Optimization of fluoride in water using alum with response surface methodology

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Original Article

Abstract

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Introduction: Fluoride counts an essential element for human health. Therefore, both low and excessive concentrations of that element in drinking water may cause health problems for the consumers. The present study aims to optimize fluoride base in drinking water using Alum response surface methodology.

Methods: The present study is an analytical research which uses surface response method based on Bax Banken model for the optimizing of variable effects in elimination of drinking water fluoride where Spectrophotometer (UNICO-(UV/VIS), model 2150 according to the method of SPADNS presented in standard methods for the examination of water and wastewater has been employed. Three variables of initial concentration of fluoride, PH, and Alum were studied in three levels (+1, 0,-1). The required numbers of samples were 17 according to the model. Experimental results were analyzed using Design Expert 7 software. The experiments were carried out randomly in order to the elimination of systematic error. The research data were analyzed using multiple regression and coefficients as well as ANOVA where ($P \leq 0.05$) determined as significant level.

Results: The results showed that initial concentration of fluoride, PH, and Alum are effective in determining the optimal sitaation. Each of these factors increases the efficiency of fluoride elimination to a certain level and after that which the efficiency decreases. In this process optimal conditions included initial concentration of fluoride3.25 mg/L, PH 6.55, and Alum concentration of 166 mg/L where in an efficient condition. Fluoride elimination equal to 76.83% with a desirability of 97.2%.

Conclusion: The results showed good agreement wbetween experimental and model predictions. It can be concluded that response surface methodology is a useful method for optimization of operating factors for the process of coagulation.

Key words: Fluride, Water, Alum

Introduction:

Low and high concentration of fluoride in water is considered a major public health concern. The recommended concentration of fluoride in drinking water is 5.0-1.5 mg/L (1). More than 200 million people in the world are facing problems due to the

high concentration of fluoride in drinking water (2). Fluorosis is a disease that caused by a high concentration of fluoride in the body of organisms. This disease has been reported around the world, including some areas of Iran (3,4). In addition, the high concentration of fluoride in drinking water can increase the risk of toxicity to aquatic organisms (5). Fluoride removal methods include coagulation and flocculation (6,7), Membrane Processes (8), adsorption on activated alumina (9,10) and ion exchange (11,12). In the recent years, the use of low prices absorbers in the reduction of fluoride in drinking water has been the focus and the research of scientists. Such materials can be referred to hydroxyapatite, calcite, Fluorspar, quartz (13), volatile ash (14), silica gel (15), coal ash (16), catalysts (17), zeolite (18), red clay (19) and bentonite (20). In this regard, regarding the fact that one of the chemicals used in water and sewage companies is Alum, and in some researches, this substance was used to remove fluoride, and had the relative favorable results. In this study, by using response surface methodology and Box-Behnken's model, the use of these chemicals in the removal of fluoride from drinking water has been optimized.

Because the typical optimization technique that is changed one variable during the study, with constant other variables, and the effect will be investigated in response results, is very time consuming and expensive. In systems that many variables are studied, these problems are more severe. This technique also does not show the interaction of different variables. Response surface methodology is a statistical design and analysis of the experimental results method and a useful technique for obtaining a valuable and meaningful version of a result, with the minimum experiments. This type of design will consider the interaction of different variables and is usable in operational parameter optimization in multi variable systems. Response surface methodology is used for modeling and analyzing problems of a favorable response that is affected by several variables, in order to obtain an optimal response (21). This method usually involves three stages of designing and running experiments, response surface modeling through regression and optimization. Therefore, RSM is a combination of mathematical and statistical techniques that is used to develop, improve and optimize the processes. One of the most common response surface designs is Box-Behnken's model. This method is very effective and flexible and offers sufficient data on the effects of variables and errors with a minimum of experiments (22).

Methods:

Experiment Design: This study is considered an analytical study. It was conducted by using response surface methodology (RSM) based on Box-Behnken's model to optimize the effect of variables effective in the removal of fluoride in drinking water, by using a spectrophotometer (UNICO- (UV/VIS) model 2150 and in accordance with the SPADNS procedure provided in standard methods for water and wastewater experiments book (23). Three variables of initial concentration of fluoride, pH and concentration of alum in three levels (-1, 0, +1) were studied that their variables and levels are provided in the table (1). The determination of variable amplitude was conducted with preliminary studies and literature review (6,7,24). The number of tests needed for applying this model was obtained from the equation $N = 2K$ $(K-1) + C_0$ (25). In this equation, N is the number of samples (tests), K is the number of factors (independent variables) and C_0 is the number of central points. Thus, in this study, box – Behnken's design with 5 central points and 17 experiments was conducted.

To evaluate the test data, the full quadratic model was used (Eq. 1). Experimental analysis was performed by using the Design Expert 7 software. To prevent systemic bias, random (26) conducted the experiments. The second order model coefficients are the interpreters of the amount of fluoride removal (response) as a function of the independent variables (factors). The research data were analyzed by using multiple regressions. The Coefficients were analyzed by using analysis of variance (ANOVA) and the amount of $(P \leq 0.05)$ was determined at the significant level.

Equation (1): General formula of fluoride removal based on the second order model
$Y = a_0 + a_1 * (F) + a_2 (pH) + a_3 (Alum$ $dose) + a_4 (F * pH) + a_4 (F * Alum dose) + a_5$

(pH * Alum dose) + a6 (F2) + a7 (pH2) + a8 (Alum dose2)

Test method: all chemicals used in this study were obtained from Merck, Germany. SPADNS method was used to measure the concentration of fluoride in the laboratory. With preparing the standard fluoride solutions with different concentrations and by using a spectrophotometer (UNICO- (UV/VIS) Model 2150 and in accordance with the instructions provided with standard methods for the Examination of Water and Wastewater book (23), first the calibration line was drawn. Then, the fluoride was measured in the considering samples. In order to perform the alum consuming optimization tests to reduce fluoride of water, a six-house jar test device was used as a batch reactor. In this study, the effect of initial fluoride concentration (2,3,4 mg/L), pH (6, 6.5 and 7) and the amount of coagulant (100, 150 and 200 mg/L) were studied in the removal efficiency.

Based on preliminary studies, the number of jar test rotations and the retention time in the slow and fast speeds were selected respectively rpm 120,

min1 and rpm30, min 20. PH adjustment was done with sulfuric acid and normal NaOH.

Table 1. The variables list and their levels

Variable name	Coded values		
	Low (-1)	Medium (0)	High (+1)
Intitial concentration of fluride	2	3	4
PH environment	6	60.5	7
Alum dosage	100	150	200

Results:

Designing the experiments and experimental results are provided in Table 2. The statistical analysis results of the variables that are summarized in Table 3, showed that the second-order statistical model is more appropriate for the design of removal fluoride experiment from drinking water by using Alum coagulant. Therefore, the final model was determined on this basis. Moreover, based on the analysis of variance, test data are in Table 3 below.

Table 2. The design matrix of variables experiment, their surfaces and the test results

Test number	Random number	Water fluoride		PH		Consuming Alum		Fluoride removal efficiency (%)
		Concentration (mg/l)	Surface	Criteria	Surface	Concentration (mg/l)	Surface	
1	9	2	-1	6	-1	150	0	36
2	11	4	1	6.5	0	100	-1	55
3	3	4	1	6	-1	150	0	59
4	4	3	0	6.5	0	150	0	73
5	8	3	0	6.5	0	150	1	75
6	5	3	0	6.5	0	150	0	78
7	12	2	-1	7	1	150	0	51
8	6	3	0	6	-1	100	-1	44.5
9	2	2	-1	6.5	0	200	1	56
10	1	3	0	6.5	0	150	0	76
11	17	2	-1	6.5	0	100	-1	51
12	13	4	1	6.5	0	200	1	65
13	14	3	0	6	-1	200	1	49
14	15	3	0	6.5	0	150	0	74
15	10	3	0	7	1	200	1	65
16	16	4	1	7	1	150	0	55
17	7	3	0	7	1	100	-1	41

Table 3. Summary of statistical characteristic in different models for fluoride removal from water by using alum

Model	R^2	R^2 Adjustment	R^2 Prediction	Standard Deviation	PRESS
Full second order	0.9772	0.9478	0.7129	2.98	784.13
Linear	0.1851	-0.0029	-0.2389	13.08	3383.80
Interaction	0.2552	-0.1916	-0.8865	14.26	5150.12
Third order	0.9946	0.9783	-	1.92	-

PRESS; Predicted residual error sum of squares

Table 4. Analysis of variance results for second-order response surface model factors in reducing fluoride

Changes Source	Sum of squares	Degrees of freedom	Mean Square	F-Value	P-value Prob > F	Results
Model	2662.62	8	296.54	33.29	<0.0001	Significant
F Concentration	200	1	200	22.45	0.0021	Significant
pH	69.03	1	69.03	7.75	0.0272	Significant
Alum Concentration	236.53	1	236.53	26.55	0.0013	Significant
F * pH	90.25	1	90.25	10.13	0.0154	Significant
pH * Alum dose	95.06	1	95.06	10.67	0.0137	Significant
F^2	434.9	1	434.9	38.6	0.0004	Significant
pH^2	1066.14	1	1066.14	119.67	<0.0001	Significant
Alum dose^2	373.03	1	373.03	41.87	0.0003	Significant
The remaining	68.61	8	8.91			
Fitting violation	53.81	4	15.85	4.28	0.0967	Not Significant
Net error	14.8	4	3.7			
The total	2731.24	16				

Table 5. Response surface regression model results to remove fluoride from drinking water by using alum

Word	Coefficient	The estimated coefficients	Standard error	The 95% confidence interval Lower limit	Higher limit
Constant coefficient	a_0	75.2	1.31	72.18	78.22
Concentration F	a_1	5	1.04	2.61	7.39
pH	a_2	2.94	1.04	0.55	5.33
Alum Concentration	a_3	5.44	1.04	3.05	7.83
F * pH	a_4	-4.75	1.46	-8.33	-1.37
pH * Alum dose	a_6	4.88	1.46	1.5	8.25
F^2	a_7	-9.04	1.43	-12.33	-5.75
pH^2	a_8	-15.91	1.43	-19.2	-12.62
Alum dose^2	a_9	-9.41	1.43	-12.7	-6.12

Equation (2): removal of fluoride efficacy based on second-order model coefficients

$Y = 75.2 + 5 (F) - 2.94 (pH) + 5.44 (Alum\ dose) - 4.75 (F * pH) + 1.25 (F * Alum\ dose) + 4.88 (pH * Alum\ dose) - 9.04 (F^2) - 15.91 (pH^2) - 9.41 (Alum\ dose^2)$

Equation (3): removal of fluoride efficacy by significant variables obtained from the second-order model

$Y = 75.2 + 5 (F) - 2.94 (pH) + 5.44 (Alum\ dose) - 4.75 (F * pH) + 4.88 (pH * Alum\ dose) - 9.04 (F^2) - 15.91 (pH^2) - 9.41 (Alum\ dose^2)$

Coefficients of quadratic model which determines the amount of fluoride removed by the independent variables of coagulant Concentration, environment pH and initial concentration of fluoride in the water, were analyzed by using test data

multiple regression analysis that are provided in Table 4.

The response of experimental system was conducted based on the general equation (1).

Multiple regression analysis was conducted to estimate the regression coefficients on the data

obtained from the tests and the coefficients were placed in the overall equation. Thus, the equation (2) was obtained. Then, a backward elimination method was used and statistically non-significant words ($P < 0.05$) were removed from the second-order model. The Coefficients for a model with P-value of each word are provided in the table (5). In equation (2), the words, which were not statistically significant, were excluded from the model. Therefore, the equation (3) provides the final statistical model with the coefficients of each term.

Table 6. Analysis results of second-order model variance to remove fluoride by alum

59.03	Mean
2.93	S.D
4.96	C.V(%)
525.44	PRESS
0.9749	R-Squared
0.9498	Adj R-Squared
0.8076	Pred. R-Squared
17.663	Adequate Precision

S.D: Standard deviation; C.V: Coefficient of variance;
PRESS; Predicted residual error sum of squares

Conclusion:

In order to obtain empirical models for predicting the response, linear relations, second and third order polynomial on the data obtained from the experiments were fitted. These models were then subjected to statistical analysis to select the appropriate model.

Figure (1a) shows that the predicted response values are fitted well with the values of model responses, so that the data are relatively on a straight line. As a result, the model can be used as a guide for moving into the design area.

Figure (1b) shows the distribution of residuals toward the fitted values. This graph is to determine the residual variance constant hypothesis. In the above diagram, no particular trend that is indicated high or low variance is observed. So, assuming constant variance will be accepted.
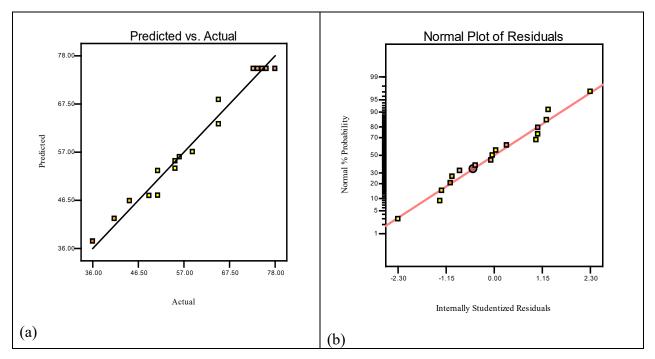

Figure 1. (a) predicted values versus actual values (b) Distribution of residuals toward the fitted values

Figure (2) is the distribution of residuals toward the experiments order and collecting data, and is used to assess the independence of residuals. In this graph, no trend can be seen that can reject the assumption of independent data. Thus, according to the analysis of the above diagrams, the selected model is suitable for data analysis.
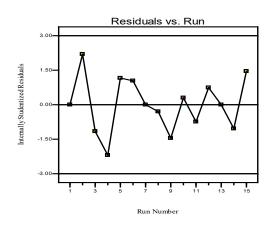
For graphical interpretation of interactions, the three dimensional regression models were used. Response surface interactions diagrams of significant factors have been derived from a quadratic equation statistically (Equation 3) are shown in Figure 3.

Response surface plots (Fig. 3) that are drawn by the software, are shown a three-dimensional view of the fluoride removal level, with different combinations of independent variables. Since the interaction of variables was significant. Therefore, the curved is clear in three-dimensional diagrams of the response surface.
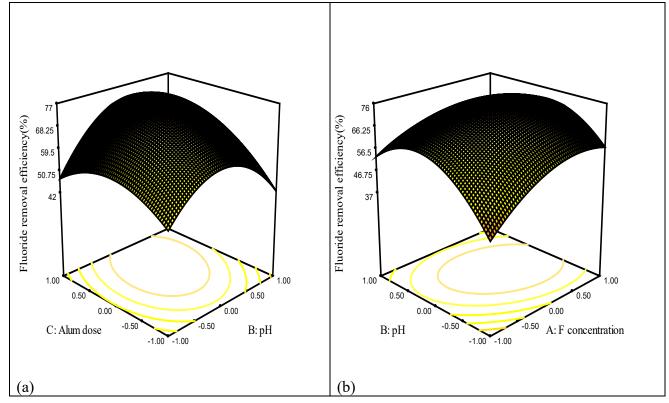

Figure 2. Distribution of residuals toward the experiments order

(a)

(b)

Figure 3. Design expert plot; response surface for fluoride removal as a function of (a) fluoride concentration and pH, and (b) pH and alum dose

Table 7. The optimum condition to remove fluoride from drinking water

Response	Fluoride concentration (mg/L)	pH	Alum concentration (mg/L)	Removal rate (%)		Error	Standard deviation	Desirability degree (%)
				Observed	Predicted			
Fluoride removal	3.25	6.55	166	77.45	76.83	0.62	0.18±	97.2

Each of two response level diagrams has a clear peak point that illustrates the importance of independent variables role, such as pH, initial concentration of fluoride and concentration of coagulant in providing maximum fluoride removal. Away from this peak point, reducing the fluoride removal efficiency is observed, so that the increase or decrease of each variable is not desirable. Figure (3) (a and b) show that the initial pH value is effective in the removal of fluoride. Based on the above figure, it is clear that the removal of fluoride amount has an increasing trend in the acidic pH range, but it decreases in inert atmosphere significantly. The highest percentage of removing fluoride is in the alum concentration of 150 mg/L and 5.6 pH, which is equivalent to 77%. When the pH will increase, the absorption rate will decrease and desorption rate will increase. Because of positive or neutral charge on the surface of the absorbent in the range of acidic pH, PH will not affect the absorbent capacity. But, in neutral and alkaline pH, due to the formation of repulsive electrical force on the absorbent surface and also the hydroxide ion competition, that have a high concentration in these conditions, with fluoride ions to occupy active sites on the absorbent surface, the efficiency of the fluoride removal will reduce by the absorbent. These results are consistent with Shims et al (27) findings that have announced a wide range for fluoride removal by aluminum hydroxides and the results of Verko et al, have announced that local kaolin in acidic pH that has many effects on fluoride removal from water, is consistent.

Moreover, based on the research results of Soshri T Pati et al., the adsorption of fluoride process on aluminum hydroxide precipitate causes the release of OH ions in the reaction. This reaction was largely dependent on pH and Optimum removal, pH is 6.5 that are consistent with the results of this study (28). Sanjel Oghlu et al have announced the pH as the most important factor in absorbing the fluoride on alum and found that acidic pH is more effective in absorbing fluoride on the

absorbent surface. Because the absorption of fluoride on the adsorbent surface releases OH anions into the environment and in the absence of pH reform, it can reduce the amount of fluoride intake that is consistent with the data obtained from this research (29).

In addition, according to the figure (3-b), with an increase in initial concentration of fluoride, the removal efficiency increases, but this process continues a little more than 3 mg/L and then the decreasing process of removal efficiency will be observed that may be due to lower absorption of fluoride on the surface of the aluminum hydroxide precipitate existing in the environment.

Process optimization and validation of tests:

To optimize the process parameters, to remove the maximum fluoride, the numerical optimization was applied. Based on the response surface and desirability functions, optimal conditions were obtained for the removal of fluoride. These conditions include the initial concentration of fluoride 3.25 mg/L, 6.55pH and the concentration of alum, 166 mg/L, fluoride removal efficiency and desirability, respectively were 76.83% and 97.2%.

To confirm the accuracy of predicted model and validity of the optimum condition, two additional tests were performed in optimum condition. The results are in the table (7).

According to this table data, the values obtained from experimental tests are consistent with predicted data by the model. These results indicate that the response surface methodology is a powerful tool for optimization of coagulation and flocculation with alum to remove fluoride from the water.

Based on the results of this study, Box-Behnken and response surface design method to determine the optimum conditions for coagulation and the flocculation process to remove fluoride was accepted. Validation results showed that these conditions are valid. The optimum condition to remove fluoride in the process, including initial concentration of fluoride 3.25 mg/L, 6.55 pH and

the concentration of alum, 166 mg/L and fluoride removal efficiency was equal to 76.83% and the degree of desirability was 97.2%, respectively

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