PROCESS OPTIMIZATION FOR FLUORIDE REMOVAL FROM WATER BY *MORINGA OLEIFERA* SEED EXTRACT

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SUMMARY: The natural coagulant *Moringa oleifera* (MO) is considered to be an efficient coagulant with some advantages over chemical coagulants. Fluoride removal, using MO seed extract was investigated. The influence of MO dosage, initial F concentration, and pH were determined and modeled using the Box-Behnken design response surface methodology. With a constant initial F concentration, it was found that increasing the MO dose resulted in increased F removal. pH had no meaningful effect on F removal. Statistical and graphical tools confirmed the adequacy of the predicted model. Based on an optimized condition, for 85.4% removal of 8 mg/L of fluoride, a coagulant dosage of 900 mg/L is needed.

Key words: Coagulation; *Moringa oleifera*; Optimization; Response surface methodology;

INTRODUCTION

High levels of fluoride can cause severe problems for humans and animals.[1-4] Fluoride (F) can be found in different concentrations in various drinking waters, foods, and air.[5-10] There are many studies related to the F content in drinking waters and the associated health problems in Iran.[11,12] Different technologies have been applied for drinking water defluoridation including adsorption, chemical coagulation flocculation, electrocoagulation, electroflotation, and membrane separation.[13-18] Common chemical coagulants such as iron and aluminum salts have been widely used for removing different contaminants from aqueous solution. Because of some limitations with these, including handling of the chemicals, the high volume of the generated sludge, and the requirements for initial and final pH adjustment, researchers have looked for new coagulants, especially natural ones.

The areas suffering from high F concentrations are mainly located in rural and remote areas, e.g., in China, India, Kenya, Tanzania, and Ethiopia.[3,4,19-23] Efficient defluoridation technologies (e.g., membrane, adsorption, and ion exchange) are, in some cases, are not practical. Applications with a low cost involving simple methods are a high priority for solving the short-term problem of high F content in drinking waters. The use of local materials is preferable and one of these materials is the seeds of the tree *Moringa oleifera* (MO) which is grown in tropical areas. It has been consumed as food in some African regions and has been applied traditionally for water clarification.

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Moringa oleifera (MO) seed has been applied as a natural coagulant for the efficient removal of different pollutants.[24-30] Some of the advantages reported for this natural coagulant are low sludge production, low pH variation through experiments, and there being no need for pH adjustments.[27, 31]

The objective of this work is to remove F from water using MO seed extract, and the optimizing and modeling of the process using Response Surface Methodology (RSM). RSM has been widely applied to optimize coagulation and flocculation processes.[15,32] RSM can reveal the effect of the main variables and their interaction, and can develop mathematical models for process prediction. For this purpose, the Box-Behnken method was applied. The design was conducted for three main variables (pH, F concentration, and MO dose) at three levels using design expert software (Stat Ease, Inc. trial version).

MATERIAL AND METHODS

Dry, mature, and brown MO rods were collected from southern parts of Iran. After skinning, the cores were well ground. A known amount (5 g) of the powdered seed was vigorously mixed (30 min) with 1L sodium chloride (1M) solution. The extraction process was followed by suspension filtration through a Whatman no. 40 filter paper. The filtrate was utilized for the experiments. More details of MO seed extraction procedure can be found elsewhere.[24, 27, 33, 34]

Synthetic F solution was prepared by dissolving a known amount of dried NaF (Merck, Germany) in distilled water. Experiments were carried out using a jar test apparatus (Lovibond®). A jar test standard procedure of 120 rpm (1 min), 20 rpm (20 min) and finally 20 minutes (for settling) was applied for all the experiments. F measurements were read by a DR/5000 (HACH, Germany) spectrophotometer using the standard SPADNS method. Removal efficiency was calculated using following equation:

$$RE\ (\%) = \frac{(Co - Ce) \times 100}{Co}$$

RE = F removal efficiency, Co = F concentration in feed solution, Ce = F concentration in treated solutions.

Box-Behnken (3 variables with 3 levels) was used to design the experiments. Table 1 shows the variables and the levels of the actual values.

Table 1. Different variables and levels for Box-Behnken design

Symbol (main variable)	Levels		
	Low level (-1)	Mild Level (0)	High level (+1)
X_1 (coagulant dosage, mg/L)	200	400	600
X_2 (pH)	4	7	10
X_3 (Initial F, mg/L)	2	5	8

RESULTS AND DISCUSSION

The results of the Box-Behnken experimental design, at different variable levels and removal predictions, for individual experiments are presented in Table 2.

Table 2. Box-Behnken design of experimental variables, levels, and removal %

Run number	Coagulant dosage (mg/L)	pH	Initial F concentration (mg/L)	Removal %	
				Experimental	Predicted
1	400	4	2	79.85	81.30
2	200	10	5	27.20	27.84
3	600	7	2	94.91	94.11
4	400	7	5	35.00	33.93
5	400	4	8	36.50	38.61
6	600	4	5	53.50	52.86
7	400	10	8	35.50	34.06
8	400	10	2	80.50	78.39
9	600	10	5	47.23	50.15
10	400	7	5	34.20	33.93
11	400	7	5	32.60	33.93
12	200	7	8	28.50	29.31
13	600	7	8	49.22	47.75
14	200	4	5	35.50	32.59
15	200	7	2	68.50	69.97

After conducting different runs for design and statistical analysis, the final equation in terms of coded factors was created as below:

$$RE\ (\%) = 33.93 + 10.64\ X_1 - 1.87\ X_2 - 21.76\ X_3 + 0.51\ X_1 \times X_2 - 1.42\ X_1 \times X_3 - 0.41\ X_2 \times X_3 + 4.56\ X_1^2 + 2.36\ X_2^2 + 21.79\ X_3^2$$

RE = F removal efficiency

The validity of a prediction model should be assessed using both graphical and numerical statistical tests such as p value, determination coefficients, and lack of fit test. Statistical analysis of variance (ANOVA) showed that the developed model was statistically significant (p value <0.05) (Table 3). In addition, from Table 3, the lack of fit test was not significant (p value >0.05) which clearly indicates the adequacy of the model. Determination coefficients, R-squared, and adjusted R-squared (0.99 and 0.98 respectively) were close, which reveals the sufficiency of the fixed model. The random distribution of the residual values through the experimental runs indicated no systematic and expected errors due to personnel or equipment during the study (Figure 1). The graphical analysis of the normal plot of the residuals indicated a normal distribution of the residuals (Figure 2).

Table 3. ANOVA for response surface quadratic model of F removal

Source	Coefficient estimate	Sum of squares	df	Mean square	F-Value	p-value Prob > F
Model	33.93	6515.21	9	723.91	91.64	< 0.0001
X_1	10.645	906.53	1	906.53	114.76	0.0001
X_2	-1.865	27.83	1	27.83	3.52	0.1194
X_3	-21.755	3786.24	1	3786.24	479.29	< 0.0001
$X_1 \times X_2$	0.5075	1.03	1	1.03	0.13	0.7328
$X_1 \times X_3$	-1.4225	8.09	1	8.09	1.02	0.3579
$X_2 \times X_3$	-0.4125	0.68	1	0.68	0.09	0.7809
X_1^2	4.559583	76.76	1	76.76	9.72	0.0263
X_2^2	2.364583	20.64	1	20.64	2.61	0.1669
X_3^2	21.78958	1753.06	1	1753.06	221.91	< 0.0001
Residual		39.50	5	7.90		
Lack of Fit		36.51	3	12.17	8.15	0.1113
Pure Error		2.99	2	1.49		

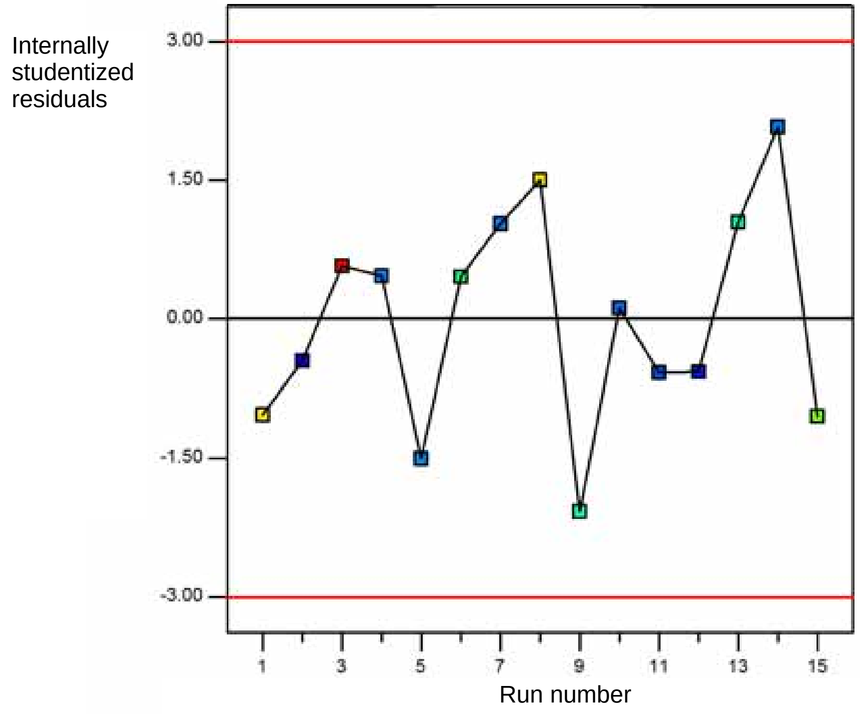

Figure 1. Residuals versus run number for F removal using *Moringa oleifera*.

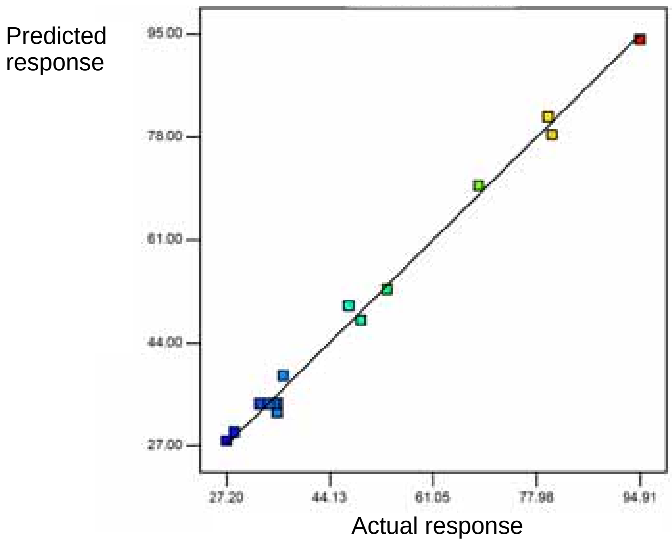

Figure 2. Normal probability plot of predicted versus actual response for F removal.

Based on the analysis of variance (ANOVA) among the independent variables, X_1 and X_3 were strongly significant (Table 3). The squared effects of these two parameters was also significant but the statistical significance of X_3^2 was greater. None of the interaction effects was significant (Table 3). The effect of each two-parameters has been presented by graphical response surface plots (Figures 3, 4, and 5). Both increasing the coagulant dosage and decreasing the F concentration resulted in increased removal efficiency but the effect of the initial F concentration was more marked (Figure 3). The effect of pH was negligible in this process (Figures 4 and 5). Essentially pH in coagulation and flocculation using MO coagulant is not an important variable. This characteristic of MO is identified as an important advantage that eliminates the costs of pH modifications and reduces the cost of the final produced sludge.

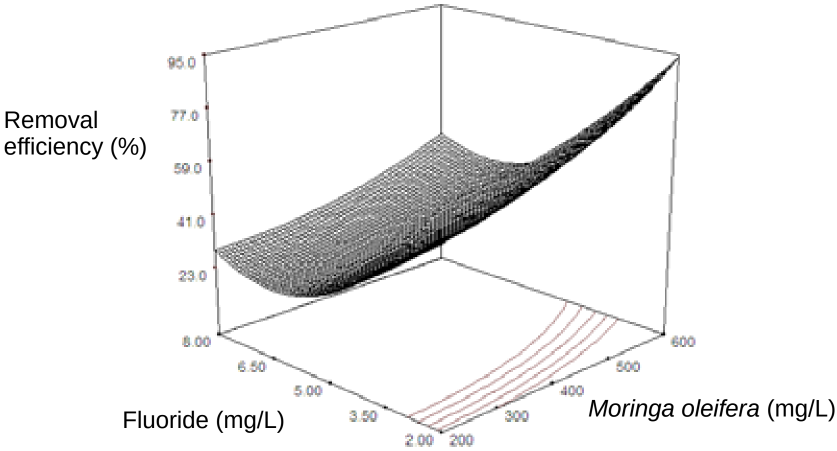

Figure 3. Response surface and contour plots for F removal efficiency. Interaction of *Moringa oleifera* dose and initial F concentration at pH of 7.

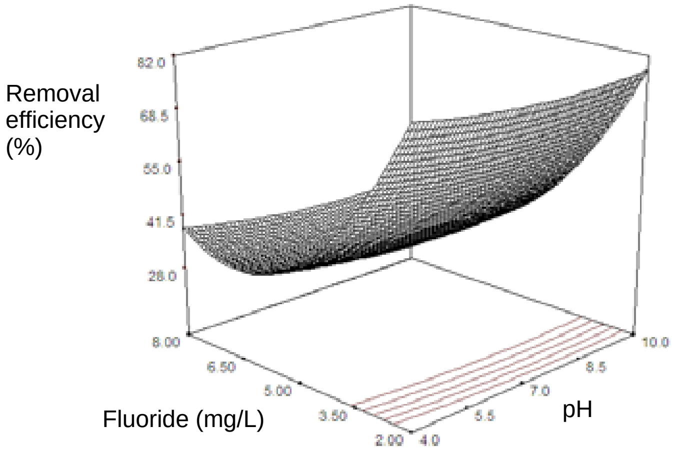

Figure 4. Response surface and contour plots for F removal efficiency. Interaction of pH and initial F concentration for *Moringa oleifera* dose of 600 mg/L.

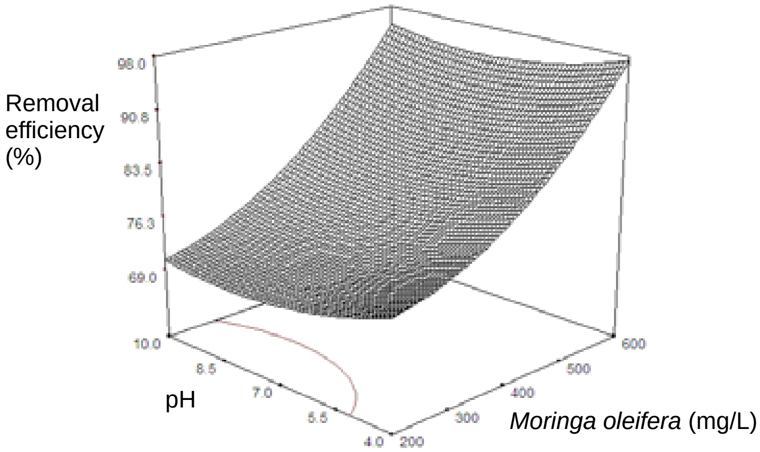

Figure 5. Response surface and contour plots for F removal efficiency. Interaction of *Moringa oleifera* dose and pH at initial F concentration of 2 mg/L.

Adding additives to natural materials is a common cause for concern. A few studies have reported on the quality of water purified by using MO as a coagulant. Analysis of MO seed extract showed the possibility of increases in some constituents. Some research revealed no change in conductivity, alkalinity, and the pH of water treated by MO seed extract.[35] The effect of MO on some parameters such as electrical conductivity (EC) and total dissolved solids (TDS) is highly related to the extraction method. In the case of extracting by tap water, there may not be significant changes in these parameters.[35] With extraction by salts (e.g. sodium chloride), the concentration of chloride and EC may increase. Because of intrinsic organic content of MO, an increase in total organic carbon (TOC) and chemical oxygen demand (COD) in the finished water can be expected.[35] Analysis of MO seed extract revealed a relatively high content of TOC (4760 mg/L) and

COD (15000 mg/L). An increase in some other parameters such as nitrate is also of concern. Ndabigengesere and Narasiah showed an increase of 0.4 to 1 mg/L in nitrate concentration. As an inherent constituent of MO seed, a value of about 110 mg/L nitrate can be found in seed extract solution.[35] The extraction using sodium chloride may increase nitrate to higher levels.[36] Application of lower and optimum dosages of MO can reduce the risk of nitrate. Ndabigengesere and Narasiah suggested that using MO after adequate purification of the active proteins could reduce these concerns significantly.[35] A problematic issue is the subsequent chlorination of the water with the possibility that the combination of the organic portion of MO and chlorine may result in new compounds forming in the water. This area needs more research. However, in the traditional application of MO in some African regions, no subsequent chlorination has been applied.

Optimization of the process, using the model at a coagulant dosage of 900 mg/L, an initial F concentration of 8 mg/L, and a pH of 7.6, resulted in 85.4% F removal. This optimized condition was evaluated through an additional experiment and the result was close to the model (85%). With real conditions, the initial concentration of F is nearly fixed, and, by using the model, the desired removal efficiency can be achieved by changing the MO dose. Applying higher concentrations of MO can result in slightly higher removal efficiencies. In tropical regions, MO can be applied as a promising solution for the removal of F from drinking water. In addition, not only is the amount of sludge generated by MO lower, by four- or five-fold compared to that produced using alum, but it is also environmentally friendly, biodegradable, and able to be used as fertilizer [35].

CONCLUSION

This study was conducted to optimize the F removal process using MO seed extract. The Box-Behnken design was applied in this study for response surface modeling. The results revealed that with an increase in the MO dosage, the F removal increased. It was also found that pH had no significant effect in the process. In other words, F removal using MO was independent of pH. A developed quadratic model was statistically adequate for the prediction of F removal. This study showed that MO can be applied as a natural coagulant for F removal for waters of relatively low fluoride content in some rural and remote areas.

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