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Fluoride removal from diluted solutions by Donnan dialysis using full factorial design

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Abstract−Excessive fluoride concentration in potable water can lead to fluorosis of teeth and bones. In the present study, Donnan dialysis (DD) is applied for the removal of fluoride ions from diluted sodium fluoride solutions. A four factor two level (2^4) full factorial design was used to investigate the influence of different physico-chemical parameters on fluoride removal efficiency (Y_F) and fluoride flux (J_F) through anion exchange membrane. The statistical design determines factors which have the important effects on Donnan dialysis performance and studies all interactions among the considered parameters. The four significant factors were initial fluoride concentration, feed flow rate, temperature and agitation speed. The experimental results and statistical analysis show that the temperature and agitation speed have positive effects on fluoride removal efficiency and the initial fluoride concentration has a negative effect. In the case of fluoride flux, feed flow rate and initial concentration are the main effect and all factors have a positive effect. The interaction between studied parameters was not negligible on two responses. A maximum fluoride removal of 75.52% was obtained under optimum conditions and the highest value of fluoride flux obtained was 2.4 mg/cm^2·h. Empirical regression models were also obtained and used to predict the flux and the fluoride removal profiles with satisfactory results.

Keywords: Fluoride Removal, Fluoride Flux, Donnan Dialysis, Anion Exchange Membrane, Factorial Design

INTRODUCTION

Fluoride occurs naturally in public water systems as a result of runoff from weathering of fluoride-containing rocks and soils and leaching from soil into groundwater. Fluoride is one of the chemical compounds that have been shown to have significant effects on people's health through drinking-water [1]. Fluoride has a beneficial effect on teeth at low concentrations in drinking-water, but excessive exposure to high levels of fluoride more than 1.5 mg/L, can lead to mottling of teeth and, in severe cases, crippling skeletal fluorosis [2].

Several defluoridation methods have been developed to improve the quality of drinking water, such as adsorption [3-5], ion exchange [6], chemical precipitation [7], electrochemical techniques [8-10], and membrane processes like reverse osmosis [11,12], nanofiltration [13-15], electrodialysis [16,17], and Donnan dialysis [18,19].

Donnan dialysis (DD) is a potentially attractive membrane separation process for concentrating valuable materials in ionic form from diluted solutions or removing undesirable ionic species from solutions. The driving force for the transport of ions is their concentration difference in the two solutions. Fundamentals of the DD process have been illustrated by authors in the above studies [18]. Although DD has slow kinetics compared to electrodialysis, it is economical, energy saving and needs simple technology [20]. Compared to an ion exchange process, DD does not need regeneration and is operated continuously [21]. However, industrial scale application of the process has not been seen up to now.

In most previous studies [22-24], the effect of some parameters on DD process is determined by varying one parameter by time, maintaining all the other parameters constant. Then, the best value achieved by this procedure is fixed and other parameters are varied by time. The disadvantage of this univariate procedure is that the best conditions cannot be attained, because the interaction effects between the parameters are discarded. Moreover, conventional methods are time consuming and require a large number of experiments to determine the optimum conditions of a process. These drawbacks of the conventional methods can be eliminated by studying the effect of all parameters using factorial design.

Design of experiments (DoE) has become one of the most popular statistical techniques since 1990s [25]. The main advantage of experimental design is that it can cover a larger area of experimental statistics and obtain unambiguous results at minimum runs. The factorial design method determines which factors have significant effects on a response as well as how the effect of one factor varies according to the level of the other factors.

The aim of the experimental work was to study the performance of Donnan dialysis process to removal fluoride ions from aqueous solutions. The effects of operating parameters, such as initial fluoride concentration, feed flow rate, temperature and agitation speed on fluoride flux and their removal efficiency were investigated. The main objective of this paper was to examine the main effects and interactions of considered parameters using a 2^4 full factorial design.

MATERIAL AND METHODS

1. Chemical Reagents

Sodium fluoride (NaF), sodium chloride (NaCl), sodium bicarbonate ($NaHCO_3$), sodium hydroxide (NaOH) and nitric acid (HNO_3)

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were reagent grade and each solution was prepared using deionzed water.

2. Membrane Conditioning Procedure

AM3 anion exchange membrane, obtained from Tokuyama Soda, has quaternary ammonium as a functional group. The ion-exchange capacity of the membrane is 2.46 meq/g with an active area of 4.52 cm^2. Before the membrane was used, it was washed with distilled water to remove impurities at 70±1 °C for 1 hour and then conditioned to convert the ions exchange sites to the desired form. The first conditioning cycle consisted of treating membrane with 200 mL HNO_3 (0.1 M) and 200 mL HCl (0.1 M) for 1 hour, to activate the membrane site functional groups, and then rinsing with distilled water. The activated anion exchange membrane was finally immersed into 200 mL NaCl (1 M) for 24 hours to completely convert the exchange sites to the desired chloride form, and then deionized water was used to wash out the residual NaCl solution.

3. Donnan Dialysis Experiments

Experiments were carried out using a laboratory cell consisting of two compartments of equal volume separated by AM3 anionic exchange membrane as shown in Fig. 1. The transport of the fluoride ions from feed compartment (F) to receiver compartment (R) was performed by two peristaltic pumps (Masterflex® L/S series). Receiver and feed tanks with 250 ml Erlenmeyer flask were used. DD experiments were carried out in a batch stirred cell. The feed compartment contained fluoride solution at different concentrations and the receiver compartment contained 0.1 M $NaHCO_3$.

4. Fluoride Analysis

The fluoride concentration was determined with a specific ion selective electrode (I.S.E 6-0502-150 fluoride ion electrode) by a Metrohm 781 pH/Ion-meter. To eliminate the interference effect ions a total ionic strength adjustment buffer (TISAB) solution was used, which contained 58 g of sodium chloride, 57 mL of glacial acetic acid and approximately 150 mL of 6 M NaOH in a volume of 1,000 mL and maintained at pH 6. The fluoride samples and the fluoride standard solutions were diluted by addition of TISAB solution with a molar ratio of 1 : 1.

5. Determination of the Flux and Removal Efficiency of Fluoride

The fluoride flux values were evaluated for all experimental conditions in order to compare the transport of fluoride ion from feed to receiver phase. The flux of fluoride ion (J_F) was determined by using the following equation:

$$J_F\ (mg/cm^2\cdot h)=Q/S * (C_0-C_f) \quad (1)$$

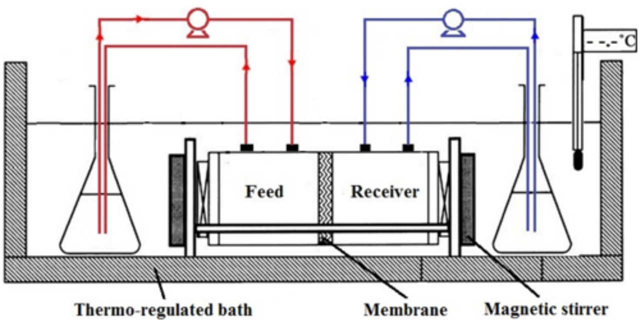

Fig. 1. Donnan dialysis laboratory cell.

where C_0 and C_f are the initial and final fluoride concentration, respectively, Q (L/h) is the feed flow rate and S is the active membrane area (cm^2).

To compare the removal of fluoride ions, the percent removal efficiency was evaluated for all experiments by the following equation:

$$Y_F\ (\%)=(C_0-C_f)/C_0 * 100 \quad (2)$$

6. Statistical Method

Factorial design determines the effects of multiple variables on a specific response and it can be used to reduce the number of experiments in which multiple factors must be investigated simultaneously [26]. The principal steps of statistically designed experiments are determination of response variables, factors, and factor levels; choice of the experimental design; and statistical analysis of the data [27]. Additionally, it can be used to find both main effects and interaction effects. Today, the most used experimental design is the 2^n factorial design, where each variable is investigated at two levels. In our study, a 2^4 full factorial design was carried out to investigate the performance of DD to removal fluoride ions from dilute solutions. Initial fluoride concentration (C), feed flow rate (Q), temperature (T) and agitation speed (A) were chosen as relevant parameters and the responses were the fluoride removal efficiency (Y_F) and the fluoride flux (J_F). Operating parameters, experimental range and coded levels are given in Table 1. A total of 20 experiments were performed according to a full factorial design with four factors (16 points of the factorial design and 4 center points to establish the experimental errors). The chosen variables for this work were set at two different levels, corresponding to the presence or absence of the experimental variables and coded as (+1) and (−1), respectively. Since interactions between these factors could be important, a linear polynomial model with first order was postulated by the following quadratic equation Eq. (3):

$$\begin{aligned}Y=&a_0+a_1C+a_2Q+a_3T+a_4A+a_{12}(CQ)+a_{13}(CT)+a_{14}(CA)\\&+a_{23}(QT)+a_{24}(QA)+a_{34}(TA)+a_{123}(CQT)+a_{124}(CQA)\\&+a_{134}(CTA)+a_{234}(QTA)+a_{1234}(CQTA)\end{aligned} \quad (3)$$

where Y is the response, a_0 is the constant term, a_1, a_2, a_3 and a_4 are the linear effects, a_{12}, a_{13}, a_{14}, a_{23}, a_{24}, a_{34} are the first-order interaction effects, a_{123}, a_{124}, a_{134}, a_{234} are the second-order interaction effects and a_{1234} is the third-order interaction effect, while the C, Q, T and A are the independent coded variables [28].

The analysis of results was achieved with statistical and graphical analysis software (Minitab Release 15, 2006). This software was used for regression analysis of the data obtained and to estimate the coefficient of regression equation.

Table 1. Experimental range and levels of independent variables

Variable	Real values of coded levels		
	−1	0	+1
C (mg/L)	5	10	15
Q (L/h)	0.4	0.7	1
A (rpm)	167	500	833
T (°C)	25	30	35

RESULTS AND DISCUSSION

1. Statistical Analysis and Modeling

A series of experiments were conducted by considering the 2^4 complete factorial design. Table 2 presents the experimental responses measured at two levels of the studied parameters. According to the results, fluoride removal efficiency varied between 34.14 and 75.52% and fluoride flux between 0.196 and 2.4 mg/cm^2·h. Higher values of fluoride removal efficiency were obtained under elevated temperature with minimum initial concentration (experiments 11, 13 and 15), and higher fluoride flux was observed at elevated initial concentration and maximum feed flow rate (experiments 8, 12 and 16).

Table 2. Full factorial design matrix for fluoride removal efficiency

Run	C (mg/L)	Q (L/h)	A (rpm)	T (°C)	Y_F (%)	J_F (mg/cm^2·h)
1	5	0.4	167	25	45.40	0.196
2	15	0.4	167	25	52.27	0.680
3	5	1	167	25	58.26	0.690
4	15	1	167	25	34.14	1.060
5	5	0.4	833	25	64.38	0.270
6	15	0.4	833	25	50.64	0.660
7	5	1	833	25	67.79	0.800
8	15	1	833	25	42.58	1.280
9	5	0.4	167	35	66.74	0.284
10	15	0.4	167	35	47.92	0.630
11	5	1	167	35	75.52	0.800
12	15	1	167	35	57.96	1.950
13	5	0.4	833	35	69.33	0.280
14	15	0.4	833	35	63.24	0.830
15	5	1	833	35	69.26	0.730
16	15	1	833	35	64.81	2.400
17	10	0.7	500	30	57.98	0.840
18	10	0.7	500	30	60.49	0.920
19	10	0.7	500	30	61.05	0.920
20	10	0.7	500	30	56.48	0.850

Table 3. Estimated effects and coefficients for fluoride removal efficiency (coded units)

Term	Effect	Coefficient	S.E coef	P-value
Constant		58.112	0.5365	0.000
C	−12.945	−6.472	0.5365	0.001
Q	1.245	0.623	0.5365	0.330
A	6.783	3.391	0.5365	0.008
T	12.360	6.180	0.5365	0.001
C * Q	−5.000	−2.500	0.5365	0.019
C * A	0.572	0.286	0.5365	0.631
C * T	1.105	0.552	0.5365	0.379
Q * A	−2.032	−1.016	0.5365	0.154
Q *T	3.725	1.863	0.5365	0.040
A* T	−2.542	−1.271	0.5365	0.152
C * Q * A	2.615	1.271	0.5365	0.099
C * Q * T	5.615	2.808	0.5365	0.014
C * A * T	5.998	2.999	0.5365	0.011
Q * A * T	−2.188	−1.094	0.5365	0.134
C *Q * A * T	−2.337	−1.169	0.5365	0.117

R-sq=0.9932

Table 4. Estimated effects and coefficients for fluoride flux (coded units)

Term	Effect	Coefficient	S.E coef	P-value
Constant		0.846	0.01087	0.000
C	0.680	0.340	0.01087	0.000
Q	0.735	0.367	0.01087	0.000
A	0.120	0.060	0.01087	0.012
T	0.283	0.142	0.01087	0.001
C * Q	0.237	0.119	0.01087	0.002
C * A	0.092	0.046	0.01087	0.024
C * T	0.249	0.124	0.01087	0.001
Q * A	0.057	0.029	0.01087	0.077
Q *T	0.229	0.114	0.01087	0.002
A* T	0.024	0.012	0.01087	0.350
C * Q * A	0.065	0.033	0.01087	0.058
C * Q * T	0.243	0.122	0.01087	0.002
C * A * T	0.088	0.044	0.01087	0.027
Q * A * T	−0.011	−0.006	0.01087	0.634
C *Q * A * T	0.014	0.007	0.01087	0.566

R-sq=0.9990

Data analysis using Minitab statistical software was used to investigate the main effects of factors, the interactions, the coefficient standard deviations and various statistical parameters of the fitted models. These parameters are shown in Tables 3 and 4 for fluoride removal efficiency and fluoride flux, respectively. The effect is the difference between the responses of two levels (high and low level) of factors; the regression model coefficients are obtained by dividing the effects by two, the standardized effects are obtained by dividing the regression coefficients by standard error coefficient [29]. The p-Value is the probability value used to determine the statistically significant effects in the model [30]. The significance of the data is judged by its p-value being closer to zero. For a 95% confidence level the p-value should be less or equal to 0.05 for the effect to be statistically significant. The Pareto plot represents the absolute values of the effects of main factors and the effects of interactions factors. A reference line is drawn to indicate that the factors which extend past this line are potentially important.

Based on data presented in Table 3 and graphical Pareto chart showed in Fig. 2, the final first-order model for fluoride removal efficiency (Y_F) in term of coded parameters is given by Eq. (4):

$$Y_F=58.112-6.472\,C+3.391\,A+6.18\,T-2.5\,C.Q+1.863\,Q.T+2.808\,C.Q.T+2.999\,C.A.T \quad (4)$$

And based on data presented in Table 4 and graphical Pareto chart in Fig. 3, the final first-order model for fluoride flux (J_F) in term of coded parameters is given by Eq. (5):

$$J_F=0.846+0.340\,C+0.367\,Q+0.060\,A+0.142\,T+0.119\,C.Q+0.046\,C.A+0.124\,C.T+0.114\,Q.T+0.122\,C.Q.T+0.044\,C.A.T \quad (5)$$

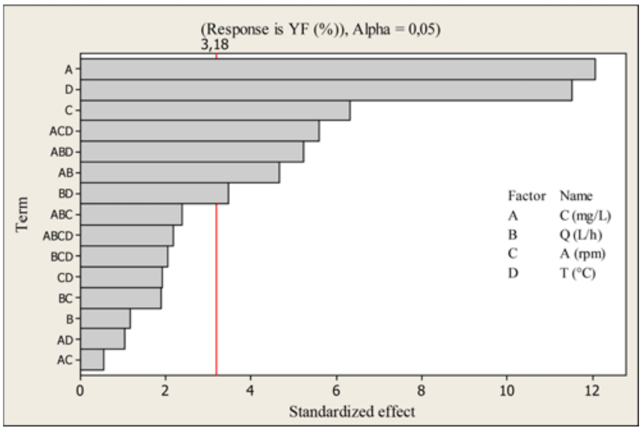

Fig. 2. Pareto chart for standardized effect for fluoride removal efficiency.

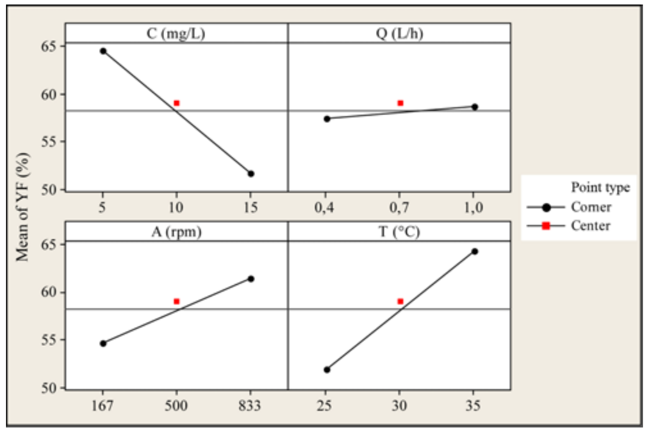

Fig. 4. Main effect plots for fluoride removal efficiency.

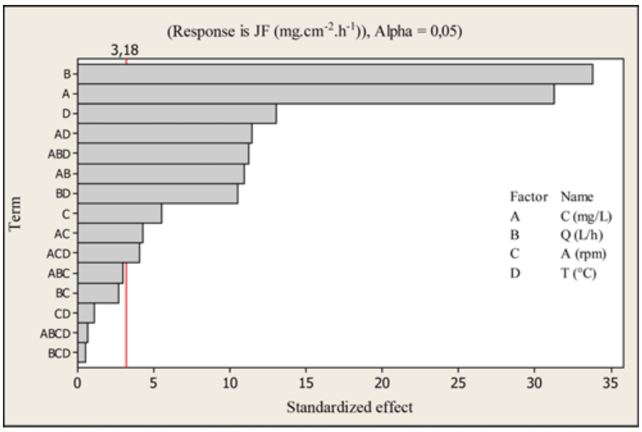

Fig. 3. Pareto chart for standardized effect for fluoride flux.

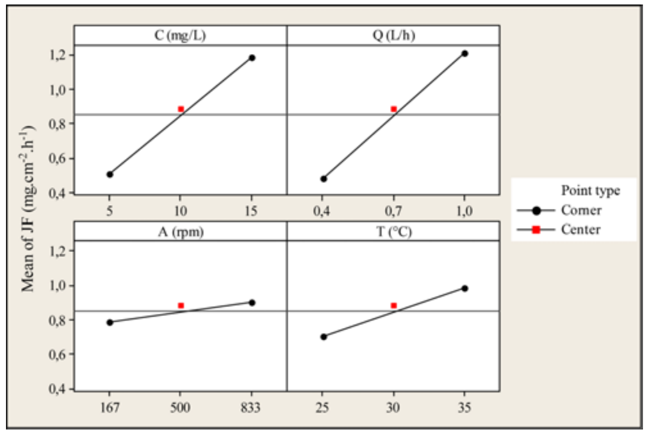

Fig. 5. Main effect plots for fluoride flux.

The goodness of fit of the model was evaluated by the coefficient of determination (R^2). The determination of the very useful statistic R^2 is allowed by calculation of the ratio of the sum of squares of the predicted responses to the sum of squares of the observed responses [31]. It is suggested that R^2 should be close to 1 for a good fit model. The estimated model for both Y_F and J_F had satisfactory R^2 values of more than 99%. In the case of fluoride removal efficiency, fitting is very good (R^2=99.32%) and only 0.68% of total variance was not explained by the model. For the fluoride flux R^2= 99.90%, which represents a high value and only 0.1% of total variance was not explained by the model. The p-value of the two models was less than 0.01, indicating that the terms in the first-order model have significant effects on the responses.

2. Main Effect Plots

The main effects were analyzed using the main effect plot for fluoride removal efficiency and fluoride flux through membrane as provided in Figs. 4 and 5. In the case of fluoride removal efficiency, initial fluoride concentration had a negative effect. At higher initial concentration, the amount of fluoride ions passing through the anion exchange membrane is very low compared to fluoride remaining in the feed compartment. The temperature of solution and agitation speed have a positive effect on removal efficiency. In the range of selected variable, fluoride removal efficiency was almost constant and was not found to vary widely with feed flow rate. On the other hand, initial fluoride concentration and temperature have the greatest effect on fluoride removal by DD. In fact, an increase of initial fluoride concentration from low to high level resulted in a 12.94% decrease in removal efficiency, whereas increase in temperature and agitation speed resulted in 12.36% and 6.78% increase in removal efficiency, respectively.

In the case of fluoride flux, all factors have a positive effect on the response. As observed, the initial fluoride concentration and the feed flow rate are the most important factors affecting the fluoride flux, while the second important factor is the temperature and the third one is the agitation speed. As a general trend, an increase of feed flow rate and initial concentration from low to high level resulted in increasing fluoride flux by 0.73 and 0.68 $mg/cm^2 \cdot h$, respectively.

Response surface plots such as contour and surface plots are useful for establishing desirable response values and operating conditions [29]. In a contour plot, the response surface is viewed as a two-dimensional plane where all points that have the same response are connected to produce contour lines of constant responses. A surface plot generally displays a three-dimensional view that may provide a clear picture of the response. These representations show the relative effects of any two variables when the remaining variables are kept constant. The chosen factors were based on the best two main effects for each response.

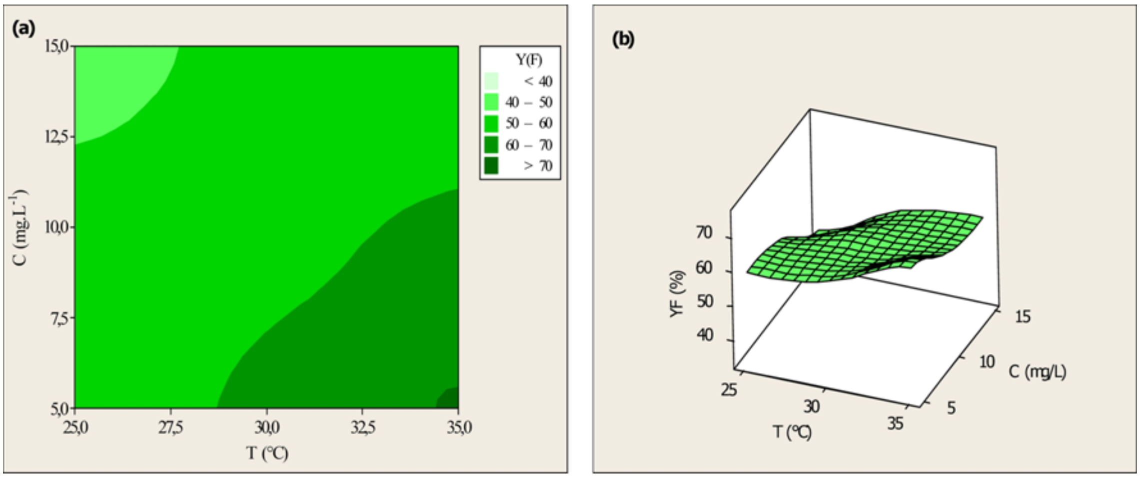

Fig. 6. Response surface plots for fluoride removal efficiency. (a) Contour plot and (b) surface plot.

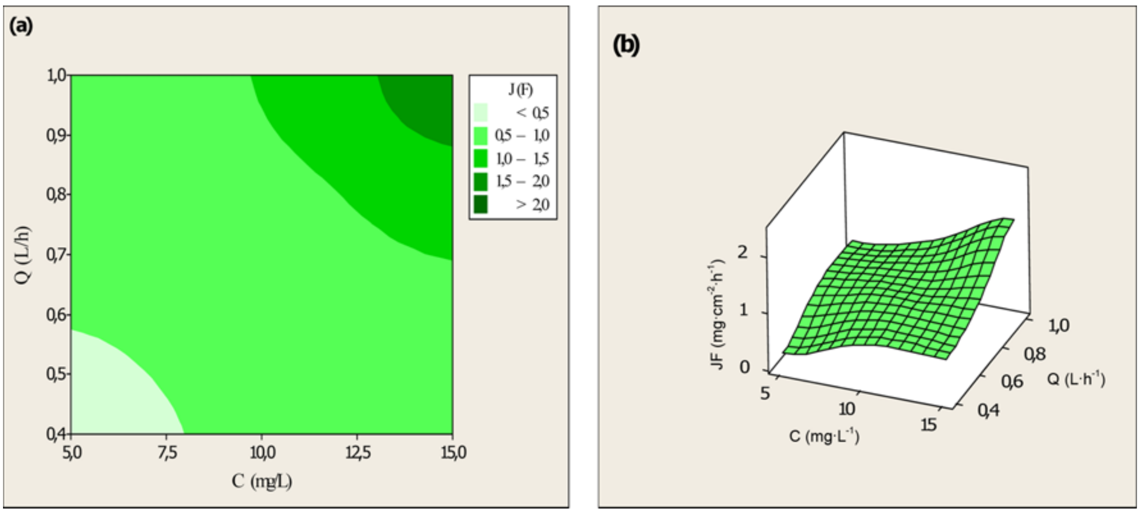

Fig. 7. Response surface plots for fluoride flux. (a) Contour plot and (b) surface plot.

Fig. 6 illustrates the contour and surface plots of fluoride removal efficiency and shows the interactive effect of initial fluoride concentration and temperature by keeping agitation speed and feed flow rate constant. As can be seen, the highest fluoride removal efficiency (Y_F>70%) occurs when the temperature is higher than 35 °C and when the initial fluoride concentration is lower than 5 mg/L, which is close to the experimental result: 70.21% (fluoride removal efficiency means of experiments number 9, 11, 13 and 15). Under these conditions (T=35 °C and C=5 mg/L), the estimated value of removal efficiency for DD of fluoride can reach an optimum value of fluoride concentration of 1.5 mg/L, which is advised by WHO for drinking water.

Response surface plots of fluoride flux obtained by DD, in Fig. 7, show the combined effect of feed flow rate and initial fluoride concentration. The fluoride flux increases (J_F>1.5 mg/cm^2·h) when the feed flow rate is higher than 0.9 L/h and initial fluoride concentration is higher than 12.5 mg/L, which is in correlation with the experimental result: 1.672 mg/cm^2·h (fluoride flux means of experiments number 4, 8, 12 and 16). After five hours of DD operation, under these conditions (Q=0.9 L/h and C=12.5 mg/L), 8.36 mg/L of fluoride ion can be reached in the receiver compartment.

CONCLUSION

A series of full factorial design experiments varying initial fluoride concentration, feed flow rate, agitation speed and temperature were performed to optimize fluoride flux and removal efficiency from diluted solutions using Donnan dialysis. According to the experimental results and statistical analysis, fluoride removal efficiency was negatively affected by the initial fluoride concentration. Decreasing the concentration of fluoride ions could enhance the fluoride removal. On the other hand, removal efficiency increased with increasing temperature and agitation speed, while the effect of feed flow rate was not significant. Moreover, this study also showed that the fluoride flux was mostly influenced by initial fluoride concentration and feed flow rate. The significant interactions found by the design of experiments are between initial fluoride concentration, agitation speed and temperature (C, A, T) and between initial fluoride concentration, feed flow rate and temperature (C, Q, T).

The factorial experiment design method is undoubtedly a good technique for studying the influence of major process parameters on response factors by significantly reducing the number of experiment and henceforth, saving time, energy and money.

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