Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2016.1177735

57 (2016) 27827–27833
December

Taylor & Francis
Taylor & Francis Group

Optimization of As(III) removal in hard water by electrocoagulation using central composite design with response surface methodology

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Received 2 December 2015; Accepted 8 April 2016

ABSTRACT

Central composite design with response surface methodology was applied to optimize the main experimental parameters such as current, time, As(III) concentration, and hardness for arsenic (III) removal in hard water by the electrocoagulation process. The main aim was to find the optimum process parameters to maximize arsenic removal from the mathematical model equations developed in this study using R software. By variance and regression analysis, the linear regression equation was established as a predicted model. The R^2 of 0.93 indicated that the equation was well fitted. The optimum condition of 99% of As(III) removal for current (A), time (min), As(III) concentration (ppb), and hardness (mg/L as $CaCO_3$) is 0.07, 37, 274, and 324, respectively. ANOVA analysis shows no significant difference between the observed and predicted values (p-value > 0.05) which shows good fit to the model.

Keywords: Central composite design; Response surface methodology; As(III); Electrocoagulation

1. Introduction

As water is one of the most vital elements on the earth, human health may be directly affected by it and one of the key categories of health risks can be related to chemical pollutants. Arsenic is a naturally occurring class one human carcinogen that is widespread in ground water in many parts of the world [1–3]. Arsenic is widely distributed in nature and is commonly associated with the ores of metals like copper, lead, and gold. Dissolved As(V) and As(III) species have been found to simultaneously exist in many contaminated groundwater. But many studies had been reported that trivalent arsenic (arsenite, As(III)) predominates in moderately reducing anaerobic environments such as groundwater [4,5].

The technologies that have been reviewed in the literature for arsenic removal from water include chemical coagulation, lime softening, adsorption on activated alumina, ion exchange, electrodialysis, reverse osmosis, nanofiltration, and electrocoagulation [6]. Most of the methods currently employed for arsenic removal from drinking water are based on As

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(III) oxidation followed by adsorption or co-precipitation of As(V) with iron and other metal oxides [7,8].

Electrocoagulation (EC), where the coagulant is *in situ* generated, is based on the electrolytic oxidation of anode materials. This water treatment technology has proven to be more effective for As(III) removal compared to chemical coagulation (using ferric ions as coagulant) [9,10]. The cell reaction, using an iron anode, is given by Eq. (1):

$$2Fe_{(s)} + 6H_2O \longrightarrow 2Fe(OH)_{3(s)} + 3H_{2(g)} \quad (1)$$

With $Fe(OH)_{3(s)}$ formation in which the pollutants (Arsenic) may co-precipitate or adsorb (Eq. (2)):

$$\begin{aligned} &Fe(OH)_{3(s)} + \text{Pollutant}_{(\text{bulk aqueous solution})} \\ &\longrightarrow [Fe(OH)_{3(s)} + \text{Pollutant on its surface}] \end{aligned} \quad (2)$$

In this study, the method of electrocoagulation is applied to remove As(III) (arsenite) in hard waters; the response surface methodology (RSM) and the central composite design (CCD) are used for the experimental design. RSM is a collection of mathematical and statistical techniques for empirical model building, evaluating the effects of several factors and searching optimum conditions. By careful design of experiments, the objective is to optimize a response (output variable), which is influenced by several independent variables (input variables). Despite the traditional approaches, which are time and energy-consuming, the application of RSM to design optimization is aimed at reducing the cost of expensive analysis methods and time. A second-order model can be constructed efficiently with CCD (which is a common method in the RSM) and the relationships between the independent variables and the dependent variables can be assessed by giving information about interaction between variables in relation to the dependent variable [11–13]. This work is aimed at finding the optimal process parameters to maximize the removal of As(III) using the mathematical model equations developed in this study.

2. Methods and materials

2.1. Chemicals

All solutions were prepared with distilled water using sulfuric acid, sodium hydroxide, hydrochloride acid, $CaCl_2 \cdot 2H_2O$, $MgSO_4 \cdot 7H_2O$, and $NaAsO_2$. Chemicals were purchased from Merck or Sigma and used as received without further purification.

2.2. Electrocoagulation experiments

The electrocoagulation treatment for As(III) removal from aqueous solution was carried out using a reactor made up of an electrolytic cell (EC) comprised with iron anode and iron cathode (15 cm × 10 cm × 15 cm) in 1.5 L capacity (Plexiglas rectangular cell). The distance between the electrodes was 15 mm and the effective area of electrodes was 50 cm^2. Prior to experiments, electrodes were chemically cleaned with HCl (15 wt.%) and rinsed with ultrapure water three times to remove the iron oxides and any passive film that may have formed. Then, they were connected to a DC power supply (0−40 V, 0−3 A). The current density studied was inside the range of 1–2 mA/cm^2. For each run, 1 L of sample was placed into the EC cell, and the pH was adjusted to seven. The arsenic solutions were filtered through Whatman Filter after settling and analyzed using inductively coupled plasma-atomic emission spectrometry (ICP-AES), (Ultima 2C, French).

The experimental removal efficiency of As(III) and the energy consumption were calculated by Eqs. (3) and (4), respectively:

$$\text{Removal efficiency } (\%) = \left(\frac{C_0 - C_t}{C_0}\right) \times 10^2 \quad (3)$$

Table 1
Independent variables and levels (coded and uncoded) of central composite design

Independent variables	Symbol	Levels of variables				
		−2	−1	0	+1	+2
Current (A)	x_1	0.05	0.0625	0.075	0.0875	0.1
Time (min)	x_2	15	26.25	37.5	48.75	60
As(III) Concentration (ppb)	x_3	50	162.5	275	387.5	500
Hardness (mg/L as $CaCO_3$)	x_4	150	237.5	325	412.5	500

$$\text{Energy consumption}\left(\frac{\text{Wh}}{m^3}\right)=\frac{\text{Eit}}{V} \quad (4)$$

where C_0 and C_t are the initial and final concentrations of As(III) in solution (ppb), E is the cell voltage (V), i is the current (A), t is the electrocoagulation time (h), and V is the volume of the treated wastewater (m^3).

2.3. Design of Experiments

Different parameters may affect the efficiency of arsenite removal which are necessary to be considered and optimized. In the first, half fractional factorial design as a screening design was carried out to determine which of the several experimental variables and their interactions present significant effects. Then the CCD was employed to investigate the As(III) removal efficiency in hard water. The RSM was used for the evaluation of the combined effects of current (x_1), time (x_2), As(III) concentration (x_3), and hardness (x_4) on the electrocoagulation process. Design generation and statistical analysis were performed using the R software [14] by response surface methodology (RSM) package [13]. R is a free and open source software environment which is used for statistical computing and graphics [14]. The ranges of independent variables and experimental conditions derived from CCD are summarized in Table 1. Total number of experiments carried out was 39, consisting of 8 axial, 16 factorial, and 15 center points.

The chosen independent variables used in this experiment are coded according to Eq. (5):

$$X_i=\frac{x_i-x_0}{\Delta x_i} \quad i=1,2,\ldots,k \quad (5)$$

where X_i is the dimensionless-coded value of an independent variable; x_i is the real value of an independent variable; x_0 is the real value of an independent variable at the center point; and Δx_i is the step change of the real value of the variable i.

The data from the design were used to create a prediction model. The empirical second-order polynomial model was shown as follows (Eq. (6)):

$$Y=\beta_0+\sum_{j=1}^{k}\beta_j x_j+\sum_{j=1}^{k}\beta_{jj}x_j^2+\sum\sum_{i<j=2}^{k}\beta_{ij}x_i x_j \quad (6)$$

where Y is the response; x_i and x_j are variables (i and j ranged from 1 to k); β_0 is the constant term; β_j is the linear coefficient, β_{ij} is the interaction coefficient, and β_{jj} is the quadratic coefficient; k is the number of independent parameters (k = 4 in this study) [15].

2.4. Statistical analysis

The experimental data were analyzed by multiple regression analysis through the generalized least square

Table 2
Independent variables and result for the As(III) removal by central composite design

Run order	x_1	x_2	x_3	x_4	Removal (%) Experimental	Removal (%) Predicted
1	+1	+1	+1	−1	98.83	98.92
2	−1	+1	−1	−1	97.83	97.95
3	−1	+1	+1	−1	99.98	100
4	0	0	0	0	99	99.01
5	−1	−1	+1	−1	98.44	98.51
6	0	0	0	0	99.15	99.01
7	+1	−1	−1	−1	98.17	98.41
8	0	0	0	0	99.18	99.01
9	+1	−1	+1	+1	98.33	98.52
10	−1	−1	−1	−1	99.37	99.54
11	0	0	0	0	99.18	99.01
12	−1	+1	−1	+1	99.77	99.95
13	−1	+1	+1	+1	99.08	99.16
14	+1	+1	−1	+1	99.93	100.2
15	+1	+1	−1	−1	99.62	99.81
16	−1	−1	−1	+1	99.21	99.43
17	+1	−1	+1	−1	97.16	97.3
18	−1	−1	+1	+1	96.75	96.87
19	+1	+1	+1	+1	99.56	99.71
20	0	0	0	0	99.15	99.01
21	0	0	0	0	99.17	99.01
22	0	0	0	0	99.17	99.01
23	+1	−1	−1	+1	99.58	99.87
24	+2	0	0	0	99.79	99.17
25	0	0	+2	0	98.05	98.24
26	0	0	0	0	99.18	99.01
27	0	0	0	0	99.11	99.01
28	0	+2	0	0	99.98	99.91
29	0	0	0	0	99.12	99.01
30	−2	0	0	0	99.2	98.84
31	0	0	−2	0	99.98	99.78
32	0	0	0	0	99.11	99.01
33	0	0	0	0	99.2	99.01
34	0	0	0	−2	98.63	98.6
35	0	0	0	0	99.17	99.01
36	0	0	0	+2	99.66	99.41
37	0	−2	0	0	98.35	98.11
38	0	0	0	0	99.12	99.01
39	0	0	0	0	99.15	99.01

Notes: Where x_1 = current (A), x_2 = time (min), x_3 = As(III) concentration (ppb), x_4 = hardness (mg/L as $CaCO_3$).

Table 3
Estimated regression coefficients for removal efficiency and model summary statistics

Coefficients	Estimate	SE	t	P
(Intercept)	1.46E+02	1.36E+01	10.76	1.89E-10
X_1	−6.06E+02	1.79E+02	−3.395	0.00249
X_2	−1.61E+00	3.47E-01	−4.646	0.000112
X_3	−7.19E-02	4.57E-02	−1.573	0.1293
X_4	−1.01E-01	4.04E-02	−2.497	0.020131
X_1:X_2	2.01E+01	4.56E+00	4.414	0.000201
X_1:X_3	8.22E-01	6.01E-01	1.368	0.18466
X_2:X_3	3.69E-03	1.17E-03	3.162	0.004355
X_1:X_4	1.38E+00	5.31E-01	2.597	0.016101
X_2:X_4	3.71E-03	1.03E-03	3.598	0.001518
X_3:X_4	6.40E-05	1.36E-04	0.471	0.64205
X_1:X_2:X_3	−4.37E-02	1.54E-02	−2.847	0.009125
X_1:X_2:X_4	−4.70E-02	1.36E-02	−3.464	0.002104
X_1:X_3:X_4	−1.02E-03	1.79E-03	−0.573	0.571923
X_2:X_3:X_4	−7.04E-06	3.47E-06	−2.029	0.05423
X_1:X_2:X_3:X_4	8.89E-05	4.56E-05	1.949	0.063545
R^2 = 0.9255, R^2 (adj) = 0.8770				
Residuals				
Min	1Q	Median	3Q	Max
−0.31803	−0.16970	0.03968	0.13385	0.59301

Notes: Where x_1 = current (A), x_2 = time (min), x_3 = As(III) concentration (ppb), x_4 = hardness (mg/L as $CaCO_3$), SE = standard error, t = student test, p = probability, R^2 = R-squared, R^2 (adj) = adjusted R-squared.

to find out the relationship between the independent and dependent variables using R software (3.0.3). The models were compared based on the coefficient of determination (R^2), adjusted coefficient of determination (R^2-adj) and Akaike's information criterion (AIC). AIC is known in the statistics trade as apenalized log-likelihood. Thus, a model for which a log-likelihood value can be obtained is shown by Eq. (7):

$$\text{AIC} = -2\log - \text{likelihood} + 2(p + 1) \quad (7)$$

where p is the number of parameters in the model, and 1 is added for the estimated variance. AIC is a measure of lack of fit of the model; when comparing two models, the smaller the AIC, the better the fit [16,17]. The coefficient of determination (R^2) and analysis of variance (ANOVA) were used to compare experimental and predicted value of the study. Also Fligner-Killeen test was used for homogeneity of variances between experimental and predicted value. Finally, the optimum condition of the experimental data was calculated using Excel software (*solved add-in*).

3. Result and discussion

3.1. Model fitting and statistical analysis

According to the created design, 39 experiments were performed and the details of the experimental conditions are provided in Table 2.

The fit of the model was verified by the coefficient of determination R^2. As shown in Table 3 the R^2 value was 0.9255 which indicated that 92.55% of the variations

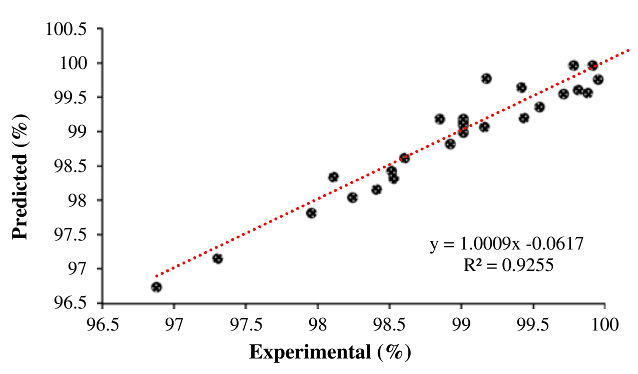

Fig. 1. Experimental As(III) removal plotted against the predicted values calculated from the RSM model.

could be explained by the predicted model. The R^2-adj value of 0.877 indicated the high degree of correlation between the observed and predicted values for the As removal efficiency.

A very high F-value (F-statistic = 19.06, much greater than unity) and a very low probability value (p-value = 1.682E-09) indicated that the model obtained was highly significant. Correlating arsenic removal efficiency (Y) with other independent variables ($X_1 - X_4$), following response surface function was utilized (in terms of actual factors) by Eq. (8):

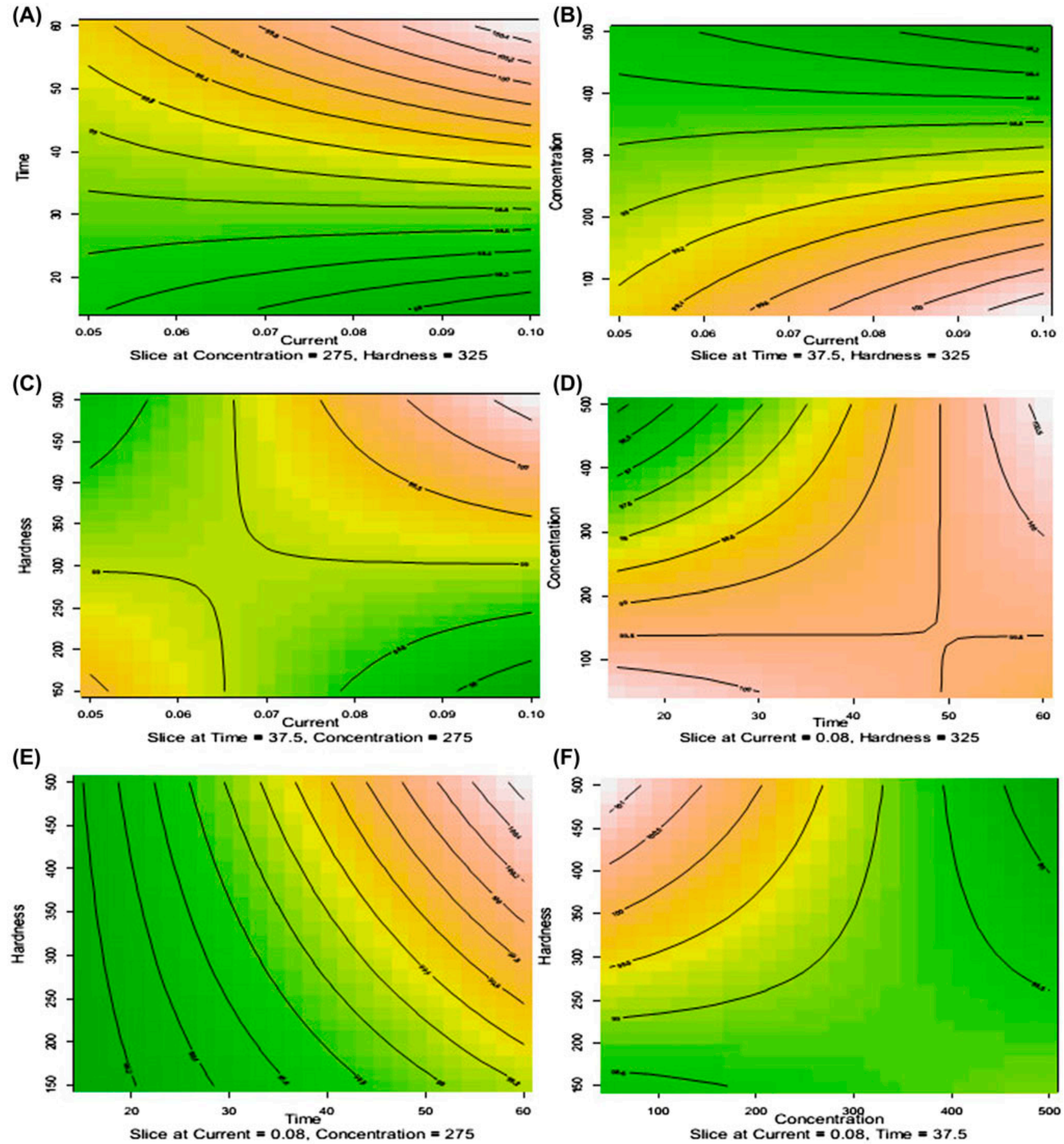

Fig. 2. Contour plots showing the effect of two variables on As(III) removal at pH 7.

$$Y(\text{removal}, \%) = 1.461\text{E}{+}02 - 6.064\text{E}{+}02\ x_1 - 1.612\text{E}{+}00\ x_2 - 7.192\text{E-}02\ x_3 - 1.008\text{E} - 01\ x_4 + 2.014\text{E}{+}01\ x_1x_2 + 8.222\text{E} - 01\ x_1x_3 + 3.692\text{E} - 03\ x_2x_3 + 1.379\text{E}{+}00\ x_1x_4 + 3.709\text{E} - 03\ x_2x_4 + 6.398\text{E} - 05\ x_3x_4 - 4.372\text{E} - 02\ x_1x_2x_3 - 4.696\text{E} - 02\ x_1x_2x_4 - 1.024\text{E} - 03\ x_1x_3x_4 - 7.038\text{E} - 06\ x_2x_3x_4 + 8.894\text{E} - 05\ x_1x_2x_3x_4 \tag{8}$$

The summary of multiple regression analysis was shown in Table 3. For each term in the models, the far along t-value to 0, and a small p-value would imply a more significant effect on the respective response variable. Therefore, the linear terms of X_1 (Current) and X_1:X_2 (Current: Time) have the largest effect on As(III) removal by electrocoagulation ($p < 0.001$). Also hardness has significant effect on As(III) removal ($p < 0.05$). But, the effect of As(III) concentration was not significant ($p > 0.05$).

Residual analysis is used to evaluate the adequacy of the model which is the difference between the observed value and the fitted value of a model. Small residual value indicates that model prediction is accurate. The average of the residuals is zero by definition, so the median should not be far from zero, and the minimum and maximum should be roughly equal in absolute value. As shown in Table 3 the median of residuals is remarkably close to zero (0.03968) and the residual standard error is small (0.2526) too. Also the model has the smallest AIC (16.77), which indicates the better the fit between other designed models.

Fig. 1 shows the comparison between the observed and predicted value for arsenite removal. It is observed a good fit of the model ($R^2 = 0.93$) with the experimental data. The result of Fligner-Killeen test confirms the homogeneity of variances (p-value > 0.05). Therefore, according to ANOVA analysis, which was used to compare the observed and predicted value, there was no significant difference between the values (p-value > 0.05).

3.2. *Influence of the removal conditions on the removal efficiency*

In order to explain the interaction effect of variables, which cannot be interpreted separately, a statistical ANOVA as well as contour and surface plots are convenient to represent precisely the model [18].

Fig. 2 shows contour plots of the model. The responses were mapped against two experimental factors while the other factors are held constant at its central level.

The current density which is the ratio of current input to the electrolytic cell to the surface area of the electrode, has the important role for controlling the reaction rate within the reactor. The amount of current density represented the coagulant dosage rate, the bubble production rate, size, and the growth of flocks, which can influence the treatment efficiency of the electrocoagulation [19]. Fig. 2(A) shows that by increasing the current and time, the As(III) removal increases. This is attributed to an increase in the amount of Fe(III) by anode dissolution, which has a strong affinity toward inorganic arsenic species and creates favorable adsorption sites for arsenic. Additionally, higher generation of hydrogen allowed by higher current helps the flotation of the flocculation matter. Also, the dissolution rate of iron increased with the increase in current density and thus a fixed amount of pollutants reacted to more $Fe(OH)_{3(s)}$ and thereby more pollutants were removed.

Fig. 2(B) and (F) shows that the efficiency decrease by increasing the As(III) concentration by increasing current and hardness of solution. Although, by increasing the current density the amount of Fe^{3+} in the solution increases, Fe^{3+} concentration was insufficient to attain high removal efficiency of arsenite when higher arsenic concentration was used. Also, Fig. 2(C) illustrates that by increasing the current and hardness at constant concentration of As(III), the efficiency will be enhanced. According to Fig. 2(D) and (E) at long contact time and increasing the As(III) concentration at constant current and hardness the As(III) removal will be improved. Similar behavior is observed by increasing hardness at constant current and As(III) concentration.

The experimental data for As(III) removal by EC at the feasible optimum condition, shown in Table 4, was 98.6% which is close to the predicted value with 99.0%. Thus, the feasible optimum condition of As(III) removal predicted is acceptable.

Table 4
Comparison of verification and predicted values of As(III) removal by electrocoagulation at feasible optimum condition

Optimum condition					
X_1	X_2	X_3	X_4	Experimental (%)	Predicted (%)
0.07	37	274	324	98.6	99.0

Notes: Where X_1 = current (A), X_2 = time (min), X_3 = As(III) concentration (ppb), X_4= hardness (mg/L as $CaCO_3$).

Electrocoagulation with iron electrodes was able to bring down 274 ppb of As(III) to 3.8 ppb, with initial hardness of 324 mg/L as $CaCO_3$, at the end of 37 min of electrolysis time. This was achieved with low electrical energy consumption such as 80.6 Wh/m^3.

4. Conclusions

This study illustrated the successful application of electrocoagulation process using Fe electrodes for treatment of As(III) pollution in hard aqueous solutions which was successfully optimized using CCD. According to the results obtained in this work, the factors that had the highest effect on most of the response variables were the current and time. ANOVA and multiple regression analysis were applied to achieve the prediction model. The predicted optimum arsenite removal was 99% using 0.07 A (1.4 mA/cm^2), 37 min, 274 ppb of As(III) and 324 mg/L as $CaCO_3$ of hardness. This research provides the basis of further research on other range of variables.

Acknowledgments

The authors of this research would like to extend a special acknowledgment to Tehran University of Medical Sciences for the financial support to carry out this project.

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