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Simulation of operation cost for nitrate removal using response surface method in electrocoagulation process

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***Abstract*— In this research, response surface methodology (RSM) was applied to model the effect of main operational variables including initial pH, initial nitrate concentration, applied current, electrode number and reaction time on the operation cost of nitrate removal by electrocoagulation. It was found that the initial pH, initial nitrate concentration and applied current are the most effective parameters on the model. According to the ANOVA (analysis of variance) results, the model presented high R^2 value of 95% for operation cost, which indicates that the accuracy of the polynomial model is acceptable. It can be concluded that RSM is a powerful tool for simulation of operation cost in electrocoagulation process for nitrate removal.**

***Keywords*— electrocogulation, operation cost, nitrate, response surface method**

I. Introduction

Electrocoagulation (EC) is one of the modern treatment methods, which has been used successfully to remove different kinds of pollutants [1]. Electrocoagulation is a process consists of creating metallic hydroxide flocs within the solution by electro-dissolution of soluble anodes usually made of iron or aluminum [2]. Three main processes occur during electrocoagulation are: electrolytic reactions at the surface of electrodes, formation of coagulants in aqueous phase, adsorption of pollutants on coagulants/ removal by sedimentation or flotation [3]. The main reactions for aluminum are as follows [4]:

At the cathode:

$$3H_2O + 3e \rightarrow \frac{3}{2}H_2(g) + 3OH^- \quad (1)$$

At the anode:

$$Al \rightarrow Al^{3+} + 3e \quad (2)$$

In the solution:

$$Al^{3+}(aq) + 3H_2O \rightarrow Al(OH)_3 + 3H^+(aq) \quad (3)$$

Nitrate is a stable and highly soluble ion with low potential for co-precipitation or adsorption [5]. Among all of the contaminants of drinking water, nitrate occupies an important place as it is generated mainly by basic human activities such as agricultural/urban runoff, disposal of untreated domestic/ urban runoff, and industrial wastewater in unsafe manner, leakage in septic systems, landfill leachate and animal manure [6]. Methemoglobinemia is one of the main health problems due to the high levels of nitrate in drinking water [7]. Conventional methods of removing nitrate from wastewater include biological decomposition, ion exchange, chemical treatment, reverse osmosis and membrane separation techniques [5, 8]. In recent years, EC has been focused on by a large number of researchers for removal of nitrate due to its high treatment efficiency, absence of sludge production, easy operation and relatively low capital cost. In particular, electrocoagulation has demonstrated an attractive alternative to the other traditional methods for treating nitrate contaminated water [8-12]. This process is limited in practice due to formation of by-products like nitrite during treatment [8].

As is well known, limitation of classical methods of studying a process such as time consuming due to large number of experiments and high cost due to using materials, can be eliminated by statistical experimental design such as response surface methodology (RSM) [13]. Many researchers applied this method for economical analysis of different pollutants by EC [14-16], but literature showed rarely has been used for nitrate [5, 8-10, 17-21].

The main objective of the present study is to model operation cost of nitrate removal as response using an electrocoagulation unit with aluminum electrodes operating in batch regime. For modelling this process the relation between operation cost and five quantitative variables (initial pH, initial nitrate concentration, reaction time, number of electrodes, current) is determined by a second order polynomial model.

II. Materials and Methods

A. *EC reactor*

A batch flow EC reactor was made in the lab from Plexiglas with dimensions of 50cm×10cm×9. Aluminum plate electrodes with the effective area of 42 cm^2 and thickness of 1mm were used in this research. Inter electrodes distance was maintained at 10 mm and electrodes were connected to a DC power supply (Micro, PW4053R, 0-5A, 0-40V) in bipolar mode. Two hotplate magnetic stirrer (Labtech Hotplate Stirrer, LMS-1003, Korea) was applied for preparing complete mixed solutions in the EC reactor. The EC reactor used in this study is shown in Fig.1.

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Figure 1. Photograph of the EC's set-up.

B. Experimental procedure

Coagulation, flocculation, settling and flotation were taking place within the EC reactor. All the experiments were carried out at room temperature. Nitrate solutions were prepared synthetically by dissolving proper amounts of $NaNO_3$ (Merck, solubility 874 g/l) and Na_2SO_4 (Merck, 99%) as supporting electrolyte in 3.7L of distilled water. The amounts of Na_2SO_4 added in each experiment are depending on the applied currents. The initial pH of the solution was adjusted before the experiment by H_2SO_4 and NaOH, and pH values were measured using pH meter (340i, WTW, Germany). Electro conductivity (EC) was recorded by EC meter (Cond 340i, WTW, Germany).

C. Experimental design and data analysis

RSM is a well-known up to date approach for constructing approximation models based on either physical experiments, computer experiments (simulations) with minimum number of experiments, as well as to analyze the interaction between parameters [22, 23]. The most popular class of second –order designs called central composite design (CCD) was used for the RSM [1].

In the present study, the CCD was selected for experimental design of the operating costs. Five factors, including (initial pH, initial nitrate concentration, current, electrode number and reaction time) with five-levels were employed for response surface modeling in the electrocoagulation process. A total of 57 experiments were carried out according to a 2^5 full factorial CCD, consisting of 32 factorial experiments, 10 axial experiments on the axis at a distance of ± α from the center, and 15 replicates at the center of the experimental domain. The value of α for rotatability depends on the number of points in the factorial portion of the design, which is given in Eq. (4):

$$\alpha = (N_F)^{\frac{1}{4}} \qquad (4)$$

Where N_F is the number of points in the cube portion of the design ($N_F = 2^k$, k is the number of factors) [13]. Therefore, α is equal to $(2^5)^{1/4} = 2.4$ according to Eq. (4).

The statistical software "Minitab", version 16.1.0 was also used for CCD and develops a simulation model. Several experiments were initiated as a preliminary study for determining the range of parameters prior to designing the experimental runs. 5-level factors were used to build models as shown in Table 1.

TABLE 1. EXPERIMENTAL RANGE AND LEVELS OF INDEPENDENT VARIABLES ACCORDING TO RSM DESIGN.

Variables	Factor	Unit	Levels				
			-α	*-1*	*0*	*+1*	*+α*
Initial pH	X_1	-	1.9	4	5.5	7	9.1
Applied current	X_2	Ampere	0.95	2	2.75	3.5	4.55
Initial concentration of nitrate	X_3	mg/l NO_3^-	160	300	400	500	640
Electrode number	X_4	-	5	8	10	12	15
Reaction time	X_5	min	61	110	145	180	229

Operating costs of the electrocoagulation process were taken as the responses of the experiments (Y_i) according to Eq. (5):

$$Y_i = b_0 + \sum_{i=1}^{n} b_i x_i + \sum_{i=1}^{n} b_{ii} x_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} b_{ij} x_i x_j \qquad (5)$$

Where Y_i is the response, b_0, b_i, b_{ii}, b_{ij} are the constant coefficient, the linear coefficients, the quadratic coefficients and the interaction coefficients, respectively, and x_i, x_j are the coded values of the variables.

D. Calculation of operating costs

Operating costs in EC process may include several items such as costs of electrodes, electrical energy, chemicals, maintenance, sludge dewatering/disposal. In this research, electrode material, electrical energy consumption and chemicals costs were taken as major cost terms in the calculation of operating costs (US$/Kg NO_3 removed) using the following equation (Eq. (6)). In order to make an economical assessment, mass depletion of the electrodes was calculated by subtracting the final weight of aluminum plates from their initial weight. Also Na_2SO_4 was major chemicals as supporting electrolyte that amounts of it depend on required current.

$$\text{Operating costs} = aC_{energy} + bC_{electrodes} + cC_{chemicals} \qquad (6)$$

Where, C_{energy} (kwh/ Kg NO_3 removed), $C_{electrodes}$ (kg Al/ Kg NO_3 removed) and $C_{chemicals}$ (gr chemicals/ Kg NO_3 removed) are consumption quantities in the experiments of nitrate removal. Coefficients a, b and c are the local prices (Iran) in the winter of 2013 are shown in Table 2.

TABLE 2. COEFFICIENTS OF OPERATING COST EQUATION.

Coefficient	Type	Value	Unit
a	Industrial electrical energy price in Iran	0.011	US$/kwh
b	Wholesale electrode material price in Iran	3.05	US$/kg Al
c	Industrial Na_2SO_4 (as major chemicals) price in Iran	342.8	US$/ton Na_2SO_4

III. Results and Discussion

A. *Development of regression model equation*

In order to study the effect of variables, experiments were performed for different combinations of the parameters using statistically designed experiments. The coefficients of the response function (Eq. 5), the P and the F values for all responses are also listed in Table 3. Also Table 4 presents the observed operating costs for the 57 experiments.

The second order polynomial equation for nitrate removal in terms of coded factors is given by the Eq. (7):

$$y = 11.41 - 0.21x_1 + 1.94x_2 - 3.29x_3 + 0.24x_4 + 0.57x_5 + \\ +0.12x_1x_2 - 0.88x_1x_3 + 0.13x_1x_4 - 1.04x_1x_5 + 0.076x_2x_3 + \\ +1.71x_2x_5 + 0.69x_3x_4 + 0.75x_3x_5 + 0.47x_1^2 + 1.09x_3^2 + 0.68x_1x_2x_5 + \\ +0.48x_1x_3x_4 - 0.88x_1x_3x_5 - 1.54x_2x_3x_5 - 1.67x_1^2x_2 \quad (7)$$

TABLE 3. ESTIMATED REGRESSION COEFFICIENTS FOR OPERATING COSTS (US $ / KG NO3 REMOVED) IN CODED UNITS.

Term	Coefficient	P-value	F-value
Constant	11.41	< 0.0001	23.90
X_1	-0.21	0.3730	0.82
X_2	1.94	< 0.0001	45.43
X_3	-3.29	< 0.0001	84.02
X_4	0.24	0.1760	1.94
X_5	0.57	0.0423	4.56
X_1X_2	0.12	0.5858	0.30
X_1X_3	-0.88	0.0011	13.41
X_1X_4	0.13	0.5420	0.38
X_1X_5	-1.04	0.0002	18.80
X_2X_3	0.076	0.8301	0.047
X_2X_5	1.71	< 0.0001	23.72
X_3X_4	0.69	0.0041	9.88
X_3X_5	0.75	0.0466	4.37
X_1^2	0.47	0.0190	6.26
X_3^2	1.09	< 0.0001	21.84
$X_1X_2X_5$	0.68	0.0053	9.26
$X_1X_3X_4$	0.48	0.0316	5.16
$X_1X_3X_5$	-0.88	0.0011	13.56
$X_2X_3X_5$	-1.54	0.0002	19.31
$X_1^2X_2$	-1.67	0.0010	13.66

The most important parameters, which affect the operation costs of nitrate removal are initial pH, initial nitrate concentration and current. While, it was found that square terms of initial pH and initial nitrate concentration and interaction terms except X_2X_4, X_4X_5 were significant to the response. Triple interaction terms of $X_1X_2X_5$, $X_1X_3X_4$, $X_1X_3X_5$ and $X_2X_3X_5$ were significant to the response.

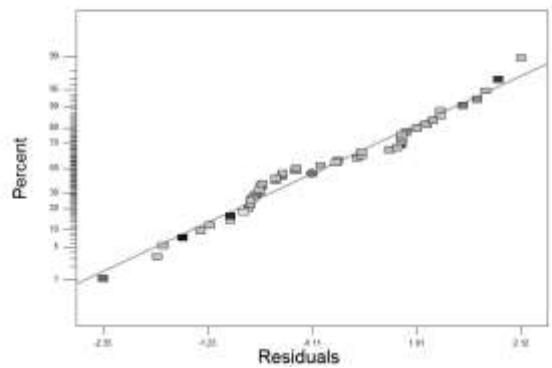
TABLE 4. RSM DESIGN AND ITS OBSERVED VALUES.

Run Number	Initial pH (X1)	Current (X2)	Initial nitrate concentration (X3)	Electrode Number (X4)	Reaction time (X5)	Observed Operating Costs (US$/Kg NO_3 removed)
42	4	3.5	500	8	110	8.39
41	5.5	2.75	400	10	145	11.14
11	4	2	500	12	110	7.91
16	4	2	300	8	180	12.00
19	5.5	2.75	400	10	145	9.72
32	7	3.5	500	8	110	7.71
12	5.5	2.75	400	10	145	12.10
50	7	3.5	300	12	110	12.85
10	5.5	4.55	400	10	145	15.41
53	7	2	500	8	110	7.64
5	5.5	2.75	400	10	145	10.65
14	7	3.5	500	8	180	9.16
25	5.5	2.75	160	10	145	25.53
52	4	2	300	8	110	3.37
3	5.5	2.75	400	10	145	12.18
51	5.5	2.75	400	10	145	11.76
18	7	2	300	8	110	7.94
2	5.5	2.75	400	10	145	12.22
17	9.1	2.75	400	10	145	13.36
45	7	3.5	500	12	180	11.48
22	7	2	500	12	110	11.64
33	7	2	300	12	180	10.81
44	7	2	300	8	180	14.47
47	5.5	2.75	400	14.8	145	10.88
13	5.5	2.75	400	10	145	11.81
35	4	3.5	300	12	110	13.11
27	5.5	2.75	400	10	145	10.68
15	4	3.5	300	8	180	19.31
1	4	2	500	8	180	14.55
57	7	3.5	300	8	110	14.55
48	5.5	2.75	400	10	145	10.94
34	4	3.5	500	12	110	8.18
28	5.5	2.75	400	10	61	11.23
23	5.5	2.75	400	10	145	12.22
26	5.5	2.75	400	10	145	11.81
24	7	2	500	12	180	8.03
21	5.5	2.75	400	5.2	145	10.46
8	7	3.5	500	12	110	9.96
4	4	3.5	500	12	180	13.02
6	7	2	500	8	180	5.71
43	4	2	300	12	180	13.53
37	5.5	2.75	400	10	145	10.68
56	4	2	500	12	180	5.90
55	1.9	2.75	400	10	145	66.41
7	4	2	300	12	110	9.10
38	5.5	2.75	640	10	145	9.57
49	7	3.5	300	8	180	20.18
29	4	3.5	300	12	180	17.60
20	5.5	2.75	400	10	145	10.94
31	5.5	2.75	400	10	229	13.64
46	7	2	300	12	110	2.63
54	4	3.5	500	8	180	13.12
30	4	2	500	8	110	5.70
40	5.5	0.95	400	10	145	6.12
36	5.5	2.75	400	10	145	12.22

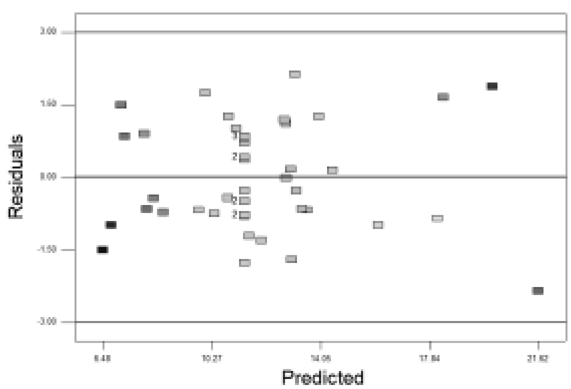
Table 5 showed the coefficient of determination (R^2) and lack of fit for operation cost of nitrate removal. High R^2 values of 95% for operation cost of nitrate removal expresses a high correlation between the observed and predicted values. Fig. 2 (a and b) compares observed operating costs with the predicted values obtained from the model. The figure indicated good agreements between the observed and predicted values.

TABLE 5. COEFFICIENTS OF DETERMINATION AND LACK OF FIT FOR OPERATION COST MODEL.

Parameter		Value
R^2		0.95
Adjusted-R^2		0.90
Predicted-R^2		0.73
Lack of fit	P-value	0.08
	F-value	2.24



(a)



(b)

Figure 2. a) Normal probability plot b) Residual versus fits plot.

The adequacy of the model was also evaluated by the residuals (difference between the observed and the predicted response value). Residuals are thought as elements of variation unexplained by the fitted model and then it expects that they occur according to the normal distribution. Normal probability plots are a suitable graphical method for judging the normality of the residuals. Observed residuals are plotted against the expected values, given by a normal distribution [24]. As seen in Fig. 2(a), the normality assumption was satisfied relatively as the points in the plot formed fairly straight line. The goodness of model fit was also examined with the plot of residuals versus fits in Fig. 2(b). For a model to be reliable, no series of increasing or decreasing points, patterns such as increasing residuals with increasing fits and a predominance of positive or negative residuals should be found. Both of plots in Fig. 2 revealed that model is adequate to describe the operation cost of nitrate removal by response surface methodology.

It can be concluded that the main effective parameters in evaluation of operation cost on nitrate removal using electrocoagulation process are: initial pH, initial nitrate concentration and current. Also according to the ANOVA results, the model presented high R-squared value of 95% and for operation cost which indicates the good accuracy of the polynomial model. Therefore, RSM is a powerful tool for simulation of operation cost on nitrate removal using EC process.

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