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Research Article

OPTIMISATION AND MODELING OF FLUORIDE REMOVAL BY ELECTROCOAGULATION IN A CONTINUOUS FLOW BIPOLAR REACTOR

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ABSTRACT

In this study an experimental design was employed to investigate the effects of different operating conditions on the removal of fluoride by electrocoagulation with aluminum electrodes. Box-Behnken design was then used for optimizing and modeling the electrocoagulation process and for evaluating the effects and interactions of variables: current density (i, A/m^2), flow rate (Q, mL/min), and initial fluoride concentration (C_0, mg/L). The proposed model fitted very well with the experimental data. R^2 adjusted correlation coefficients (AdjR^2: 0.98) for fluoride removal efficiency showed a high significance of the model. The model predicted for a maximum removal of fluoride (95.07%) at the optimum operating conditions (120 A/m^2, 120 mL/min and 30 mg/L) after the EC process was 94.76% at the same optimum operating conditions.

Keywords: Electrocoagulation; Fluoride removal; Modeling; Optimization; continues flow.

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1. INTRODUCTION

The importance of water in the human economy continues to grow and the supply of good quality water is becoming increasingly difficult, both because of the growing population and its standard of living that accelerated development of modern industrial techniques. The discharge of untreated water from the industrial activities such as semiconductor, fertilizers industries, electroplating, glass, and steel, ceramic into the natural environment can result contamination of surface water and groundwater [1].

Fluoride ions in water have beneficial and harmful effects on the environment and humans. Excessive consumption of fluoride causes dental or skeletal fluorosis. When there is an ideal amount of 1 mg/L in drinking water, fluoride helps prevent teeth decay [2]. Several methods have been developed to remove excess fluoride from water, such as adsorption [3], chemical precipitation [4,5], membrane separation [6,7] and electrocoagulation [8].

EC is a polluted water treatment technique that has been proven effective for the treatment of certain soluble or colloidal pollutants. Water containing nitrates, fluorides, arsenic, lead, etc. can be treated by this process [9,10].

The optimization of the EC process can make a notable contribution to eliminating fluorides. The efficiency of this electrochemical process depends on the composition of the aqueous solution (conductivity of the water), the nature of the coagulant (Fe or Al) introduced as well as the structure of the pollutants. This operation based on the generation of metal cations, through the passage of the electric current in an electrochemical cell; the electrodes may consist of various metals which are chosen so as to optimize the treatment process, the two metals commonly used are iron and aluminum. These generated metal cations and the hydroxide metal formed could adsorb or neutralize the polluted particles. These neutralize particles agglomerate to form flocks that are susceptible to decantation [11,12].

The objective of this study was to evaluate removal of fluoride from aqueous solution containing high fluoride concentrations by the EC process using continuous flow bipolar reactor with Al electrodes. The R S M was used to develop a mathematical model to describe the effects and relationships of independent variables for the main process using three operating parameters such as current density, flow rate and initial fluoride concentration to maximize fluoride removal efficiency.

2. EXPERIMENTAL METHODS

2.1. Experimental setup and procedure

The reactor used in this study is a bipolar electro-coagulator in continuous mode. It consists of a parallelepiped shaped glass cell. The synthetic effluent is pumped into the electrochemical cell containing three aluminum plates used as electrodes (two of dimensions 20 × 10 cm, and one of 17 × 10 cm) and deposited vertically in the reactor (size 7 × 10 × 17 cm). The gaps between the two adjacent electrodes were kept constant at 1 cm for all the experiments. The electrodes are connected a digital DC power supply (Metrix AX502, 0–2.5 A and 0–30 V). The electrochemical cell has a volume of about 1.250 L (Fig. 1 shows the installation of the experimental device). An agitator has been put in place in which the effluent is homogenized, to prevent the formation of foams which can disturb the reactions and the flow of the effluent and prevent the proper functioning of the EC (Fig. 1).

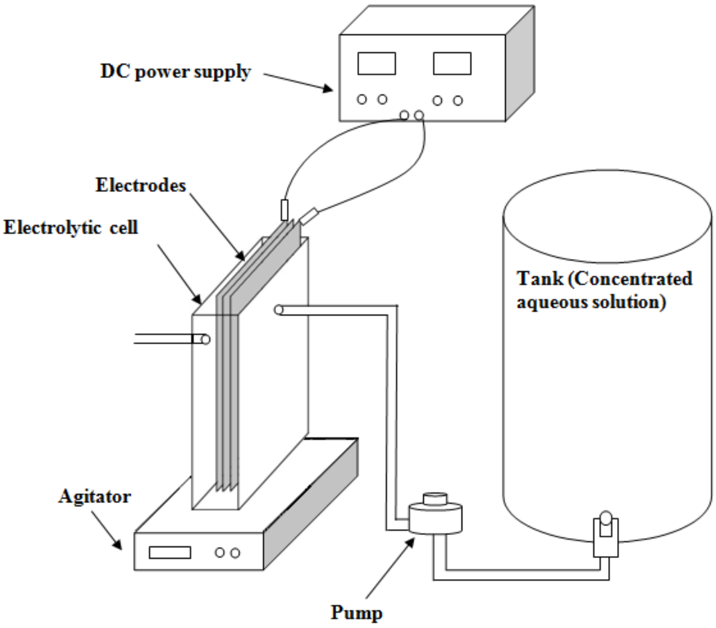

Fig.1. Installation of the experimental device

In this study, we used aluminum electrodes. These electrodes are immersed in the solution. One of the factors that affect the efficiency of the process is the state of the electrodes, so before each test, they must be cleaned to avoid all kinds of impurities: rinsing with distilled water; rinsing with the NaOH solution (10 %); and rinsing with distilled water.

A synthetic solution of sodium fluoride was prepared (dissolution of NaF at 99 % purity in tap water + NaCl), at a conductivity of 2.1 mS/cm, and at an initial pH of 8.1-8.3.

During the experiment, samples are taken at defined times. At each interval, 100 ml are taken in a beaker and after 20 minutes of decantation, 10 ml of the solution are taken with a syringe.

2.2. Analysis

The measurement of the concentration of fluoride ions in solution is carried out by the standard ionometric method described by Ming et al. [13] and taken up by various authors [14]. This analytical method is based on the use of a fluoride ion selective electrode (Jenway Fluoride Combination Ion Selective Electrode). A calibration curve has been established to estimate the concentration of fluoride ions in solution. To prevent the fluoride ions from being complexed with other ions (Al^{3+}, Fe^{3+}, Cu^{2+}, Ca^{2+}, etc.), a buffer solution TISAB was added to the samples before determining the fluoride ion concentration. The pH values were determined using pH-meter (type Hanna Instruments). The conductivity was measured by conductivity meter (type Hanna model EC2015).

2.3. Box–Behnken design

The Box–Behnken experimental design is used to optimize the treatment process parameters affecting the removal of fluoride by electrocoagulation. Flow rate (X_1), current density (X_2) and initial concentration (X_3) are input variable parameters. The interval of the allowed values for these factors was deduced from the preliminary tests carried out (Table 1). The factor levels were coded as –1 (low), 0 (central point or middle) and 1 (high).

The rate of fluoride removal, Y (%) was chosen as a response of the studied system and it was calculated by the following equation:

$$Y(\%) = \left[\frac{[F^-]_i - [F^-]_f}{[F^-]_i}\right] \times 100 \quad (1)$$

Where $[F^-]_i$ and $[F^-]_f$ are the concentration of the fluoride before and after the treatment, respectively.

For this response (Y), a polynomial model of the second degree shown in Eq. 2 is established to quantify the influence of the variables, where X_1, X_2 and X_3 are the independent variables representing solution flow, current density and initial concentration, respectively; β_0 is a constant; β_1 , β_2 and β_3 are the coefficients representing the linear weight of X_1, X_2 and X_3, respectively; β_{12}, β_{13} and β_{23} are the coefficients representing the interactions between the variables; β_{11}, β_{22} and β_{33} coefficients representing the quadratic influence of X_1, X_2 and X_3.

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 \quad (2)$$

Table 1. Experimental design levels of chosen variables

Variables	Levels in Box–Behnken design		
Coded level	Low (-1)	Middle (0)	High (+1)
Flow rate, mL/min	100	150	200
Current density, A/m^2	40	80	120
Intial concentration mg/L	30	50	70

3. RESULTS AND DISCUSSION

3.1. Effect of pH

The value of pH solution is an important factor in the electrochemical process. The effect of pH is studied by taking four values (4, 6, 8, and 10). All other parameters are kept constant: C_0 = 50 mg/L, Q = 150 mL/min, i = 80 A/m^2, Cd (solution conductivity) = 2.1 mS/cm. We took samples in time when the treatment is stable (after the residence time). The results of these experiments are shown in Fig.2.

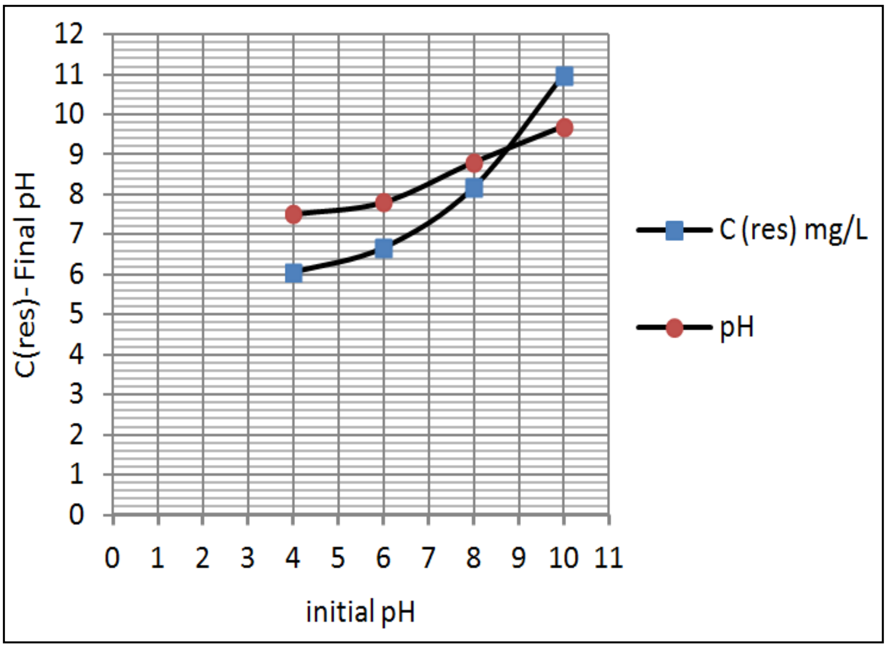

Fig.2. Effect of initial pH on fluoride removal by E. (C_0 = 50 mg/L, Q = 150 mL/min, i = 80 A/m^2, Cd (solution conductivity) = 2.1 mS/cm)

The fluoride removal mechanism has been characterized as precipitate and adsorb of fluorides on $Al(OH)_3$ [15], From Fig.2, it is noted that when the initial pH is increased from 4 to 6, the final pH increases from 7.6 to 7.8 and the C_{res} (residual concentration) increases from 6 to 6.7, and when the pH increases from 8 to 10, the final pH decreases from 8.8 to 9.7, and the residual concentration increases from 8.2 to 11.

When the initial pH is 4, the pH increased to 7.6 at the end of treatment, When the pH increases, Al^{3+} combines with the OH^- ions to successively give the ionic species $Al(OH)^{2+}$, $Al(OH)_2^+$, and $Al(OH)_3$. In the pH range between 5 and 8, the most common species in solution is aluminum hydroxide $Al(OH)_3$ with a maximum of 95% to pH 6.5 [16]. The amorphous precipitates of $Al(OH)_3$ are capable of adsorb the fluoride ions [17] as shown by Eq.3:

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

The complexation of F^- and Al^{3+}, AlF^{2+}, AlF_3 may occur and subsequent precipitation of Cryolite (Na_3AlF_6).

$$Al^{3+} + 6F^- \rightarrow AlF^{3-}_6 \quad (4)$$

$$AlF^{3-}_6 + 3Na^+ \rightarrow Na_3AlF_{6\,(s)} \quad (5)$$

The increases of C_{res} at initial pH 6 due to $Al(OH)_4^-$ ion begins to form at pH 6 and reaches its maximum of 90% of the aluminum present in the solution to pH 9.5. The rest of the aluminum being in the form of aluminum hydroxide $Al(OH)_3$ and $Al(OH)_5^{2-}$.

3.2. Statistical analysis

The combined effects of solution flow rate, current density, and initial concentration for fluoride removal were monitored. Table 2 shows the data resulting from the experiments of the effect of the three variables on the treatment. The experimental results were analyzed through an RSM design to obtain an empirical model for the best response. The predicted results by the model are shown in Table 2.

Table 2. Box-Behnken design consisting of experiments for the study of the three factors that are expressed in coded and actual levels with experimental and predicted values for fluoride removal, *Y*(%).

N. exp	Coded level			Actual level of variables			Percentage of removal	
	X_1	X_2	X_3	Q	i	C_i	Y(%)	Y(%)
1	-1	-1	0	100	40	50	75.52	75.75
2	+1	-1	0	200	40	50	67.34	67.03
3	-1	+1	0	100	120	50	89.68	89.99
4	+1	+1	0	200	120	50	81.48	81.24
5	-1	0	-1	100	80	30	89.69	89.11
6	+1	0	-1	200	80	30	80.82	80.78
7	-1	0	+1	100	80	70	86.11	86.14
8	+1	0	+1	200	80	70	76.42	76.99
9	0	-1	-1	150	40	30	81.35	81.69
10	0	+1	-1	150	120	30	93.73	93.99
11	0	-1	+1	150	40	70	76.65	76.38
12	0	+1	+1	150	120	70	92.88	92.53
13	0	0	0	150	80	50	84.73	83.64
14	0	0	0	150	80	50	82.35	83.64
15	0	0	0	150	80	50	83.84	83.64

The coefficients values of Eq.2 were calculated and tested for their importance using the NEMRODW software and are listed in Table 3.

The term “signif.” is values are used as a tool to check the significance of each coefficient, wich in turn, can indicate to the variables and their interactions. On the Table 3 we can see the star mark indicating the intensity of the significance of the coefficients: For *** very significant, ** significant and insignificant for no star.

Table 3. Estimation and statistics of the coefficients

Standard deviation of the response	0.920
R^2	0.994
R^2_A	0.983
$R_{pred.}$	0.961
PRESS	28.014
Number of degrees of freedom	5

Name	coefficient	*F*. inflation	Standard deviation	*t*.exp	Signif.
β_0	83.640		0.531	157.38	<0.01***
β_1	-4.367	1.00	0.325	-13.42	<0.01***
β_2	7.114	1.00	0.325	21.86	<0.01***
β_3	-1.691	1.00	0.325	-5.20	0.348**
β_{11}	-4.014	1.01	0.479	-8.38	0.0397***
β_{22}	-1.121	1.01	0.479	-2.34	6.6
β_{33}	-3.634	1.01	0.479	7.59	0.0632***
β_{12}	-0.005	1.00	0.460	-0.01	99.2
β_{13}	-0.205	1.00	0.460	-0.45	67.5
β_{23}	0.962	1.00	0.460	2.09	9.1

**** Very significant, ** significant and insignificant for no star*

The mathematical expression of the relationship of fluoride removal with the three variables (X_1, X_2 and X_3) is given below in terms of coded factors. Eq.6 predicts the rate of fluoride removal:

$$Y\,\% = 83.64 - 4.367X_1 + 7.114X_2 - 1.691X_3 - 4.014X_1^2 - 1.121X_2^2 - 3.634X_3^3 - 0.005X_1X_2 - 0.205X_1X_3 + 0.692X_2X_3 \quad (6)$$

The good correlation between the values measured and those predicted by the model confirms the quality of this model. In addition, the model gives a value of $R^2 = 0.994$. This value confirms that the equation of the model is very reliable. This also indicates that the terms of the model are significant.

Table 4. Variance analysis for the response surface mod

Source of variation	Sum of squares	Degrees of freedom	Mean square	*F*	Signif.
Regression	705.8855	9	78.4317	92.5694	<0.01***
Residues	4.2364	5	0.8473		
Validity	1.3442	3	0.4481	0.3098	82.1
Error	2.8922	2	1.4461		
Total	710.1219	14			

Table 4 shows the variance analysis (ANOVA) results for the fluoride Y response (%). The represented *F* ratio is used to determine the statistical significance of the extraction-elution process. The *F* value is a ratio of two independent estimates of the experimental error.

The analysis of the variance of these responses showed that the model is highly important. This importance is shown by the value of *F*-statistic (the ratio of the mean square due to the regression of the root mean square to the real error) (the ratio = 92.5694) and a very small value of signif. (Meaning <0.01). The low value of "Signif" indicates that the model is considered statistically significant.

3.3. Effects of variables on fluoride removal

The effects of variables on fluoride removal are shown in Fig.3. The three dimensions and two plots of the interaction response surface between varying flow rate and current density influencing the removal of fluoride, where the initial concentration is held at a constant value (30 mg/L).

The response surface of the fluoride removal shows that the percent increase in fluoride removal with increasing current density and decreasing flow rate at any current density, the decrease in flow rate increasing the resident time in the reactor.

According to Faraday's law, increasing the current and time causes an increase in the production of ions. This results an increase in flocs formation in the solution, thus improving the removal efficiency. In addition, the rate of generation of H_2 (g) increases with increasing current density. In addition, as noted by researchers [1, 18], the high rate of hydrogen production is allowed by strong currents, which prefer the flotation of the flocculated material.

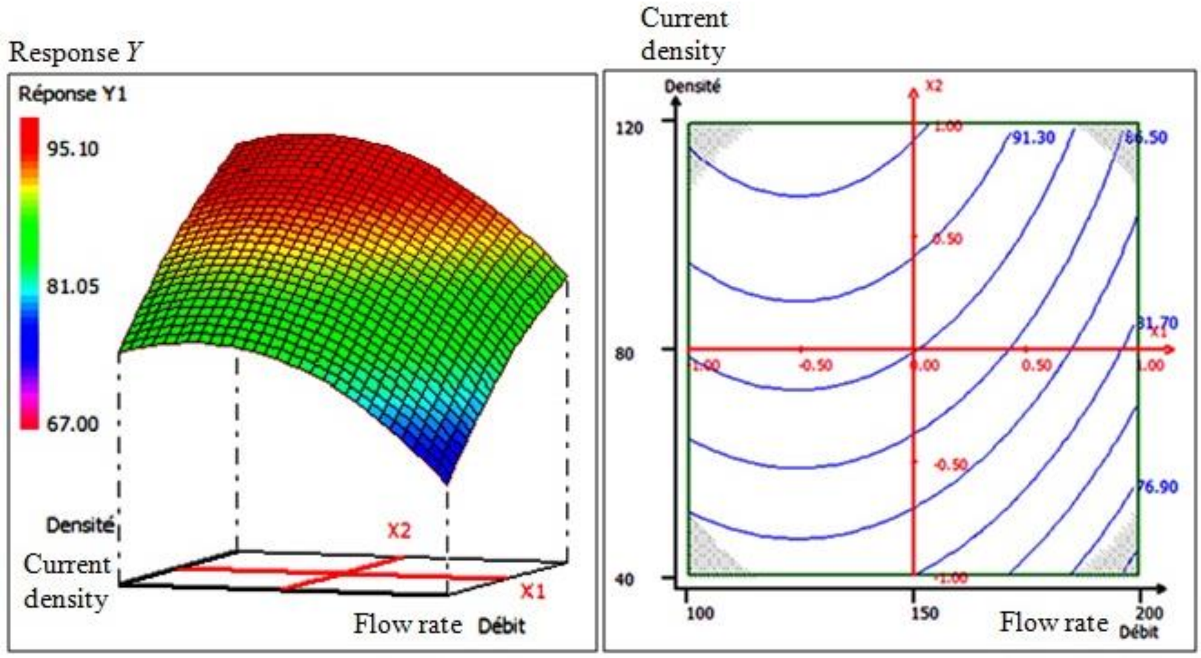

Fig.3. Graphic representation in 2 and 3 dimensions (iso-response curve)

3.4. Search for the optimum

Optimization of operating conditions was achieved by optimizing the equation model. The optimum of the variables values for maximum fluoride removal efficiency found by the NEMRODW software, the optimum current density was found to be 120 A/m^2 and the flow rate 125 mL/min, and the initial concentration 30 mg/L. These results are almost in agreement with the experimental results, (Table 5).

This confirms that the Box-Behnken design could be effectively used to optimize the process parameters, which are complex processes, using the experimental statistics model.

The response surface model developed in this study to predict the effectiveness of fluoride removal in water may be considered adequately applicable. An analysis of the variance showed a strong coefficient of determination value ($R^2 = 0.996$) by satisfactorily adjusting the second order regression model with the experimental data.

Table 5. Optimal values of experimental parameters for maximum fluoride removal.

Flow rate (mL/min)	Current density (A/m^2)	Initial concentration (mg/L)	The rate of fluoride removal, *Y* (%)	
			Experimental	Predictive
120	120	30	94.76	95.07

4. CONCLUSION

In the present study, the performance of electrochemical treatment in fluoride removal was investigated by focusing on the influence of operating parameters, using a surface-response method, in particular the Box-Behnken plane. The operational parameters in this process play a more important role in the treatment efficiency; the optimal values of experimental parameters for maximum fluoride removal flow rat 120 mL/min, current density 120 A/m^2, 30 mg/L initial concentration. The current density and the pH remain among the most significant factors. The response surface models developed in this study to predict fluoride removal efficiency were considered adequate. An analysis of the variance showed a strong coefficient of determination value (R^2=0.99) by satisfactorily adjusting the second order regression model with the experimental data.The results of this study indicate that EC is a very effective process for the removal of fluoride; in addition, it is modelable and optimizable with the response surface method.

Electrocoagulation is a complex process involving many mechanisms, to achieve optimum performance and future advances in the application of this technology, more effort must be made to better understand the fundamental mechanisms of operations, improving the design of the reactor in terms of shap and effluent flow.

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