedral hexaaquaions, $[Fe(H_2O)_6]^{3+}$, gives a red-brownish gelatinous precipitate of hydrous oxide [11-13].

The sulfidic compound was removed in the form of metal sulfide in the presence of iron or aluminum anode. Sulfite and sulfate ions are getting removed possibly by adsorption on metal oxides/hydroxides. Sulfite and sulfate ions are possibly enmeshed in the porous metal oxide/hydroxide precipitate [14]. In the electrocoagulation process, some parameters such as initial pH, reaction time, initial concentration, current density and some other parameters were considered as effective factors but

a methodology is required to optimize these parameters and to identify their interactions. Response surface methodology (RSM) is an efficient experimental tool based on statistical analysis to determine optimal conditions for a multivariable system. Statistical optimization can determine the role of each component and the interactions among the parameters, which can save time, decrease the need for instrumentation, chemicals, and manpower [15, 16]. In the present investigation, the electrode sulfurization technique is explored for instantaneous and effective removal of sulfate ion with the lowest sludge rate production. Optimization of operating conditions and effective parameters like working time, pH, sulfate concentration and current density has been done using RSM.

MATERIALS AND METHODS

Synthetic wastewater

All reagents such as HCl, NaOH, Na_2SO_4, $BaCl_2$, $MgCl_2.6H_2O$, Sodium acetate ($CH_3COONa.3H_2O$), KNO_3, acetic acid (CH_3COOH (99%)) were prepared in analytical grade, and deionized water was used in all preparations. Stock solution of sulfate (SO_4^{-2}) was made by adding the specific values of sodium sulfate (Na_2SO_4) in deionized water. The synthetic wastewater was prepared from the stock solution by dilution. The desirable concentrations of sulfate were fabricated according to design of experiment runs. For all test the pH was adjusted using 1 M HCl and 1 M NaOH.

Electro-desulfurization setup

Electro-desulfurization was carried out in the batch reactors with a 500 mL capacity using iron (Fe/Fe) electrodes with a monoplar mode. Other appurtenance of electro-desulfurization unit consist of the DC power supply (TEK-8051, 30 V and 5 A double), and two electrodes with the dimensions $140 \times 60 \times 2$ mm at a fixed distance of 1.5 cm. The contents of the electrocoagulation react or were gently aerated with a magnetic rotator (Alfa, HS-860) with 70 rpm. **Fig. 1** shows the experimental set-up. Before starting-up the each test, electrodes impurity were cleaned with 1 M H_2SO_4 and rinsed with deionized water.
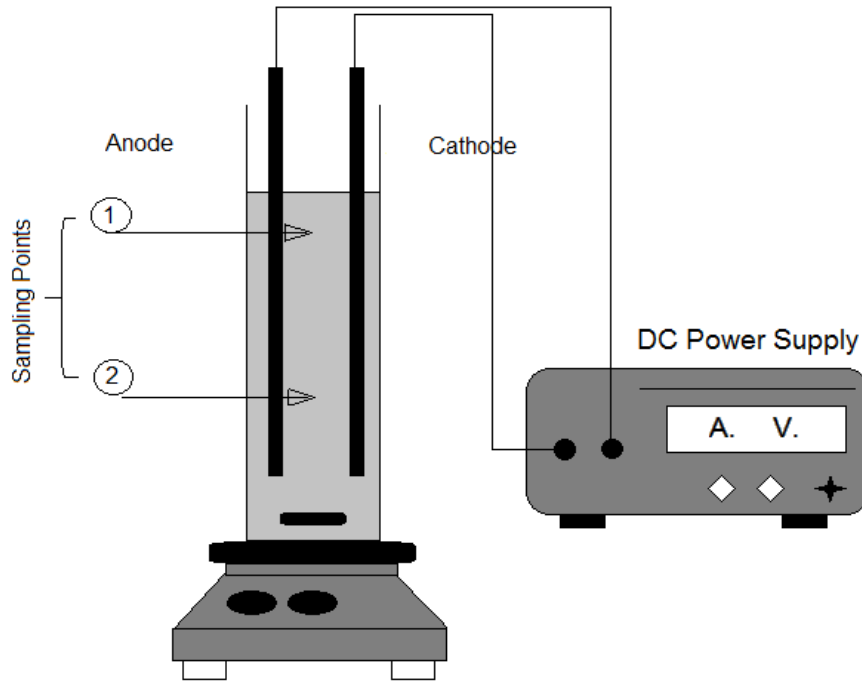
Fig. 1 Experimental set-up.

Sampling and analytical method

The samples were collected from the two points of reactor (upper and lower portions) and were filtered by Watman 0.45 μm to remove the flock and interference material. The residual sulfate was determined according to Environmental Protection Agency (EPA) procedure (Turbidimetric Method 9038)[17].Sulfate concentration was measured by turbidimetric method by UV-spectrophotometer at 420 nm (Rayleigh UV 9200, China). The other experiments were performed regard to standard methods for the examination of water and wastewater[18].

Electrochemical experiments based on RSM

RSM is a collection of mathematical and statistical techniques for empirical model building. By careful design of experiments, the objective is to optimize a response (output variable) which is influenced by several independent variables (input variables). Central composite design (CCD) was widely used for fitting a polynomial model. By using this method, modeling is possible and it requires only a minimum number of experiments. It is not necessary during the modeling procedure to know the detailed reaction mechanism since the mathematical model is empirical. According to CCD method with total number of $2k + n_\alpha + n_0$ trials, where k is the number of independent variables, n_α is axial points and n_0 center points. In this work using Design-Expert 7.1.4a 8 (2^3)

factorial design,6 (2×3) axial points with 6 central points was selected. The behavior of the system is explained by the quadratic polynomial empirical model.

$$y = \beta_0 + \sum_{i=1}^{3}\beta_i X_i + \sum_{i=1}^{3}\beta_{ii} X_i^2 + \sum_{i<1}^{3}\sum_{j=1}^{3}\beta i_j X_i X_j + \varepsilon \quad (5)$$

where, y is the expected value of the response variable, β_0, β_{ii}, β_{ij} are the model parameters, X_i and X_j are the coded factors evaluated. In this study, y represents the sulfate removal and sludge generation in the different empirical models.

Confirmation experiments

To check the validity of the models, a confirmatory experiment was done at optimal values predicted by the models. Values of sulfate removal and amount of sludge generation obtained from mentioned experiment were compared with the results predicted by the models and checked to be in the range of low and high confidence intervals.

RESULTS AND DISCUSSION

Statistical analysis

Influent pH, time, initial sulfate concentration and current density for a three-factor-five-level CCD design were used to determine the optimal values. Table 1 showed the range sand levels of the variables in this study. Each factor was varied at

five different levels while the other parameters were kept constant. Once the desired ranges of the variables had been defined, they were coded to lie at±1 for the factorial points, 0 for the center points, and ±α for the axial points [19].The experimental conditions and their responses designed using CCD method is shown in Table 2. A total of 20 experiments were required for this procedure. In order to investigate the effect of each factor including initial pH, initial sulfate concentration and current density on the response of the system, analysis of variance (ANOVA) results were calculated as shown in Table 3.

This statistical tool is required to test the significance and adequacy of the model. The mean squares (MS) were calculated as MS=SS/DF, where: SS is the sum of squares of each variation source and DF is the degrees of freedom[15, 16].The Fischer variation ratio (F-value) is a measure of how well the factors describe the variation in the data about the mean. Data has some variation around its mean value; the greater the F-value from unity, the more acceptable is this variation. The amount of p-value values for the models which were less than 0.05 (<0.0001) indicated that the models were statistically significant with a 95% confidence interval.

Table 1. Experimental variables at different levels used for the bioleaching experiment.

Factor	-α	-1	0	+1	+α
A: pH	5	6	7	8	9
B: Initial sulfate conc. (mg/l)	40	80	120	160	200
C: Current density (mA/cm^2)	4	8	12	16	20

Table 2. Experimental plan based on CCD and the results.

Run	A:pH	B: Initial Sulfate Conc. (mg/l)	C: Current Density (mA/cm^2)	Sulfate Removal %	Sludge generation (g)
1	8	80	8	48.8	0.04
2	6	160	16	45	0.21
3	7	120	12	47.1	0.09
4	5	120	12	43.6	0.11
5	8	160	8	42.4	0.05
6	7	120	12	49.6	0.11
7	7	40	12	55.0	0.10
8	6	80	8	33.3	0.04
9	7	200	12	30.3	0.01
10	8	160	16	59.8	0.08
11	7	120	4	26.6	0.03
12	7	120	12	49.7	0.11
13	7	120	12	49.5	0.09
14	7	120	12	49.5	0.11
15	6	80	8	48.8	0.1
16	6	80	16	55	0.22
17	8	80	16	50.5	0.1
18	6	160	8	42.5	0.12
19	8	160	16	74.34	0.2
20	7	120	20	73.9	0.18

Table 3. ANOVA for response surface models applied.

Response	Model	ANOVA					
		Source	S.S.	Df	M.S.	F Value	Prob> F
Sulfate removal	quadratic	Model	5449.0797	9	605.45	27.55973	< 0.0001
		A-pH	2734.9248	1	2734.92	124.4915	< 0.0001
		B-Conc.	392.03108	1	392.03	17.84493	0.0004
		C-Current	1323.1091	1	1323.10	60.22683	< 0.0001
		AB	2.6405383	1	2.64	0.120195	0.7324
		AC	163.3284	1	163.32	7.434573	0.0130
		BC	10.465232	1	10.46	0.476368	0.4980
		A^2	644.2403	1	644.24	29.32528	< 0.0001
		B^2	99.96883	1	99.96	4.550498	0.0455
		C^2	0.0773501	1	0.077	0.003520	0.9533
		Residual	439.37531	20	21.96		
		$(R^2 = 0.92$	$R^2_{adj}= 0.89)$				
Sludge generation	quadratic model	Model	0.0152038	9	0.002	38.00663	< 0.0001
		A-pH	0.0039784	1	0.004	89.50644	< 0.0001
		B-Initial sulfate Conc.	0.0039784	1	0.004	89.50644	< 0.0001
		C-Current density	0.005251	1	0.005	118.1392	< 0.0001
		AB	0.0003151	1	0.00031	7.088352	0.0150
		AC	0.0003516	1	0.00035	7.909538	0.0108
		BC	0.0002031	1	0.0002	4.568549	0.0451
		A^2	0.0007176	1	0.0007	16.14495	0.0007
		B^2	0.0002626	1	0.00026	5.908249	0.0246
		C^2	3.161E-05	1	0.00003	0.711155	0.4090
		Residual	0.000889	20	0.00004		
		$(R^2=0.94$	$R^2_{adj}=0.91)$				

Sulfate removal

The model equation for coded values in a quadratic model fitting the experimental results for sulfate removal can be seen in Eq. (6).

$$\text{Removal} =48.63+10.67A-4.04B+7.42C+0.41AB+3.19AC+0.81BC+4.80A^2-1.89B^2+0.053C^2 \quad (6)$$

where A is pH, B is initial sulfate concentration and C is current density (mA/cm^2). It should be noted that polynomial models are reasonable approximations of the true functional relationship over relatively small regions of the entire space of independent variables [20]. Fig. 2 shows the predicted data (date that was gathered from model to percentage of metals recovery) versus actual data (data that was gathered from experimental condition to percentage of metals recovery). Results show the very good agreement between the experimental and predicted values. The relatively high R^2 and adjusted R^2 (R^2adj) (0.92 and 89 respectively) values that presented in Table 3 indicate that the modified quadratic model is capable of representing the system under the given experimental conditions.
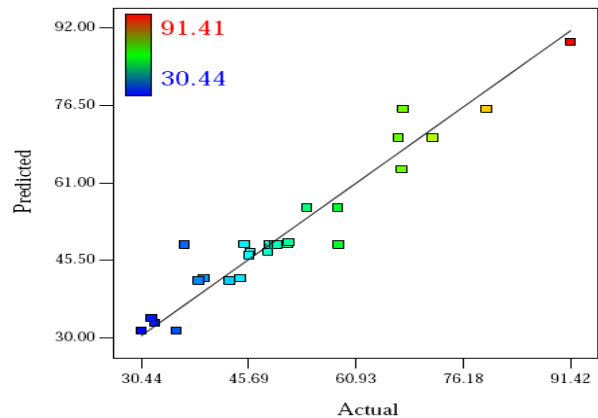

Fig. 2. Predicted vs. actual values for sulfate removal.

Fig.3 shows the sulfate removal efficiency contour plots. There is clearly in Fig. 3a a combined effect of pH and initial sulfate concentration on sulfate removal at a constant current density (16 mA/cm^2). The maximum sulfate removal (>73%) was observed for initial sulfate concentration of 80 mg/l and pH of 8.
Fig. 3b shows combined effect of initial pH and current density on the sulfate removal at a constant initial sulfate concentration of 80 mg/l. With current density increasing from 8 mA/cm^2 to16

mA/cm^2, the sulfate removal efficiency increased. The maximum sulfate removal (>73%) was observed for the current density 16 $mA/cm^2$and initial pH 8. Current density increasing result in higher production of iron complexes means coagulant concentration was increased in the aqueous phase; therefore the efficiency of sulfate was increased that is compatible with Faraday's law.
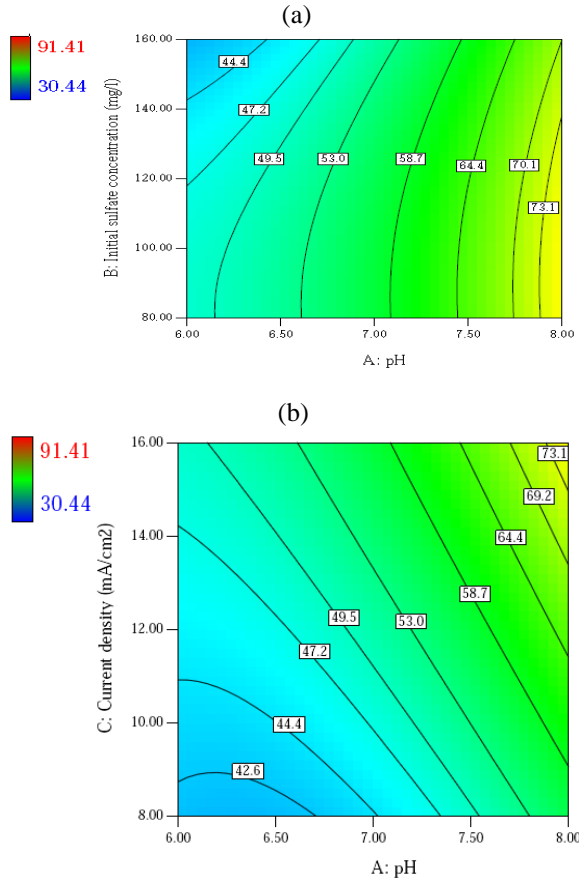

(a)

(b)

Fig.3. Contour plots of the interactive effect for sulfate removal: **(a)** effect of initial pHand initial sulfate concentration at the constant current density of 16 mA/cm^2 and **(b)** effect ofinitial pH and current density at the constant initial sulfate concentration of 80 mg/l.

Sludge generation

The model equation for coded values in the quadratic model fittingthe experimental results of sludge production can be seen in Eq.(7):

$$Sludge\ generation = 0.074 + 0.013\ A + 0.013B + 0.015C + 4.438E\text{-}003AB + 4.688E\text{-}003\ AC + 3.563E\text{-}003BC + 5.062E\text{-}003A^2 - 3.062E\text{-}003B^2 + 1.063E\text{-}003\ C^2 \quad (7)$$

where A is pH, B isinitial sulfate concentration and Cis current density (mA/cm^2).Fig.4 shows the actual and the predicted sludge generation. The clustering of the points around the diagonal line

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indicates a satisfactory correlation between the experimental data and the predicted values, confirming the robustness of the model.R^2 and adjusted R^2 (R^2adj) were found to be 0.94 and 0.91, respectively indicating that actual and predicted sludge generation were in agreement. The effect of pH and initial sulfate concentration on the amount of sludge generation is shown in Fig. 5a. According to this figure amount of sludge will be decreased from 0.13 g to 0.06 g by pH decreasing from 8 to 6 and initial sulfate decreasing from 160 mg/l to 80 mg/l at a constant current density 16 mA/cm^2.

Fig. 5b shows the interaction between pH and current density. According to this figure, the amount of sludge generation decreased by the decreasing of pH from 8 to 6 and the current density from $16mA/cm^2$to 8 mA/cm^2 at a constant initial sulfate 120 mg/l. It should be say that in the pH below of isoelectric point (iep), iep of iron oxide/hydroxide was 7.7, the mechanism of removal sulfate is precipitation and in the pH higher than it the mechanism of removal sulfate is adsorption[14].By increasing the current density, the bubble flux and in turn the collision probability is increased. At the same time, the dissolution of anode and in turn concentration of metal ions also increases. At higher current densities the consumption of electrodes is high[14]. Thus current density plays an important role in achieving optimum results.
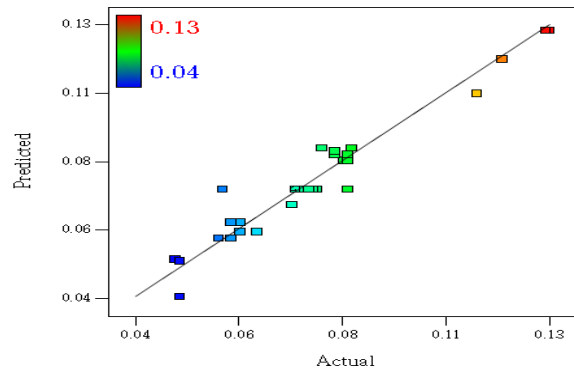

Fig.4. Predicted vs. actual values for sludge production.

Process optimization

In the numerical optimization, a minimum and a maximum level must be provided for each parameter. The goals are combined into an overall desirability function. Desirability is an objective function that ranges from zero outside of the limits to one at the goal. The program seeks to maximize this function. By starting from several points in the design space chances improve for finding the best local maximum are high[21]. A multiple response method was applied for optimization of any

combination of two goals namely sulfate removal and sludge generation. Level of all parameters within the range of investigation was set for maximum sulfate removal and minimum sludge generation. According to numerical optimization by Design-Expert 7.1.4, at optimal conditions as follows: pH 8, initial sulfate concentration 80 mg/l and current density 12 mA/cm^2, the maximum sulfate removal and minimum sludge generation were predicted as 68.5% and 0.075 g, respectively.

Confirmatory experiments

To test the validity of the optimized conditions given by the model, an experiment was carried out with the parameter suggested by the model. Table 4 presents the results of the experiment conducted at the optimal conditions and showed that verification experiment and the predicted values from fitted correlations were in close agreement at a 95%confidence interval. These results confirmed the validity of the model, and the experimental values were determined to be quite close to the predicted values. Under these conditions, the experimental value for the sulfate removal and sludge generation was found to be 68.5% and 0.075 g, respectively. The 95% confidence interval (C.I.) is the range in which the process average was expected to fall 95% of the time.

Kinetic study

Fig. 6 shows the trend of sulfate removal efficiency under optimal conditions including initial pH 8, initial sulfate concentration 80 mg/l and current density 16 mA/cm^2. Accordingly, large portion of sulfate was removed in first 5 min, and then the removal efficiency is increased, gradually. Maximum removal efficiency was determined around 85% at endpoint of 90 min. To evaluate the kinetics of sulfate removal, two of the most used kinetic models pseudo-first order (Eq. 8) and pseudo-second order (Eq. 9) were fitted to experimental results. The equation of two used kinetic are define as following[22]:

$$\ln C_t = \ln C_0 - k_1 t, \quad (8)$$
$$\frac{1}{C_t} = k_2 t + \frac{1}{C_0}, \quad (9)$$

where $C_0$is the initial sulfate concentration and C_t is the sulfate concentration after time t; k_1 and k_2 are the first and second-order kinetic constants, respectively. The linear equations of the kinetic plots and their correlation factor were shown in the Fig. 7. The kinetic constants values of the k_1 and k_2 were obtained about0.0214 min^{-1} and 0.0008l.g^{-1}min^{-1}, respectively. The correlation factor (R^2) of the straight lines was 0.97 for the pseudo-first order and 0.95for the pseudo-second order. It was evident that the correlation coefficient for the pseudo-first-order kinetic model was higher than pseudo-second order; therefore the removal of sulfate using electrocoagulation method follows the pseudo-first-order kinetic model for the entire process.
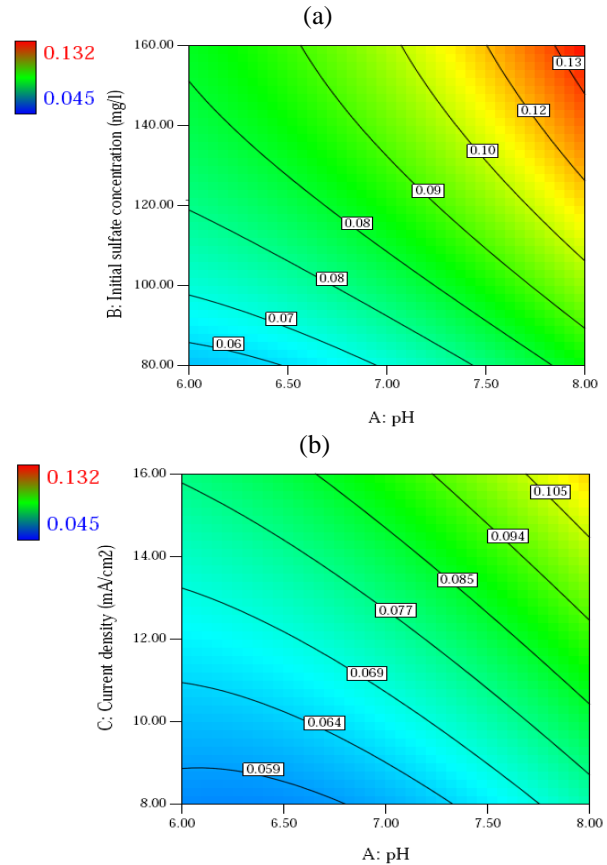
Fig.5. Contour plots of the interactive effect for sludge production: (a) effect of initial pHand initial sulfate concentration at the constant current density of 16 mA/cm^2 and (b) effect of initial pH and current density at the constant initial sulfate concentration of 120 mg/l.
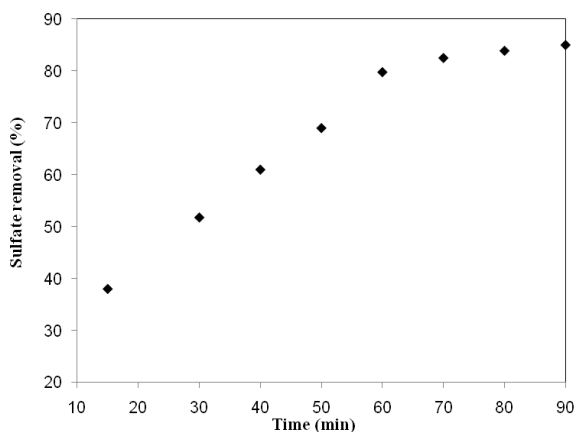
Table 4. Verification of the model at optimum condition.

Response (%)	Target	Correlation Predicted (%)	Confirmation Experiment (%)	95% CI Low	95% CI High
Sulfate removal (%)	Maximize	66.6	68.5±0.2	62.2	71
Sludge generation (g)	Minimize	0.07	0.075±0.005	0.06	0.08

Fig. 6. Sulfate removal efficiency vs. time under optimal condition (initial pH 8, initial sulfate 80 mg/l and current density 12 mA/cm^2).
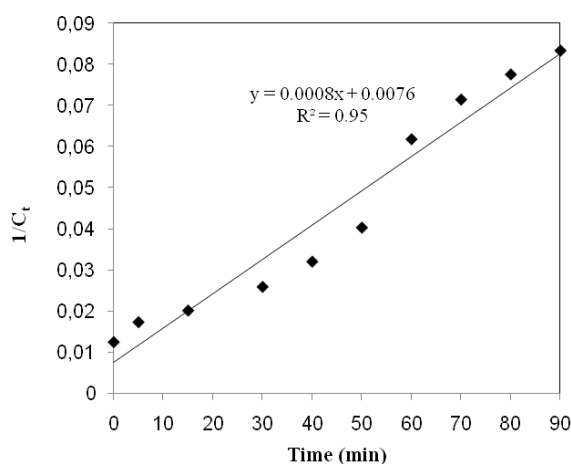
(a)

$y = -0.0214x + 4.2522$
$R^2 = 0.97$

(b)

$y = 0.0008x + 0.0076$
$R^2 = 0.95$
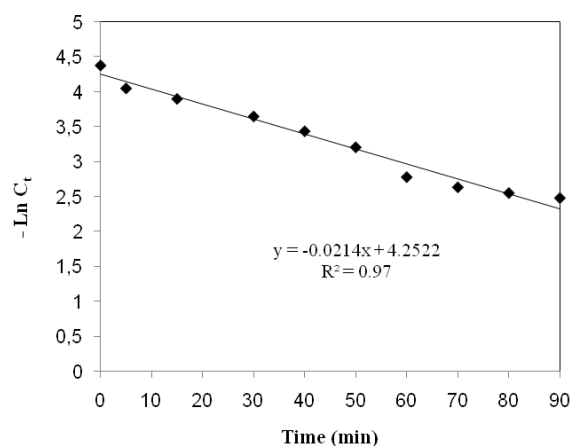
Fig. 7. The plots of the kinetic model **(a)** Pseudo first order **(b)** Pseudo second order.

CONCLUSION

Removal of sulfate from synthetic effluents was studied using electrocoagulation method.CCD was fitted with a modified quadratic model polynomial

equation for both sulfate removal and sludge production. The optimum values for variables were pH 8, initial sulfate concentration 80 mg/l and current density 12 mA/cm^2.Maximum sulfate removal and minimum sludge generation were obtained as 68.5% and 0.075g, respectively. The kinetics of sulfate removal was investigated using the pseudo-first and second order models. Results showed the experimental data were better described by pseudo-first order and was selected as overall kinetic removal of sulfate.

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