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Multiobjective optimization for minimum residual fluoride and specific energy in electrocoagulation process

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ABSTRACT

In the present paper, 2^4 factorial design method was employed for optimization of two responses: residual fluoride and specific energy consumed. The study was based on interaction effect of four factors namely, current, initial fluoride concentration, time, and inter-electrode distance. A regression model equation was developed which was validated by high R^2 values of 98.78 and 99.80% for residual fluoride and specific energy consumed, respectively. Optimization was targeted for residual fluoride concentration less than 1 mg/l and minimum specific energy consumption. The optimized conditions as suggested by the model for initial fluoride concentration 6 mg/l were: applied current—0.27 A, inter-electrode distance—20 mm, treatment time—46.70 min, specific energy—5.85 J/mg, and residual fluoride—0.77 mg/l. These results were used for experimental verification, which was in good agreement with the predicted results.

Keywords: Regression model; Fluoride; Electrocoagulation; Specific energy

1. Introduction

Fluoride contamination in groundwater is a major public health concern of the present time. Excessive exposure to fluoride either from drinking water or from other sources like food, drugs, cosmetics, industrial sources etc. can result into adverse health effects. Health problems associated with high concentrations of fluoride intake are dental fluorosis and skeletal fluorosis [1]. Severity of the fluorosis depends upon the amount of fluoride ingested and the tenure of exposure. In dental fluorosis, excessive fluoride can cause yellowing of teeth, white spots, and pitting or mottling of enamel. The most common symptoms of chronic fluoride exposure are skeletal fluorosis, which can lead to permanent bone and joint deformation [2]. Therefore, fluoride removal has been very important to environmental engineers. The desirable fluoride level in drinking water as set by Indian standards of drinking water is 1 mg/l.

The electrocoagulation (EC) process has been demonstrated as an effective choice for defluoridation by researchers [3,4]. A renaissance has been experienced by EC process. Reduced sludge production, no requirement for chemical handling, and ease of operation are some of the advantages of this process [5]. EC process generates sludge at the

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rate of 80–100 g per 1,000 l (on dry basis) [6]. EC has been suggested as an alternative to conventional coagulation [7,8].

EC process is an amalgamation of different processes. In the process of EC for fluoride removal, Aluminum anode is used to dose the water with a coagulating agent, and hydrogen gas is generated from cathode by electrolysis of water. The electrode reactions are outlined below [9]:

$$\text{Anodes: } Al(s) \rightarrow Al^{3+} + 3e^- \tag{1}$$

$$\text{Cathodes: } 2H_2O + 2e^- \rightarrow H_{2(g)} + 2OH^- \tag{2}$$

The Al^{3+} ions further react to form a solid $Al(OH)_3$ precipitate (Eq. (3)). $Al(OH)_3$ flocs are formed by the process of EC and these flocs entrap other particles remaining in the solution. They act as adsorption sites and help in the removal process. The basic principle of the process is depicted in Eq. (4) [9]:

$$Al^{3+} + 3H_2O \leftrightarrow Al(OH)_{3(s)} + 3H^+ \tag{3}$$

$$Al(OH)_3 + xF \leftrightarrow Al(OH)_{3-x}F_x + xOH^- \tag{4}$$

The tiny bubbles of the H_2 gas help the flocs to float in an upward direction and form a stable floc layer at the top surface of the reactor.

The EC process is highly dependent on the pH of the solution [10,11]. It will affect on the speciation of Al and will have a significant influence on the defluoridation mechanism. Since aluminum hydroxide is an amphoteric hydroxide, pH is a sensitive factor for the formation of $Al(OH)_3$ flocs. The solid $Al(OH)_3$ is most prevalent between pH 6 and 8, and above pH 9, the soluble species $Al(OH)_4^-$ is the dominant. It is for this reason that in the present study, the pH value of the sample was set to 6.

The aim of this study is to find the optimum process parameter settings for fluoride removal by EC process. The objective of optimization was to achieve residual fluoride <1 mg/l, consuming minimum specific energy. Design of experiments was used for modeling and analyzing the influence of control parameters on response values. Experiments were conducted using a monopolar EC batch process. Four critical parameters were considered: initial fluoride concentration, current, time, and inter-electrode distance.

2. Materials and methods

2.1. EC apparatus

A reactor of 2 L effective volume was used to conduct the batch experiments. Two aluminum electrodes with the purity of 98.99% and surface area of 1,270 mm^2 were used. Electrodes were connected to a DC power supply (Testronix, 230V DC) in monopolar configuration and a variable transformer was used to control the current intensity. The batch EC cell with monopolar electrode connection is shown in Fig. 1.

2.2. Experimental procedure

Fluoride containing samples were synthetically prepared in the laboratory by mixing NaF and NaCl (as supporting electrolyte) in tap water. The electrical conductivity of the prepared samples was measured and it was kept in the range 0.99–1.01 mS/cm. Initial pH of the solution was adjusted to 6 using HCl for all experiments. Magnetic stirrer was used to ensure complete mixing. Samples were taken at the end of the experiments from the reactor. All the experiments were accomplished at room temperature. Fluoride concentration was determined using ion selective electrode method [12] with a fluoride selective electrode (Thermo Scientific Orion 5-Star meter, 9609BNWP fluoride electrode). Conductivity and pH of the samples were measured using a calibrated conductivity meter (Lutron CD 4302) and pH meter (Electronics India deluxe 101), respectively.

2.3. Experimental design and data analysis

The present paper aims to find the optimum conditions of residual fluoride and specific energy consumed. These objectives are affected by the following factors, namely: applied current, inter-electrode

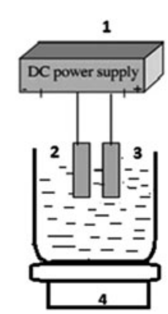

Fig. 1. Diagram of the experimental setup. (1): DC power supply, (2): electrodes, (3): EC reactor, and (4): magnetic stirrer.

Table 1
Levels used for process parameters

Variables	Factor	Level (−1)	Level (+1)
A	Current (A)	0.15	0.75
B	Inter-electrode distance (mm)	20.00	40.00
C	Initial fluoride concentration (mg/l)	4.00	6.00
D	Electrocoagulation time (min)	10.00	50.00

distance, treatment time, and initial fluoride concentration. Changing the settings of these process parameters have a significant influence on the residual fluoride and specific energy consumed. Design of experiment enables to study not only the main effects but also the interaction effects between the parameters.

Further, the choice of the two levels of factors used in two-level experiments also depends on the factor. For the present analysis, factors have the limits of the range which can be easily expressed using two settings such as high and low levels. These two settings for each factor encompasses the complete range that has been found feasible based on the previous studies and experimentally determined values. Using two levels also reduces the number of experiments that needs to be performed without affecting the

Table 2
Factors and response values of full factorial design

Run	A: Current (A)	B: Inter-electrode distance (mm)	C: Initial fluoride concentration (mg/l)	D: Time (min)	Residual fluoride (mg/l)	Specific energy consumed (J/mg)
1	0.75	20.00	6.00	10.00	1.86	11.59
2	0.75	20.00	6.00	50.00	0	40
3	0.15	40.00	6.00	10.00	5.38	7.25
4	0.75	40.00	4.00	50.00	0	114.84
5	0.15	20.00	6.00	50.00	0.91	2.799
6	0.15	20.00	6.00	10.00	3.48	3.8
7	0.75	20.00	6.00	50.00	0	39.37
8	0.15	40.00	4.00	10.00	2.82	4.25
9	0.75	20.00	6.00	10.00	2.03	11.9
10	0.15	20.00	4.00	10.00	2.29	1.57
11	0.15	20.00	4.00	10.00	2.3	1.58
12	0.75	20.00	4.00	50.00	0	70.78
13	0.15	20.00	4.00	50.00	0.701	4.09
14	0.75	20.00	4.00	50.00	0	70.78
15	0.15	40.00	6.00	50.00	2.48	6.39
16	0.15	40.00	4.00	10.00	2.78	4.11
17	0.15	20.00	6.00	50.00	0.86	2.77
18	0.75	40.00	4.00	50.00	0	114.84
19	0.15	20.00	4.00	50.00	0.685	4.07
20	0.75	40.00	6.00	50.00	0	73.43
21	0.75	40.00	4.00	10.00	0.391	25.45
22	0.75	40.00	6.00	10.00	2.01	22.08
23	0.75	20.00	4.00	10.00	0.574	16.52
24	0.15	40.00	6.00	10.00	5.53	9.57
25	0.15	40.00	4.00	50.00	0.195	6.6
26	0.15	40.00	6.00	50.00	2.43	6.3
27	0.75	40.00	4.00	10.00	0.336	25.07
28	0.75	40.00	6.00	50.00	0	73.43
29	0.75	40.00	6.00	10.00	1.89	21.44
30	0.15	40.00	4.00	50.00	0.201	6.61
31	0.75	20.00	4.00	10.00	0.524	16.29
32	0.15	20.00	6.00	10.00	3.61	1.19

efficacy of the selected DOE model. Further, optimum settings of parameters can then be found between the low and the high range of the selected factorial levels. A total of 32 experiments were conducted using 2^4 factorial design with a single replicate. Table 1 presents the levels used for process parameters in factorial design.

Experimental data was analyzed using Design Expert 8.0.7.1, and regression model equation was obtained for the two responses. Contour plots and

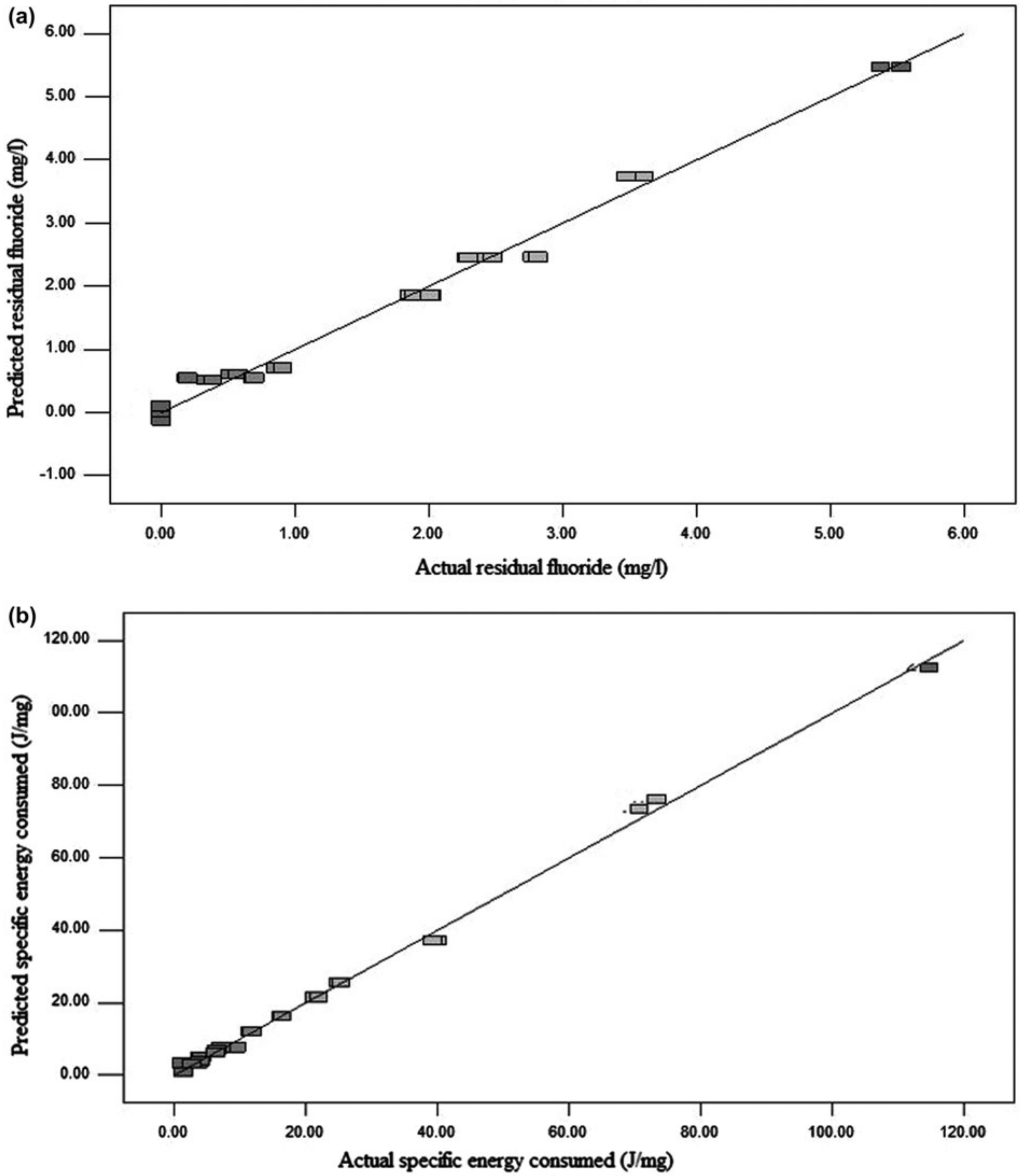

Fig. 2. Parity plot for the actual and predicted value of (a) residual fluoride (mg/l) and (b) specific energy consumed (J/mg).

Table 3
ANOVA for residual fluoride (mg/l)

Source	Sum of squares	df	Mean square	F-value	p-value Prob > F	
Model	73.80	10	7.38	169.58	<0.0001	Significant
A	22.84	1	22.84	524.91	<0.0001	
B	1.37	1	1.37	31.46	<0.0001	
C	10.90	1	10.90	250.38	<0.0001	
D	26.91	1	26.91	618.27	<0.0001	
AB	1.68	1	1.68	38.70	<0.0001	
AC	1.42	1	1.42	32.65	<0.0001	
AD	3.20	1	3.20	73.44	<0.0001	
BC	1.67	1	1.67	38.49	<0.0001	
CD	2.46	1	2.46	56.59	<0.0001	
ABC	1.34	1	1.34	30.89	<0.0001	
Residual	0.91	21	0.044			
Lack of Fit	0.87	5	0.17	58.23	<0.0001	Significant
Pure Error	0.048	16	2.976E-			
Cor Total	74.71	31				

Note: $R^2 = 98.78\%$ and R^2 (adj) = 98.19%; df, degree of freedom.

residual plots were also developed using the program. The statistical adequacy of the models was justified through analysis of variance (ANOVA) for regression model, and residual plots were used to examine the goodness of models fit. The quality of the fit of polynomial model was also expressed by the coefficient of determination, R^2. Finally, optimum values of factors were obtained by setting a target in the program.

3. Results and discussions

3.1. Development of regression model equation

The results of two responses; residual fluoride and specific energy consumption were measured, and presented in the design matrix (Table 2). A regression model equation was developed between the response and input variables. The regression model equation for residual fluoride and specific energy consumed in terms of coded factors are given by Eqs. (5) and (6), respectively.

$$\begin{aligned}\text{Residual fluoride} = {} & +1.43 - 0.85 \times A + 0.22 \times B + 0.58 \\ & \times C - 0.91 \times D - 0.24 \times A \times B \\ & - 0.22 \times A \times C + 0.33 \times A \times D \\ & + 0.24 \times B \times C - 0.28 \times C \times D \\ & - 0.21 \times A \times B \times C\end{aligned} \tag{5}$$

$$\begin{aligned}\text{Specific energy consumed} = {} & +26.78 + 21.93 \times A \\ & + 5.89 \times B - 5.67 \times C \\ & + 13.07 \times D + 4.09 \times A \\ & \times B - 6.43 \times A \times C \\ & + 12.98 \times A \times D + 4.56 \\ & \times B \times D - 3.55 \times C \times D\end{aligned} \tag{6}$$

The coefficient of first-order terms indicates the main effects, while second- and third-order terms indicate the interactions among the concerned factors. It can be noticed that when the effect of a factor is positive and

Table 4
ANOVA for specific energy consumed (J/mg)

Source	Sum of squares	df	Mean square	F-value	p-value Prob > F	
Model	32,666.14	11	2,969.65	892.48	<0.0001	Significant
A	14,232.42	1	14,232.42	4,277.32	<0.0001	
B	1,547.92	1	1,547.92	465.20	<0.0001	
C	742.48	1	742.48	223.14	<0.0001	
D	6,425.22	1	6,425.22	1,930.99	<0.0001	
AB	841.93	1	841.93	253.03	<0.0001	
AC	887.46	1	887.46	266.71	<0.0001	
AD	6,072.60	1	6,072.60	1,825.02	<0.0001	
BD	399.04	1	399.04	119.92	<0.0001	
CD	631.02	1	631.02	189.64	<0.0001	
ABD	470.78	1	470.78	141.48	<0.0001	
ACD	415.29	1	415.29	124.81	<0.0001	
Residual	66.55	20	3.33			
Lack of Fit	59.89	4	14.97	35.96	<0.0001	Significant
Pure Error	6.66	16	0.42			
Cor Total	32,732.69	31				

Note: $R^2 = 99.80\%$ and R^2 (adj) = 99.68.

Table 5
Actual and predicted values of residual fluoride

Predicted value (mg/l)	Actual value (mg/l)
2.43	2.47
0.20	0.18
0.19	0.22
0.34	0.37
0.57	0.60
2.3	2.36
2.03	2.00
3.61	3.56
5.38	5.30

the factor was changed from low to high level, the value of residual fluoride increases. On the contrary, when the effect is negative and the factor was changed from low to high level, residual fluoride decreases.

It can be observed from the Eq. (5) that current and time show negative effect, while initial fluoride concentration and inter-electrode distance show positive effect on the residual fluoride concentration. Also, it can be seen that current and time show the greatest effect on the residual fluoride concentration. Researchers have stated that in most electrochemical processes, current and time are the key parameters for controlling the reaction rate in the reactor [13]. From Eq. (6), it is observed that only initial fluoride concentration shows negative effect while current, distance between electrodes, and time show positive effect on specific energy consumption.

3.2. Validation of the model

The adequacy of the model was assessed through ANOVA. ANOVA is a statistical technique that subdivides the total variation in a set of data into component parts associated with specific sources of variation for the purpose of testing hypotheses on the parameter of the model [14]. The ANOVA results for residual fluoride and specific energy consumed are shown in Tables 3 and 4, respectively. A *p*-value lower than 0.0001 indicates that the model is statistically significant, and that the model terms are significant at 95% probability level [15]. In this case, $p < 0.0001$ suggests that regression model equation fitted well with the experimental results. Also, high R^2 values of 98.78 and 99.80% for residual fluoride and specific energy consumed, respectively, expresses a high correlation value between the actual and predicted values. Fig. 2(a) and (b) compares actual residual fluoride and specific energy consumed with the predicted values obtained from the model. The comparison of actual and predicted values of residual fluoride is also presented in tabular form in Table 5. The Fig. 2 indicated good agreement between the actual and predicted values. The adequacy of the model was also evaluated by the residuals (difference between the actual and the predicted response value). Normal probability plots are a suitable graphical method for judging the normality of the residuals [16]. The normal probability plots for residual fluoride and specific energy consumed are illustrated in Fig. 3(a) and (b).

3.3. Comparison of results with literature

The effect of current and time had negative value which indicates that higher the factor value, more is the decrease in final fluoride concentration. This result is in good agreement with Emamjomeh and Sivakumar [4], who explained that time and current determines the Al dose and higher the dose, quicker is the fluoride removal process. Drouiche et al. [17] have also illustrated that the increase in electrolysis time decreases the fluoride content. It has also been concluded by Emamjomeh and Sivakumar [4] that as the inter-electrode distance is increased, the resistance between electrodes also increases, and final fluoride concentration increases. Similar conclusion is made in the present study. The same conclusion is also mentioned by Zhang et al. [18]. Drouiche et al. [19] have also mentioned in their study that lesser inter-electrode distance give better treatment efficiency. The effect of initial fluoride concentration had a positive value, which indicates that amount of final fluoride concentration increases when initial fluoride concentration is increased. A similar conclusion was made by Zhu et al. [8]. Also Drouiche et al. [20] have mentioned that for a given amount of coagulant generated by EC, there is an increase of adsorption capacity at lower fluoride concentrations because there are more available adsorption sites for fluoride ions.

3.4. Contour plots for various operating parameters

The Figs. 4 and 5 show the interaction effect of various factors. The interactions which were having a significant effect on the response values are being illustrated in the contour plots. For residual fluoride as a response, factors A and D show a negative effect and factors B and C show a positive effect. For specific energy consumed factors A, B, and D show a positive effect while factor C show a negative effect on the response. On increasing factor B, specific energy consumed decreases for a simple reason that when initial fluoride concentration is increased, more fluoride is available for removal per Joule of energy spent.

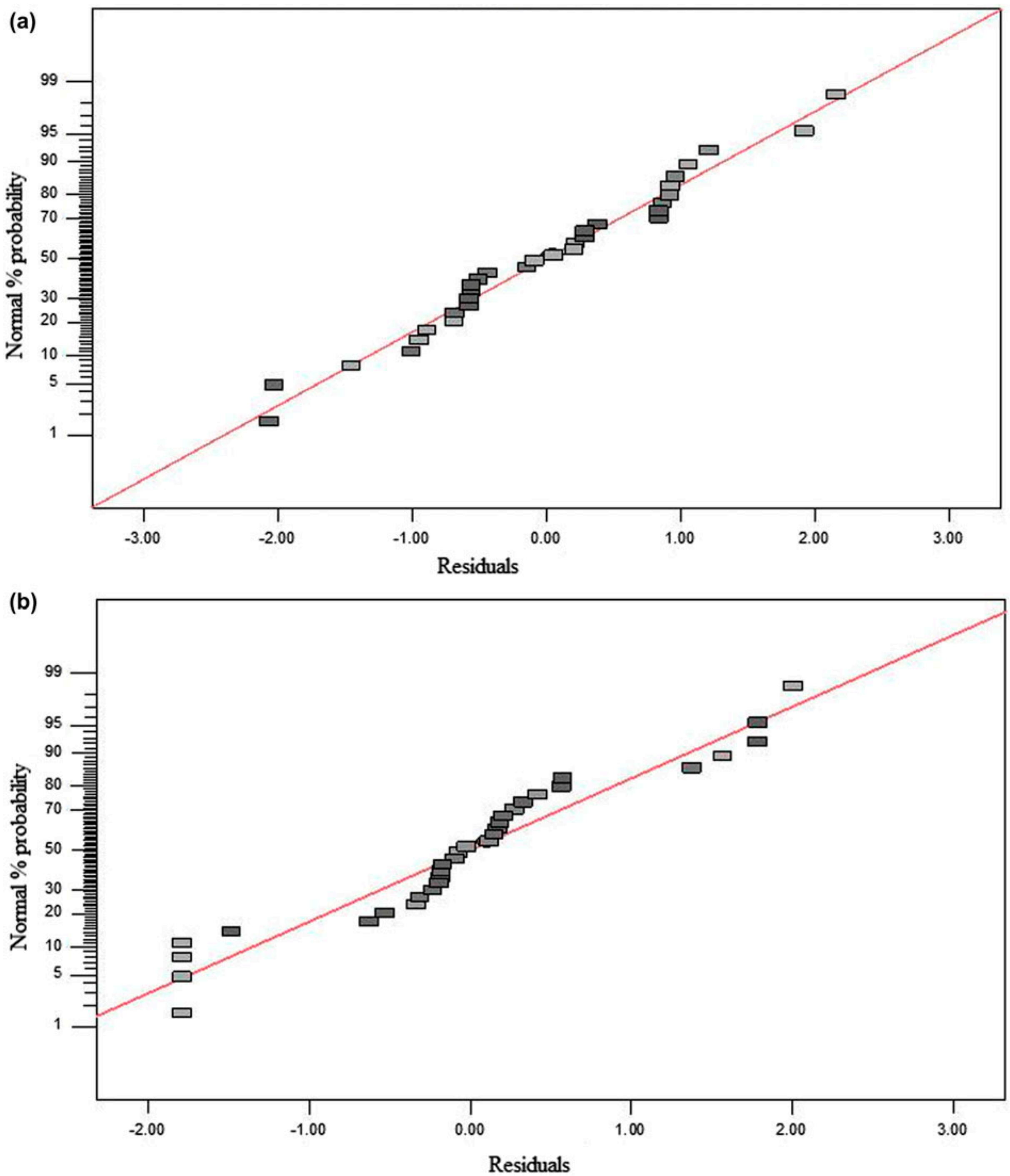

Fig. 3. Normal probability plots (a) residual fluoride (mg/l) and (b) specific energy consumed (J/mg).

3.5. Fluoride removal optimization

The main objective of the optimization is to determine the optimum values of variables for residual fluoride concentration less than acceptable limit for drinking water. In optimization, the target residual fluoride was defined as <1 for minimum specific energy and for initial fluoride concentration of 6 mg/l. The optimization results are shown in Table 6. The experimental verification of these optimum conditions confirms good agreement with the predicted results.

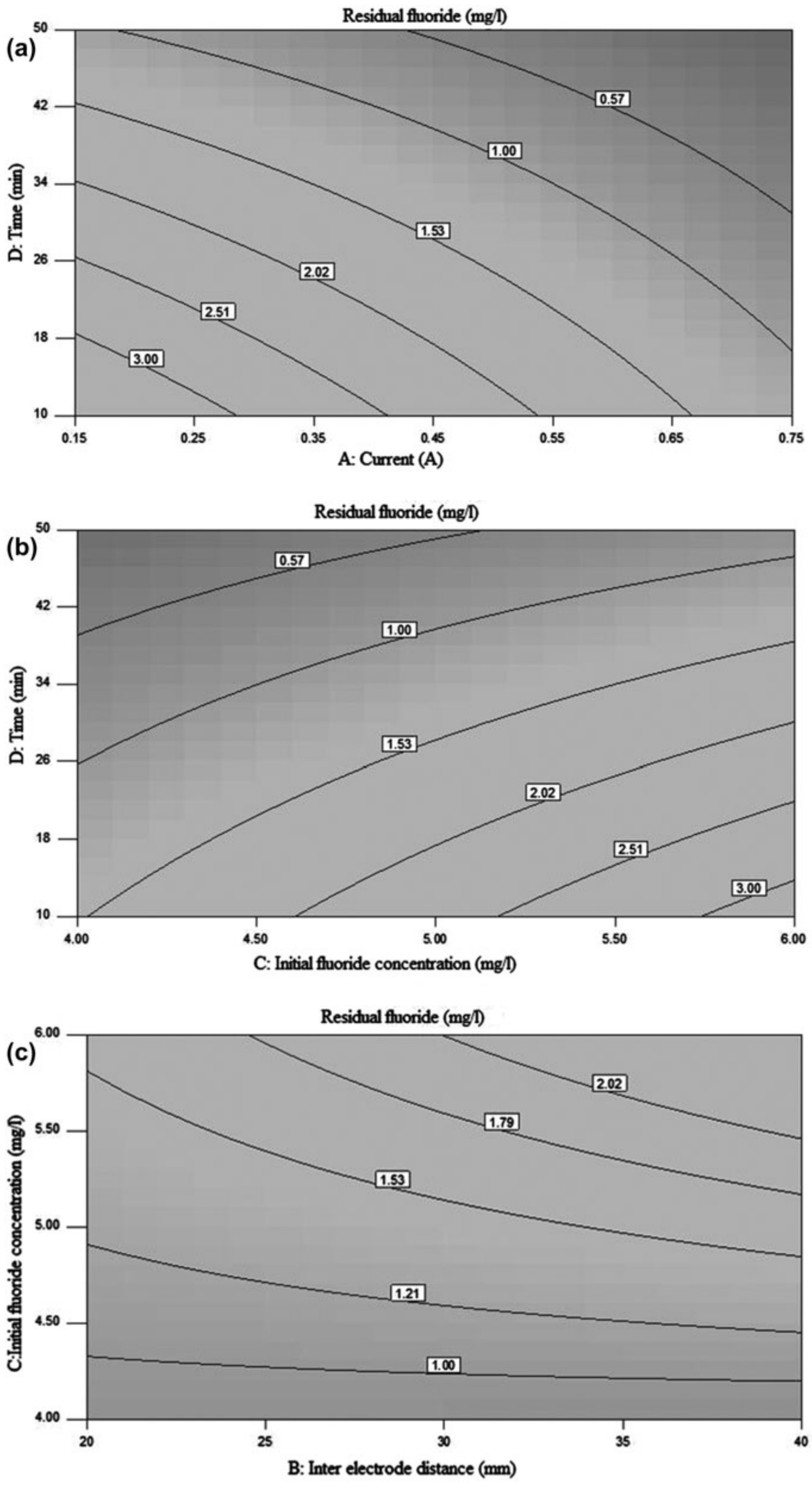

Fig. 4. Contour plots for residual fluoride as a function of (a) time and current, (b) time and initial fluoride concentration, and (c) initial fluoride concentration and inter-electrode distance.

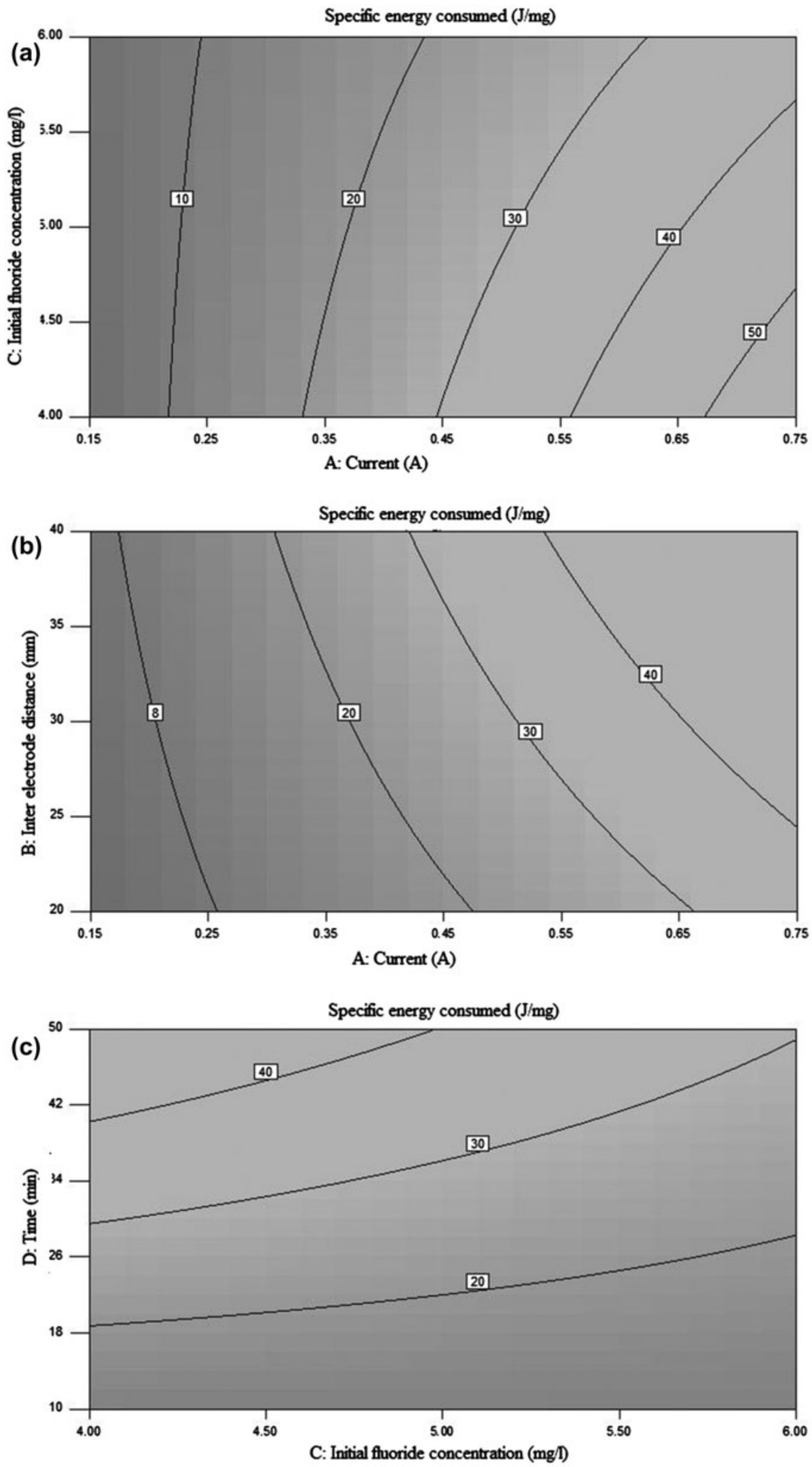

Fig. 5. Contour plots for specific energy consumed as a function of (a) initial fluoride concentration and current, (b) inter-electrode distance and current, and (c) time and initial fluoride concentration.

Table 6
Optimum values of fluoride removal

Variables	Unit	Values from optimization
Initial fluoride concentration	mg/l	6.00
Current	A	0.27
Inter-electrode distance	mm	20.00
Time	min	46.70
Specific energy consumption	J/mg	5.85
Residual fluoride (predicted)	mg/l	0.77
Residual fluoride (experimental)	mg/l	0.69

4. Conclusions

In the present study, the full factorial design was employed as an experimental design tool to explain the effect of main operating parameters and their interactions on the removal of fluoride and specific energy consumption as major responses for batch EC process. For this purpose, effect of current, initial fluoride concentration, distance between the electrodes, and time were evaluated on residual fluoride concentration and specific energy consumption. According to the ANOVA results, the model presents high R^2 values of 98.78 and 99.80% for residual fluoride concentration and specific energy consumption, respectively, which indicates that the accuracy of the polynomial models was good for both models. An experiment was done in optimum conditions which confirmed that the model and experimental results are in close agreement (0.69 mg/l residual fluoride from the experiment compared to 0.77 mg/l from the model). This suggests that full factorial design was successfully employed in the present study for experimental design and analysis of results.

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