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Optimization studies for water defluoridation by adsorption: application of a design of experiments

Meral Mouelhi, Ikhlass Marzouk, Béchir Hamrouni*

Faculty of Sciences of Tunis, Desalination and Water Treatment Research Unit, University of Tunis El Manar, El Manar II, 2092 Tunis, Tunisia, Tel. +216 71 871 282; emails: mouelhimeral@gmail.com (M. Mouelhi), ikhlassmarzouk@gmail.com (I. Marzouk), bhamrouni@gmail.com (B. Hamrouni)

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ABSTRACT

Fluoride in groundwater is a worldwide problem. In Tunisia, it is one of the most abundant constituents occurring in groundwater, creating a major problem in safe drinking water supply. This paper aims to examine the fluoride removal from aqueous solutions by adsorption on activated alumina (AA) using a two-level full factorial design. For this sake, four operating parameters supposed to affect the removal efficiency were chosen: initial fluoride concentration, pH of the solution, adsorbent dose, and temperature. Factors that influence the fluoride removal efficiency were evaluated statistically by using factorial plots: the Pareto chart, main effect, interaction effect, normal probability plots, and the cube plot. Analysis of variance and *P*-value significant levels were used to check the significance of the effect on percentage removal. The statistical analysis allowed verifying that the four studied parameters have an influence on the fluoride elimination (*P*-values ≤ 0.05 and *F*-values >4.49). It was found that increasing adsorbent dose enhances significantly the fluoride removal efficiency (from 62.3 to 98.4%). In the second part of the study, suitability of AA for natural waters defluoridation was investigated. The technical viability of the process was verified in the case of groundwater sample as the percentage removal reached 76.3% at optimal conditions.

Keywords: Fluoride removal; Adsorption; Water treatment; Alumina; ANOVA; Factorial design

1. Introduction

Fluorine is a common element that is extensively distributed in earth's crust and exists as fluorides in a number of minerals, such as fluorspar, cryolite, or fluorapatite.

Traces of fluorides are present in numerous waters, with greater concentrations often associated with groundwater. Although optimum levels of fluoride in drinking water have beneficial effects on teeth, an excessive exposure to fluoride causes adverse effects such as dental and skeletal fluorosis [1].

The World Health Organization has set a guidance value of 1.5 mg L^{-1} for fluoride in drinking water [2].

Because of the permanent risks, fluoride removal from water with high fluoride content becomes necessary.

Several methods have been developed in wastewater treatment technology for fluoride removal. Advanced treatment technologies have proved to be efficient, as in the case of membrane separation

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*Corresponding author.

processes such as electrodialysis [3,4], Donnan dialysis [5], nanofiltration, and reverse osmosis [6,7]. Although membrane use has received universal acceptance, a number of limitations have slowed its use. These techniques involve, indeed, a high investment cost and require high technology for operation and maintenance.

Electrocoagulation process has also been used for defluoridation [8,9]. However, the shortcomings of this method are the high cost associated with the use of metal salts (aluminum sulfate, calcium hydroxide, etc.) and the generation of toxic sludge.

Thus, alternative techniques for reducing the fluoride amount in water have been developed.

Numerous investigations have focused on defluoridation by adsorption. The principle behind this technique is that fluoride is transported by diffusion from the bulk phase to the solid surface where it binds with the surface or interface between two phases by either chemical or physical forces.

Compared to other techniques, adsorption process is considered as an ideal and appropriate separation technique because of convenience, ease of operation, and simplicity of design.

Various media have been investigated to find out an economical and efficient defluoridating adsorbent, e.g. minerals, clays [10,11], or biosorbents [12–15]. Bhatnagar et al. [16] have written a comprehensive review on fluoride removal from water by adsorption. Different adsorbents used for defluoridation were compared. It was concluded that among the different adsorbents appropriate for the fluoride removal, activated alumina (AA) appeared to be an interesting media combining a high efficiency with a low-cost process. Removal of fluoride by AA is an established treatment technology that has been and still is practiced both by small- and large-scale water treatment enterprises. It was classified by WHO and the USEPA as one of the best demonstrated available technologies for fluoride removal [17].

Several factors influencing the adsorption of fluoride onto AA such as adsorbent dose, pH of the solution, initial concentration of fluoride, and temperature have been considerably studied and reported. Previous researchers use the traditional one-variable-at-a-time experiments to determine the individual effect of various factors on adsorption processes [18–20]. However, factorial design technique can be employed to provide a large amount of information and reduce the number of experiments, time, and overall research cost. The most important advantages of this technique are that the effects of individual parameters as well as their relative importance are obtained and that the interactional effects of two or more variables can be known [21]. Recently, a number of investigations have been conducted using this technique to model pollutant adsorption process [22–24]. Nevertheless, there are limited studies concerning the application of this method to the adsorption of fluoride. One of the goals of this study is to apply a two-level design of experiment in order to determine the influence of these parameters and their interactions on the removal efficiency of fluoride.

Preliminary tests of fluoride adsorption were carried out with AA to assess the different factors suspected to affect the fluoride sorption.

In addition, a case study was performed to estimate the feasibility and potential of this process under natural conditions.

2. Materials and methods

2.1. Materials

2.1.1. Activated alumina

The acid AA used in this study was purchased from Sigma-Aldrich and dried at 110°C for 24 h. This adsorbent was characterized by a particle size of 150 mesh, a pore diameter of 58 Å, a surface area of 155 $m^2 g^{-1}$, a melting point of 2,040°C, and a molecular weight of 101.96 g mol^{-1}.

Morphology of Al_2O_3 was characterized by scanning electron microscopy.

An image of the surface of AA particles is illustrated in Fig. 1.

Fig. 1(a), at 300× magnification, shows that the AA particles have a spherical shape and are of different sizes; moreover, the surface of an AA particle is fractured and rough (Fig. 1(b)). The elemental chemical composition of the alumina surface is determined by means of the X-ray microanalysis probe (energy dispersive spectroscopy) coupled to the microscope and the spectrum is depicted in Fig. 2. The EDX study revealed the presence of Al_2O_3 (87.96%) and CO_2 (12.04%).

2.1.2. Reagents

All the reagents used were of analytical grade. Double-distilled water was used in all the experiments. A stock solution of 1,000 mg L^{-1} fluoride was prepared by dissolving 2.21 g of sodium fluoride (Sigma-Aldrich) in double-distilled water. A total ionic adjustment buffer solution (TISAB) was used to adjust pH and to prevent interference of complexing ions during the measurement. A 1 L solution containing NaCl (58 g), trisodium citrate (3 g), glacial acetic acid

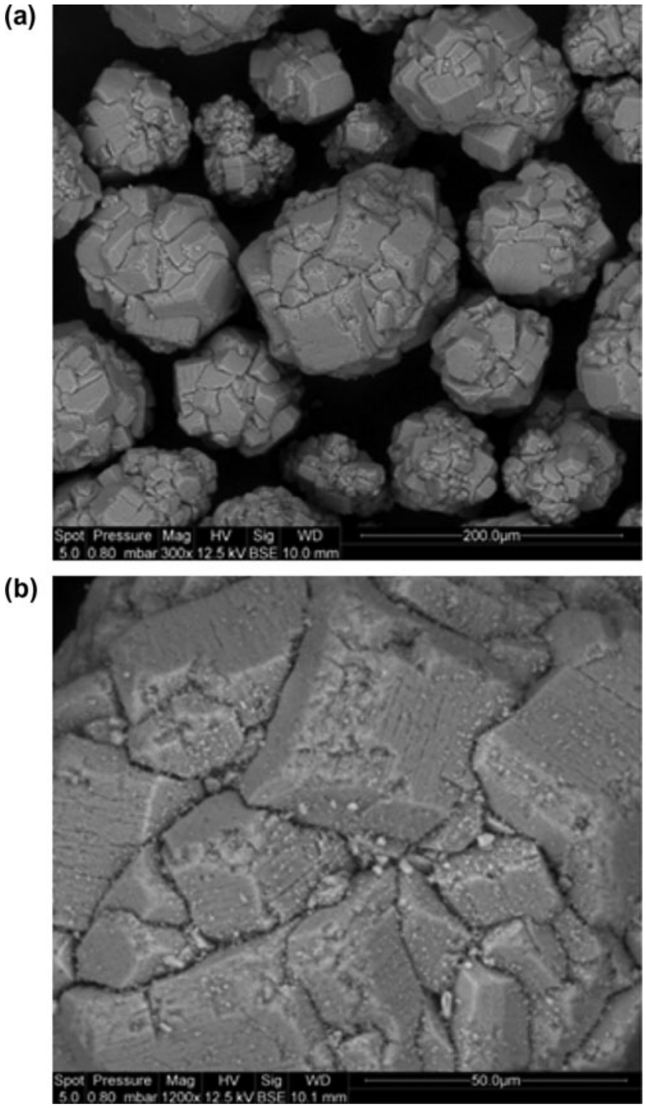

Fig. 1. Photomicrography of the surface of an activated alumina particles: magnification factor = 300 (a) and magnification factor = 1,200 (b).

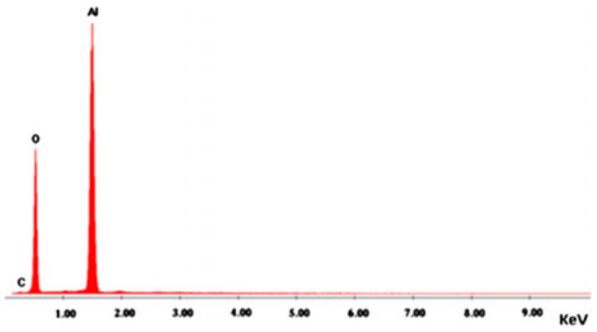

Fig. 2. Energy dispersive spectrum of the activated alumina surface.

(57 mL), and an appropriate amount of NaOH (5 M) was prepared in order to adjust pH at 5.3.

2.2. Batch adsorption experiments

All batch fluoride sorption studies were carried out in a high-density polyethylene bottles which were kept in an orbital shaker with thermostatic control (Grant OLS 200).

A varying amount of AA was added to each bottle containing initially 100 mL of fluoride with initial concentration 5 mg L^{-1} and stirred at 130 rpm until equilibrium was attained. The pH values of the solution were measured by a pH meter. Samples were withdrawn after a definite time interval and filtered through Whatman No 1 filter paper (0.45 μm). The residual fluoride concentration was determined using a potentiometer (Radiometer Analytical, ION Check 45), equipped with a fluoride ion selective electrode (sens ION model 51928). The concentration of fluoride in a water sample was determined by a calibration curve, which was prepared with standard solutions of fluoride concentrations ranging from 0.1 to 10 mg L^{-1}. The amount of adsorption at equilibrium (q_e, mg g^{-1}) was calculated according to Eq. (1)

$$q_e = (C_0 - C_e) \times \frac{V}{m} \tag{1}$$

The removal percentage of fluoride was calculated using Eq. (2):

$$\%\text{Removal} = \frac{C_0 - C_e}{C_0} \times 100 \tag{2}$$

where C_0 and C_e are the initial and equilibrium concentrations (mg L^{-1}), V is the volume of solution (L), and m is the weight of AA (g). In all figures, the error bars represent the standard deviation of three identical experimental points.

2.3. Validation of the analytical method

In order to validate the analytical protocol for determining residual fluoride concentration, some parameters have been studied. Linearity as well as specificity and fidelity tests were carried out with five replicates. The definitions and procedure for validation parameters have been applied according to the French method validation standard NF XPT 90-210 [25]. Experimental validation of the analytical method is given by Table 1.

Table 1
Validation of the analytical method

Test	Experimental value	Critic value	Conclusion	
Linearity	$F_l = 4{,}156.66$	$V_{Cl} = 8.53$	Linear	Linearity approved
	$F_{nl} = 3.93$	$V_{Cnl} = 6.23$	No curvature	
Specificity	$t_{obs} = 3.219$	$t_{(2,0,975)} = 4{,}303$	Slope equal to 1	Specific
	$t'_{obs} = 1.270$		Origin intercept is equal to 0	
Cochran	$C_{xobs} = 0.393$	$C_{cochran,\ \alpha=5\%} = 0.721$	Point group is considered no aberrant	
		$C_{cochran,\ \alpha=1\%} = 0.629$	Point group is considered no suspect	
Fidelity	$CV_r = 0.439\%$; 0.441%; 0.192%; 0.599%	$CV_r < 5\%$	Repeatable	Faithful
	$CV_R = 0.418\%$	$CV_R < 5\%$	Reproducible	

3. Results and discussion

3.1. Parameters affecting the adsorption

Adsorption processes are affected by several factors, such as initial pH, initial concentration of fluoride, adsorbent dose, and temperature. The main purpose of this study is to establish the ideal conditions of the adsorbent capacity.

3.1.1. Influence of pH

For the removal of fluoride from aqueous solutions by adsorption, pH is considered to be an important parameter. The effect of pH was determined by studying adsorption at an initial fluoride concentration of 5 mg L^{-1} with adsorbent dose of 1 g/100 mL of AA over a pH range of 4–12, keeping the other parameters constant at 25°C. The pH adjustments were made either with 0.1 M HCl or 0.1 M NaOH. The effect of pH on the adsorption of fluoride by AA is shown in Fig. 3.

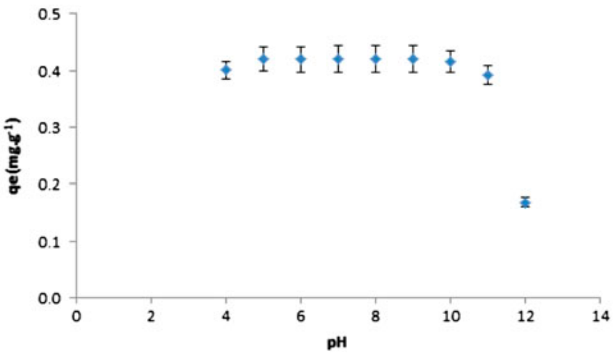

Fig. 3. Effect of pH on equilibrium adsorption capacity.

For pH values below pH 5, the main fluoride species present in acidic solutions are positively charged AlF^{2+}, AlF_2^+, and AlF_3 [26] species as well as the surface of Al_2O_3. Therefore, the adsorption of fluoride is retarded for acidic solutions because of the electrostatic repulsion. At acidic pH (pH 3), hydrofluoric acid was formed and hence the adsorption of fluoride occurred. A progressive decrease in fluoride removal was observed with an increase in pH (from pH 10) and this can be attributed to the competition for active sites by excessive amounts of hydroxide ions. So, it can be concluded that the optimum removal was between pH 6 and 9. Gong et al. [27] observed similar results using different types of aluminas and confirmed that the fluoride adsorption was strongly dependent on pH.

3.1.2. Influence of adsorbent dose

The effect of adsorbent dose on the amount of fluoride adsorbed was studied for two concentrations of fluoride. As it can be shown in Fig. 4, defluoridation capacity decreases from 0.8544 to 0.1489 mg g^{-1} (initial concentration of fluoride $C_0 = 5$ mg L^{-1}) and from 1.404 to 0.647 mg g^{-1} (initial concentration of fluoride $C_0 = 20$ mg L^{-1}) for 0.5–3.0 g/100 mL dosage of AA.

In addition, an increase in the fluoride removal percent is observed by increasing adsorbent dose. This may be due to the increase in availability of surface active sites resulting from the increased dose. However, it can be seen that after dosage of 2.0 g/100 mL in the case of $C_0 = 5$ mg L^{-1} and 3.0 g/100 mL in the case of $C_0 = 20$ mg L^{-1}, there was no significant change in percentage removal of fluoride. This is due to the overlapping of active sites at higher dosage, thus reducing the net surface area.

3.1.3. Influence of contact time

Fig. 5 shows the progression of adsorption reaction, the percentage removal of fluoride by AA after different contact times; as contact time increases, fluoride

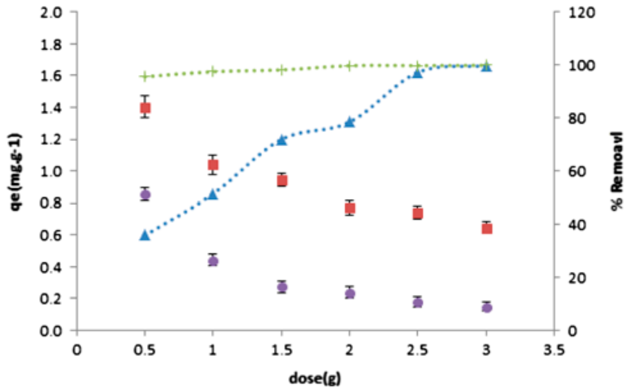

Fig. 4. Effect of adsorbent dose on equilibrium adsorption capacity: $C_0 = 5$ mg L^{-1}: %removal (+), q_e (■); $C_0 = 20$ mg L^{-1}: %removal (▲), q_e (●).

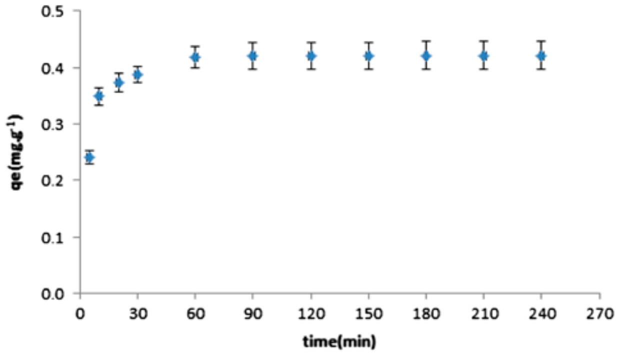

Fig. 5. Influence of contact time on equilibrium adsorption capacity.

removal also increases initially, but then gradually approaches a more or less constant value, reaching equilibrium in about 60 min. For further optimization of other parameters, this contact time was considered as the equilibrium time.

3.2. Statistical analysis

The use of statistical design of experiments is advantageous as it allows obtaining optimal conditions through a relatively smaller number of systematic experiments. The design determines which factors have important effects on a response as well as how the effect of one factor varies with the level of the other factors [28–30]. In this investigation, the factorial of the type 2^4, which consists on performing 16 experiments, was applied. The variables and levels for the experiment are presented in Table 2. Each factor was studied at both low and high levels. The higher level was designated as (+) and the lower value was designated as (−).

The regression equation with four parameters and their interaction with each other can be given by the following expression:

$$\begin{aligned}\%R = {} & b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4 + b_{12}X_1X_2 \\ & + b_{13}X_1X + b_{14}X_1X_4 + b_{23}X_2X_3 + b_{24}X_2X_4 \\ & + b_{34}X_3X_4\ldots\end{aligned} \tag{3}$$

where $\%R$ represents the experimental response, X_i is the coded variable (−1 or +1), b_i represents the estimation of the principal effect of the factor i for the response $\%R$, whereas b_{ij} represents the estimation of interaction effect between factor i and j for the response. The coefficient b_0 represents the average value of the response of 16 assays. The coefficients of the polynomial model were calculated by means of statistical analysis software MINITAB 15. The predicted responses were expressed in terms of percentage removal ($\%R$). The order in which the experiments were made was randomized to avoid systematic errors. The experimental design matrix for fluoride removal by adsorption from aqueous solutions is given in Table 3.

The effects, regression coefficients, standard errors (SE), and T values (standardized effects) are summarized in Table 4.

The regression model coefficients are calculated by dividing the net effects by two. The standardized effects were obtained by dividing the regression coefficients by standard error. The mathematical model representing fluoride removal efficiency ($\%R$) in the experimental region studied can be expressed by Eq. (4):

Table 2
The 2^4 factorial design for fluoride adsorption onto AA

			Experimental region	
Variables	Factors	Unit	Minimum value (−1)	Maximum value (+1)
X_1	Adsorbent dose (A)	g	0.5	1.5
X_2	pH (B)	–	5	9
X_3	Initial concentration of fluoride (C)	mgL^{-1}	5	20
X_4	Temperature (D)	℃	10	40

Table 3
Studied parameters in their reduced and normal forms

Experiment	*A* (g)	X_1	*B*	X_2	*C* (mg L^{-1})	X_3	*D* (°C)	X_4	%*R*
1	0.5	−1	5	−1	5	−1	10	−1	62.3
2	1.5	1	5	−1	5	−1	10	−1	98.4
3	0.5	−1	9	1	5	−1	10	−1	49.4
4	1.5	1	9	1	5	−1	10	−1	90.0
5	0.5	−1	5	−1	20	1	10	−1	46.5
6	1.5	1	5	−1	20	1	10	−1	73.8
7	0.5	−1	9	1	20	1	10	−1	38.5
8	1.5	1	9	1	20	1	10	−1	62.0
9	0.5	−1	5	−1	5	−1	40	1	94.7
10	1.5	1	5	−1	5	−1	40	1	98.3
11	0.5	−1	9	1	5	−1	40	1	77.9
12	1.5	1	9	1	5	−1	40	1	99.3
13	0.5	−1	5	−1	20	1	40	1	72.3
14	1.5	1	5	−1	20	1	40	1	99.3
15	0.5	−1	9	1	20	1	40	1	51.8
16	1.5	1	9	1	20	1	40	1	87.0

Table 4
Statistical parameters for a 2^4 design

Term	Estimated coefficient	SE	*T*	*P*
Constant	75.094	2.032	36.95	0.000
A	13.419	2.032	6.60	0.001
B	−5.606	2.032	−2.76	0.040
C	−8.694	2.032	−4.28	0.008
D	9.981	2.032	4.91	0.004
D * B	1.669	2.032	0.82	0.449
D * C	0.706	2.032	0.35	0.742
A * D	−2.519	2.032	−1.24	0.270
B * C	−0.969	2.032	−0.48	0.654
B * D	−0.469	2.032	−0.23	0.827
C * D	1.219	2.032	0.60	0.575

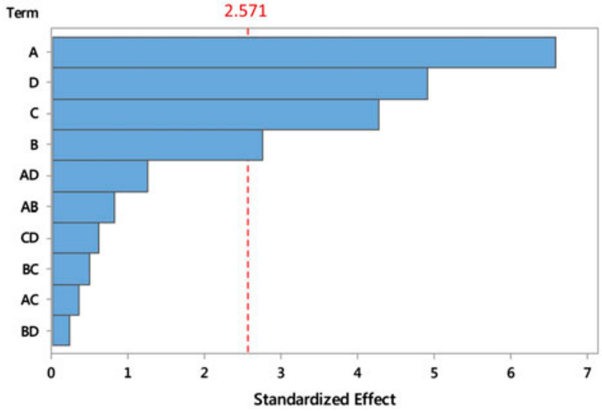

Fig. 6. Pareto chart for standardized effects.

$$\%R = 75.10 + 13.42X_1 - 5.59X_2 - 8.68X_3 + 9.99X_4 + 1.56X_1X_2 + 0.72X_1X_3 - 2.53X_1X_4 - 0.98X_2X_3 - 0.46X_2X_4 + 1.22X_3X_4 \quad (4)$$

3.2.1. Student's test

To determine whether the calculated main and interaction effects were significantly different from zero, a Student's test was carried out with a confidence level of 95%. The relative importance of the various investigated factors and their interactions are illustrated in the Pareto chart (Fig. 6). Accordingly, all the studied parameters seem to be highly influent on the experimental response since the absolute values of their coefficients are higher than the *t* value ($t = 2.571$, for $\alpha = 0.05$, and 16 degrees of freedom). Moreover, it can be seen that the first-order interactions are negligible implying that the main factors are independent of each other.

3.2.2. Analysis of variance

The obtained model was validated using the analysis of variance method (ANOVA). The sum of squares (SS) and mean square (MS) of each factor as well as *P*-value and the *F*-ratio were determined by choosing an α risk of 5%. Results are summarized in Table 5.

P-value is the probability value that is used to determine the statistically significant effects in the model. The importance of the data can be judged by its *P*-ratio, with values closer to zero denoting greater

Table 5
Analysis of variance

Source	Degrees of freedom	Sum of squares (SS)	Mean square (MS)	*F*-value	*P*-value
A	1	2,881.01	2,881.01	43.60	0.001
B	1	502.88	502.88	7.61	0.040
C	1	1,209.30	1,209.30	18.30	0.008
D	1	1,594.01	1,594.01	24.12	0.004
A * B	1	44.56	44.56	0.67	0.449
A * C	1	7.98	7.98	0.12	0.742
A * D	1	101.51	101.51	1.54	0.270
B * C	1	15.02	15.02	0.23	0.654
B * D	1	3.52	3.52	0.05	0.827
C * D	1	23.77	23.77	0.36	0.575
Error	5	330.38	66.08		
Total	15	6,713.91			

significance. For a 95% confidence level, the *P*-value should be less than or equal to 0.05 for the effect to be considered statistically significant [31]. The *F*-ratio is defined as the ratio of the respective mean square effect and the mean square error. Since for an α risk of 5%, 1 degree of freedom, and 16 factorial tests $F_{0.05,1,16}$ is equal to 4.49, all the effects with *F* values higher than 4.49 are significant. According to Table 5, we can confirm once again the statistical significance of the studied parameters on the modification of the response as the corresponding *P*-values are less than α (0.05) and *F* values are higher than $F_{0.05,1,16}$ (4.49).

3.2.3. Normal probability plots

To identify the "real" effects, a normal probability plot is used. One point on the plot is assigned to each effect. According to the normal probability plots, the points which are close to a line fitted to the middle group of points represent those estimated factors that do not have any significant effect on the response variables. Points far away from the line likely represent the "real" factor effects [32]. Normal probability plot of standardized effects is represented in Fig. 7. This graph coincides with the analysis performed for significant results. All the studied factors are characterized by square signs situated away from the centerline which confirms their statistical significance.

To graphically verify the normality assumption for data, a normal probability plot was performed by plotting data against a theoretical normal distribution in such a way that the points should form an approximate straight line. Fig. 8 shows that the experimental data come from a normal distribution since the experimental points follow a straight line. We can then validate the modeling of the fluoride removal result by the linear polynomial model.

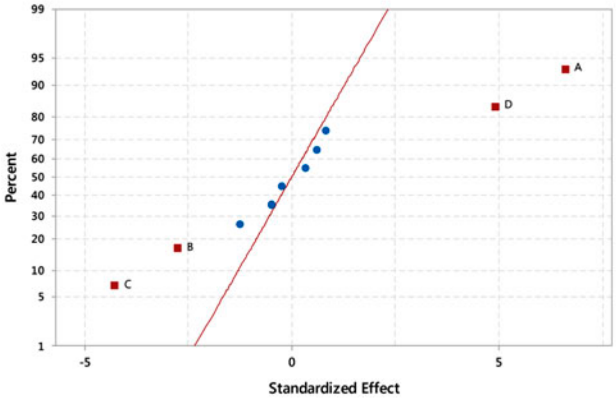

Fig. 7. Normal probability plot of standardized effects at alpha = 0.05. Effect type: not significant (●), significant (■). Factors: dose (A), pH (B), concentration (C), and temperature (D).

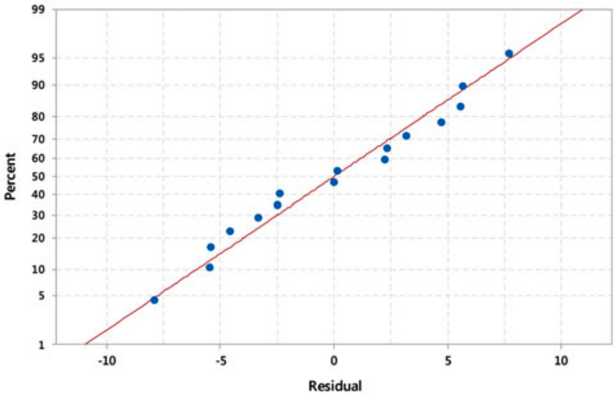

Fig. 8. Normal probability plot of residuals for fluoride removal efficiency.

3.2.4. Main and interaction effects

The main effects of each parameter on the fluoride removal percentage are shown in Fig. 9. From the analysis of the graphs and the coefficients of Eq. (4), we can conclude that adsorbent dose is the most important variable on the fluoride removal efficiency since its coefficient is the largest (13.419). The positive sign of this coefficient means that the intensification of this parameter increased the amount of fluoride removed. That is also observed in the case of effect of temperature. However, the effect of pH and initial fluoride concentration factors are negative since a decrease in %*R* is observed when these factors change from low to high.

The plots of the interaction effects are also studied and they are shown in Fig. 10. The parallel lines in this figure indicate that there is no interaction between the two factors. It can be seen that there is no significant interaction between all factors. Interactions between adsorbent dose and pH as between pH and initial concentration of fluoride are both negative. A positive interaction effect was observed between temperature and dose, and between temperature and concentration.

For a better understanding of the relationship between factors and a response, a cube plot was carried out (Fig. 11). The cube plot indicates that increasing adsorbent dose from 0.5 to 1.5 g enhances significantly the fluoride removal efficiency by 36.1% (from 62.3 to 98.4%) at low temperature (10˚C), while at higher temperature (40˚C), changes in adsorbent dose do not have a greater effect (an increase of only 3.6%). In addition, increasing initial fluoride

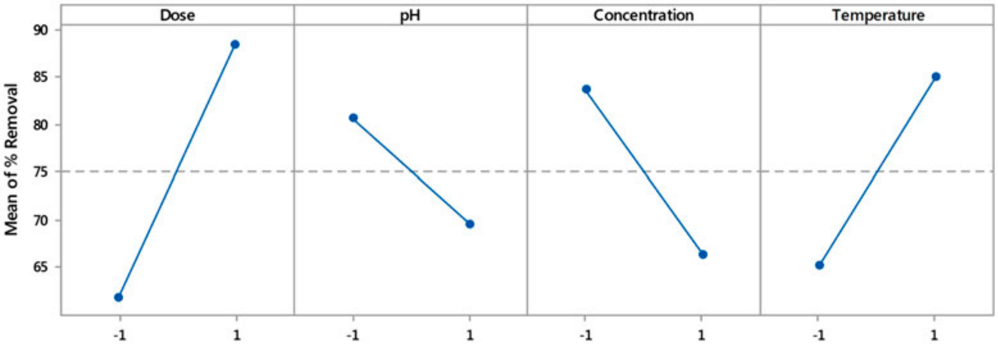

Fig. 9. Main effects plot for fluoride removal.

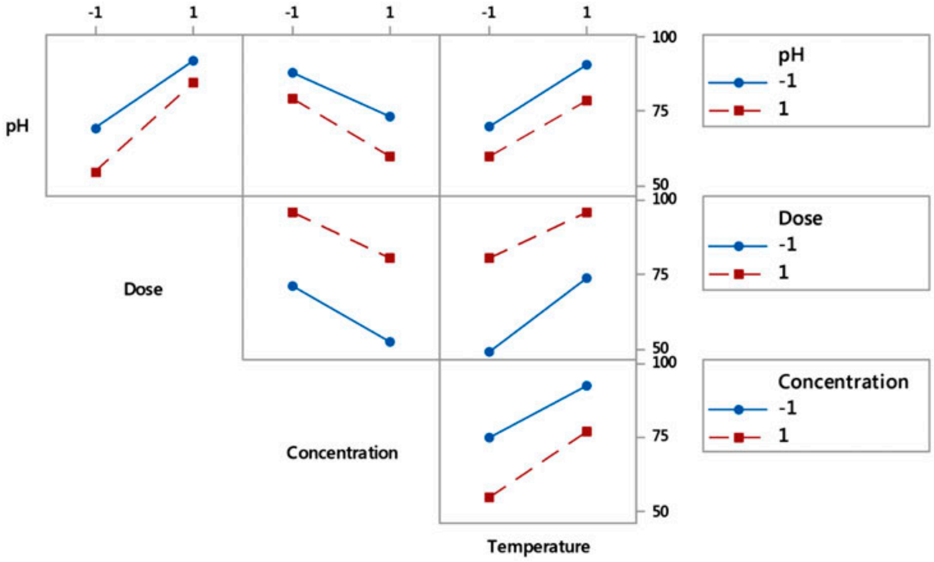

Fig. 10. Interaction effects plot for fluoride removal.

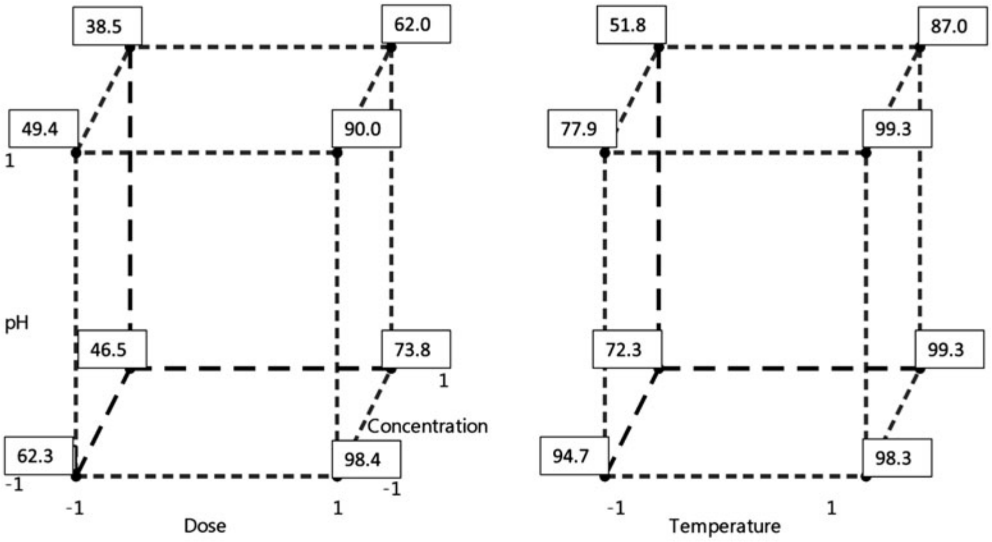

Fig. 11. Cube plot for fluoride removal.

concentration from 5 to 15 mg L^{-1}, at higher adsorbent dose (1.5 g), diminishes the response from 98.4 to 73.8% which means a decrease of 24.6% at lower temperature. A variance of only 1% is observed at higher temperature. This means that both the effect of adsorbent dose and initial fluoride concentration are higher when the temperature is low. Other interactions showed no important features for discussion.

Besides, the maximum adsorption of fluoride was 99.3%. This high percentage was obtained using the optimal conditions, namely higher temperature (40°C) and adsorbent dose of 1.5 g. Moreover, if the initial concentration of fluoride is high (20 mg L^{-1}), it is better to work under the lowest pH (pH 5).

Table 6
Characteristics of real water samples

Characteristics	Sample A	Sample B
Origin	Groundwater	Seawater
pH	6.98	7.64
Conductivity (mS cm^{-1})	4.22	53.70
Turbidity (NTU)	178	1.65
Initial fluoride concentration (mg L^{-1})	5.95	5.28
%Removal	76.30	42.57

3.3. Case study

The main objective of this study is to validate the suitability of AA for the water defluoridation by investigating the removal efficiency of fluoride in real natural waters.

We chose to work on two natural water samples obtained from different sources. The characteristics of these samples are presented in Table 6.

This study was performed under optimal conditions found previously (a sample volume of 100 ml with adsorbent dose of 1 g L^{-1} and stirred in thermostatic bath for 90 min at 25°C). The results confirm the effectiveness of the defluoridation by AA under natural conditions. These returns reveal that in the case of groundwater, the fluoride removal percentage reaches 76.3%, while only 42.6% was reached for the defluoridation of the seawater sample. The difference can be attributed to the complexity of the seawater matrix with high concentrations of carbonate and sulfate. Moreover, the removal rates of fluoride were relatively low in comparison with the removal rate from synthetic wastewater. This may be due to the presence of the organic compounds and other ions which may competitively adsorb on AA, leading to a decrease in fluoride removal. It will be quite important to investigate the influence of organic matter and co-present ions on the fluoride adsorption. It is also important to note that this technique is very effective in the treatment of water intended for human consumption, as it has helped reduce the fluorine content in the standard required by the WHO (1.5 mg L^{-1}) and this without any pretreatment confirming that the defluoridation by AA is a cost-effective solution.

4. Conclusions

The full factorial design applied allowed the simultaneous investigation of four factors executing only 16 experiments and the evaluation of the most important factors for fluoride removal. From the statistical analysis, it was determined that all the studied parameters seemed to be highly influent and significant, with *t*-values greater than 2.571. Adsorbent dose and temperature had a positive effect, whereas pH and initial concentration of fluoride exhibited a negative influence on removal efficiency. However, interaction effects were non-significant on fluoride adsorption. The maximum adsorption of 99.3% was obtained using the optimal conditions (40°C and 1.5 g of adsorbent). Moreover, this defluoridation process appeared to be effective for natural waters treatment since the percentage removal reached 76.6% in the case of groundwater under optimal conditions and with no pretreatment.

List of symbols

C — concentration (mg L^{-1})
q_e — amount of adsorption at equilibrium (mg g^{-1})
C_0 — initial concentration (mg L^{-1})
C_e — equilibrium concentration (mg L^{-1})
V — volume of solution (L)
m — weight of activated alumina (g)
b_i — estimation of the effect of the factor i
b_{ij} — estimation of the interaction effect between factor i and j for the response
X_i — coded variable

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