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Fluoride removal from aqueous solution by Purolite A520E resin: kinetic and thermodynamics study

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ABSTRACT

Fluoride in drinking water above permissible level causes dental and skeletal fluorosis. Fluoride removal operations have been conducted first on a "model" water solution (i.e. distilled) in which the fluoride concentration has been varied, and second on underground water (Louza 2) using the Purolite A520E resin. Batch sorption studies were carried out to determine the effect of initial fluoride concentration, agitation time, adsorbent dose, co-ions, and temperature on the removal of fluoride by the resin. The amount of fluoride ions removed per unit mass of Purolite A520E resin, at 30°C from 5 $\mathrm{mg\,L^{-1}}$ fluoride ion solution, was estimated to be 2 $\mathrm{mg\,g^{-1}}$. The experimental data fitted well to the Langmuir and Freundlich isotherms. Thermodynamic parameters such as ΔH°, ΔS°, and ΔG° were calculated, indicating that the adsorption process was spontaneous and endothermic. The fluoride content was reduced to 1.20 from 3.39 $\mathrm{mg\,L^{-1}}$ by treating Louza 2 water with the Purolite A520E resin (2 $\mathrm{g\,L^{-1}}$, shaking time 30 min). The fluoride saturated resin was regenerated with sodium chloride solution. All the regeneration experiments were carried out at room temperature. Desorption efficiency of the resin was studied using 6% NaCl solution as eluent. It was observed that more than 98% desorption could be successfully made. The cost of the produced cubic meter of water is estimated to 0.25 €/m^3.

Keywords: Drinking water; Defluoridation; Exchange resin; Purolite A520E

1. Introduction

Environmental fluoride has received much attention on account of the fact that an optimum concentration has been found to reduce the incidence of dental decay. Low levels of fluoride are required for humans and animals and have beneficial effects on tooth and bone structures. However, the ingestion of excessive fluoride, mainly through drinking water, causes dental and skeletal fluorosis [1]. The optimum fluoride level in drinking water for general good health set by the World Health Organization WHO is considered to be between 0.5 and 1.5 $\mathrm{mg\,L^{-1}}$ at temperature ranging from 12 to 25°C [2]. In the south of Tunisia, especially in the regions of Gafsa, Metlaoui, and Redayef, fluoride contents in drinking water are significantly higher than drinkability standards (Table 1) [3]. Concentrations

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higher than this can lead to fluorosis, which causes a serious health problem for the population.

Several methods have been tried to remove excessive amounts of fluoride from drinking water, namely, adsorption [3–5], chemical addition to cause precipitation [6,7], ion exchange [8–10], reverse osmosis/nanofiltration [11–14], Donnan dialysis [15], and electrodialysis [16].

Iminodiacetate resins [17] such as chelex 100 and Amberlite IRC-178 are widely used [18] but with insignificance in selectivity [19,20]. Other chelating resins that are employed for such purpose are 4-viny pyridine-divinylbenzene/acrylonitrile-divinylbenzene copol ymers, Amberlite IRA-400, Biorad AGMP-1, silica-based C18 support, Amberlyst A-26, Dowex-2, and Merrifield chloromethylated resins [21]. Unfortunately, current resins are often not specific to the defluoridation of water. Indeed, the affinity of the ion exchange vis-à-vis the fluoride ion is generally lower than for other ions. It follows a prior elimination of all other anions which is not always desirable. The problem of cost of resin regeneration severely limits the use of processes [13].

This study will contribute to the removal of fluoride from aqueous environments as well as in the field of analytical and environmental chemistry. The used resin Purolite A520E provides good stability, high sorption capacity for ions, and good flexibility in working conditions such as durability and chemical stability toward hard environments. It could be regenerated successfully. The Purolite A520E resin has been used only for nitrates removal [22]. Fluoride removal operations have been conducted first on a "model" water solution (i.e. distilled) in which the fluoride concentration has been varied, and second on underground water (Louza 2) using the Purolite A520E resin. The sorption studies of fluoride were carried out to evaluate sorption isotherms, too. The equation isotherms, such as Langmuir and Freundlich, were successfully used to model the experimental data.

2. Experimental

2.1. Materials

All reagents used were of commercially available high-purity Analar grade (Merck or Aldrich, India). A stock solution of 250 mg L^{-1} fluoride was prepared by dissolving 552.5 mg of sodium fluoride (Merck, Germany) in 1.0 L of distilled water and all synthetic (model) solutions for removal experiment and analysis were prepared by appropriate dilution from the freshly prepared stock solution. A Tunisian underground water from south of Tunisia (Louza 2) was treated in this study. The water has particularly high levels of fluorides ($[F^-] = 3.39$ mg L^{-1}), which represents a permanent risk for the rural population, which relies on underground water (wells) for its daily consumption.

Before use, the Purolite A520E resin was washed in distilled water to remove the adhering dirt and then dried at 50°C. After drying, the resin was screened to obtain particle size range of 0.3–1.2 mm. The main characteristics of Purolite A520E resin, a macroporous anion-exchange resin, are given in Table 2.

2.1.1. Ionic analysis methods

The analytical procedures utilized in this study were those recommended by Afnor [23]. Calcium and magnesium concentration was successively obtained by complexometric determination with EDTA on the same water sample. Alkalinity: determination of OH^-, CO_3^{2-}, and HCO_3^{2-} concentrations of the sample were carried out by neutralization of a given volume of water by hydrochloric acid 0.02 M in the presence of phenolphthalein and helianthin. Chlorides and sulfates were analyzed by ion chromatography in an AS11 4 mm column (DIONEX). However, this analytical method was imprecise for fluorides owing to the high amount of chloride ions. Fluoride concentrations were measured on a SevenMulti^{TM} instrument (Mettler Toledo) using a perfectION^{TM} (Mettler Toledo) ion selective electrode for fluoride. TISAB III (58 g of NaCl, 57 mL of CH_3COOH, and approximately 150 mL of 6 M NaOH in a volume of 1,000 mL) was used to maintain pH 5.3, to control ionic strength and de-complex fluoride. The calibration of the ion meter was done with fluoride solutions of 10, 1.0, and 0.1 mg L^{-1} concentrations. pH was measured using the same instrument.

2.1.2. Batch tests

All experiments were carried out twice and the adsorbed fluoride ion concentrations reported were the means of duplicate experimental results. The reproducibility of the concentration measurements

Table 1
Fluoride concentration of drinking waters from Gafsa regions (south of Tunisia)

	Metlaoui Louza 1	Metlaoui Louza 2	Redayef Tabeddil	Om Elarayes	Gafsa FM4	Foum El Maaza
$[F^-]$ (mg L^{-1})	2.88	3.39	2.73	2.80	2.61	2.20

Table 2
Physicochemical properties of resin Purolite A520E

Skeleton	Polystyrene cross-linked with divinylbenzene of the macroporous type
Functional groups:	Quaternary ammonium
Physical aspect	Opaque cream spherical beads
Granulometry	0.3–1.2 mm
Ionic form	Cl^-
Humidity	45–52%
Limit of temperature	100°C
Limits of pH	0–14
Real density	1.06

was within 2%. Batch-wise adsorption study was carried out for fluoride at room temperature, i.e. 30 ± 1°C. The sample solution (100 mL) containing fluoride ion (5 mg L^{-1}) was taken in 200 mL beaker flask. The resin (0.2 g) was added and the mixture was agitated for a fixed period of time. The shaking speed was 120 strokes per min throughout the study.

Batch sorption studies have been carried out to determine the effect of initial fluoride concentration, agitation time, adsorbent dose, co-ions, and temperature on the removal of fluoride by the resin.

To determine the equilibrium sorption time, experiments were conducted by varying contact time of 2, 4, 6, 8, 10, 12, and 14 min to a solution containing initial concentrations of 5 mg L^{-1} and 2 g L^{-1} of resin.

To study the effect of an increase in the amount of resin on fluoride removal, experiments were conducted by varying the amount of 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, and 3.5 g L^{-1} to a solution containing an initial fluoride concentration of 5 mg L^{-1}. The samples were agitated up to equilibrium and the fluoride residual concentrations were determined.

The effect of sulfate SO_4^{2-} and hydrogenocarbonate HCO_3^{2-} on the defluoridation process using Purolite A520E was found by spiking synthetic fluoride solution ($[F^-] = 5$ mg L^{-1}) with different concentrations of co-ions (SO_4^{2-}, HCO_3^{2-}) and investigated for fluoride removal rate.

At the end of each experiment, the resin was filtered and the residual fluoride content was measured. The amount of adsorption at equilibrium, Q_e (mg g^{-1}), was calculated by:

$$Q_e = (C_i - C_e)V/W \quad (1)$$

where C_i and C_e are the initial and equilibrium liquid phase concentrations (mg L^{-1}), respectively, V the volume of solution (L), and W the weight of the Purolite A520E resin used (g).

3. Results and discussion

3.1. Effect of shaking time and initial concentration

The effect of shaking time on the adsorption of fluoride onto the Purolite A520E resin was studied. It was evident from the Fig. 1 that 2 mg g^{-1} of fluoride was removed within 10 min. The equilibrium was established within 10 min and showing a slight increase. This might be due to the fact that once a certain amount of fluoride ions gets adsorbed onto Purolite A520E resin within a given time (<10 min), no more removal occurs afterwards, i.e. the removal (or doping) level might have been reached. Further experimental work was carried out at 30 min shaking time in order to avoid sorption error.

The amount of fluoride ions removed per unit of Purolite A520E resin (Q_e, mg g^{-1}) at different initial fluoride concentrations and temperature is collected in Table 3. The results reveal that the amount of fluoride adsorbed per unit mass of Purolite A520E resin increased with the increase in initial fluoride concentration and rise in temperature. The variation of Q_e with temperature indicates that the process is endothermic in nature.

3.2. Effect of Purolite A520E dose

Adsorbent dose is a significant parameter because this concludes the capacity of an adsorbent for a given initial concentration of the adsorbate at the operating conditions. The effect of Purolite A520E dose on the removal of fluoride ions for the initial fluoride concentration of 5 mg L^{-1} was studied and is shown in Fig. 2.

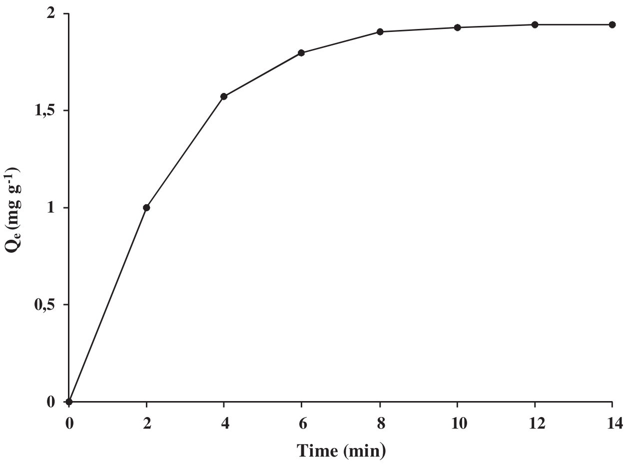

Fig. 1. Effect of shaking time on the removal of fluoride ions by Purolite A520E resin. ($[F^-]_i = 5$ mg L^{-1}, dose of resin 2 g L^{-1}, temperature 30°C).

Table 3
Equilibrium parameters for the removal of fluoride ions per unit mass ($mg\,g^{-1}$) of Purolite A520E

	C_e ($mg\,L^{-1}$)			Q_e ($mg\,g^{-1}$)		
$[F^-]_i$ ($mg\,L^{-1}$)	30°C	40°C	50°C	30°C	40°C	50°C
2.5	0.40	0.36	0.33	1.05	1.07	1.08
5	0.87	0.84	0.78	2.06	2.08	2.11
7.5	1.75	1.70	1.67	2.87	2.90	2.91
10	2.88	2.83	2.75	3.56	3.58	3.62

It was observed that the value of Q_e increased with a decrease in dose of Purolite A520E resin. This increase in fluoride removal was due to the availability of a higher number of fluoride ions per unit mass of resin. The maximum removal fluoride was found to be 5.32 $mg\,g^{-1}$ at a Purolite A520E resin dose of 0.05 g/100 mL and initial fluoride concentration of 5 $mg\,L^{-1}$. Further experiments were carried out using 0.2 g of resin per 100 mL of fluoride ion solution, as it exhibited appreciable removal capacity, for the optimization of adsorption parameters.

3.3. Sorption–desorption mechanisms

The mechanism of fluoride removal by Purolite A520E resin is shown in Fig. 3. The fluoride saturated resin was regenerated with 6% sodium chloride solution. The method used consisted of brewing the resin in NaCl solution (10 g of resin/1,000 mL of NaCl solution) during one hour at a stirring speed of 120 strokes per min. The concentration of fluorides was then measured in this solution following filtration. The resin was removed, washed in distilled water, and then dried at 50°C. It was observed that more than 98% desorption could be successfully made.

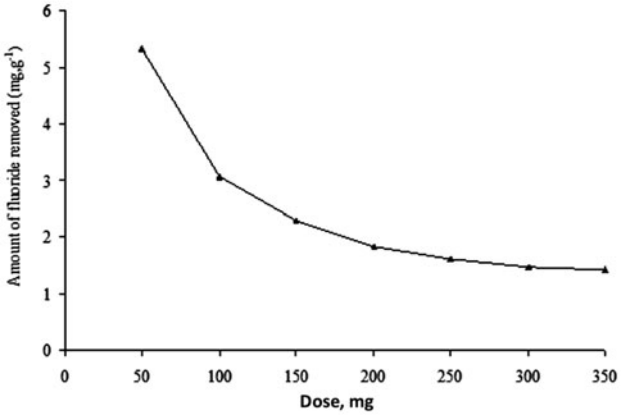

Fig. 2. Effect of resin dose on the removal of fluoride ($[F^-]$ = 5 $mg\,L^{-1}$, shaking time 30 min, V= 100 mL, and T= 25°C).

3.4. Adsorption isotherms

Investigation of data by isotherm is the main parameter required for the design of an adsorbent and it is important for calculating the adsorption capacity of the adsorbent system. Several models have been used for this purpose. The mathematical expressions Freundlich and Langmuir are used in this study [24,25]. The goodness of fit was discussed using correlation coefficient, r.

Freundlich [$\log Q_e = \log k + (1/n)\log C_e$], Langmuir [$(C_e/Q_e = (1/Qb) + (C_e/Q)$] equations were applied, where Q_e is the amount of fluoride ion adsorbed per unit mass of the adsorbent and C_e is the amount of fluoride ion in liquid phase at equilibrium. k, n, Q, and b are Freundlich, Langmuir constants, respectively. These equations are applied to correlate the amount of the fluoride adsorbed per unit amount of the adsorbent and the initial concentration of adsorbate is in the range of the 2.5–10 $mg\,L^{-1}$ using 0.2 g of resin per 100 mL of adsorbate and 30 min shaking time.

The Langmuir and Freundlich models are widely used isotherms. The analytical equation of Langmuir model was plotted. C_e/Q_e vs. C_e gives a straight line, indicating that the Langmuir adsorption is also followed by the adsorption data very well (Fig. 4). From the intercept and slope, the values of Q and b have been evaluated and compiled in Table 4. The sorption capacity of Purolite A520E resin was found in the average 5 $mg\,g^{-1}$ while it was 3 $mg\,g^{-1}$ without shaking the solution.

The essential characteristic of Langmuir isotherm can be expressed in terms of a dimensionless constant, separation factor R_L, which describes the type of isotherm [26] and is calculated by:

$$R_L = 1/(1 + bC_i) \tag{2}$$

where C_i is the initial concentration of fluoride ions and b is the Langmuir isotherm constant.

Values of $R_L < 1$ represent favorable adsorption and values greater than 1.0 represent unfavorable adsorption. The values of R_L (Table 5) calculated were 0.09–0.37, showing that our system is favorable.

The Freundlich adsorption isotherm based on heterogeneous surface was applied for the fluoride removal by adsorption. The constants of Freundlich adsorption model were calculated by plotting graph log Q_e vs. log C_e. Linear plots of log Q_e against log C_e

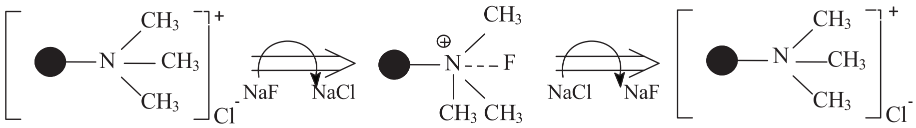

Fig. 3. Mechanism of fluoride sorption on Purolite 520E resin and its desorption.

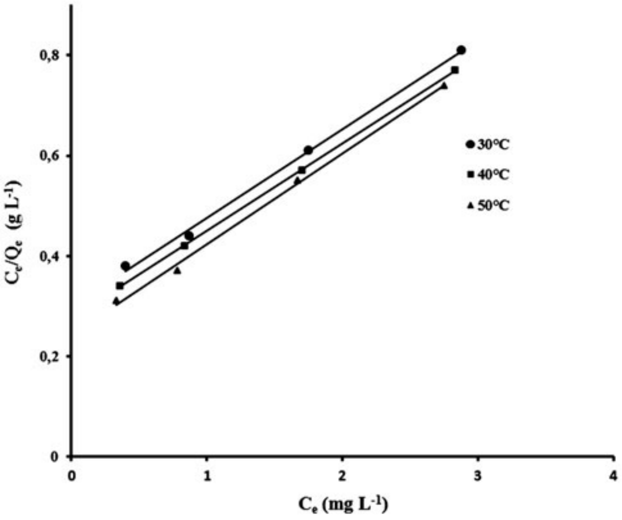

Fig. 4. Langmuir isotherm for the removal of fluoride by Purolite A-520E resin.

Table 4
Langmuir and Freundlich isotherm constants for the removal of fluoride by Purolite A520E resin

Isotherm	Statistical parameters constants	Temperature		
		30℃	40℃	50℃
Langmuir	r	0.99	0.99	0.99
	Q (mg g^{-1})	5.26	5.23	5.15
	b (L mg^{-1})	0.68	0.75	0.93
Freundlich	r	0.97	0.98	0.98
	n (mg g^{-1})	1.51	1.56	1.74
	k (g L^{-1})	1.90	2.05	2.22

Table 5
Langmuir isotherm constant R_L

[F$^-$]$_i$ (mg L^{-1})	R_L (mg L^{-1})		
	30℃	40℃	50℃
2.5	0.37	0.34	0.30
5	0.23	0.21	0.17
7.5	0.16	0.15	0.12
10	0.13	0.11	0.09

(Fig. 5) indicate the applicability of the Freundlich isotherm. From the intercept and slop, the values k and$1/n$ have been evaluated and compiled in Table 4. The results indicated that the adsorption capacity, k, increased with a rise in temperature suggesting that the removal of fluoride ions by Purolite A520E is an endothermic process. Furthermore, the values of adsorption intensity (n) for fluoride ion are in the range of 1.51–1.74. The values of n lie between 1 and 10, indicating favorable adsorption [26].

3.5. Thermodynamic parameter

The standard free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) were calculated from the variation of equilibrium constant k_0 with temperature. The values of k_0 were determined by the reported method [27]. The thermodynamic parameters were calculated using the following equations:

$$\Delta G^\circ = -\mathrm{RT}\ \mathrm{Ln}\, k_0 = \Delta H^\circ - T\Delta S^\circ \quad (3)$$

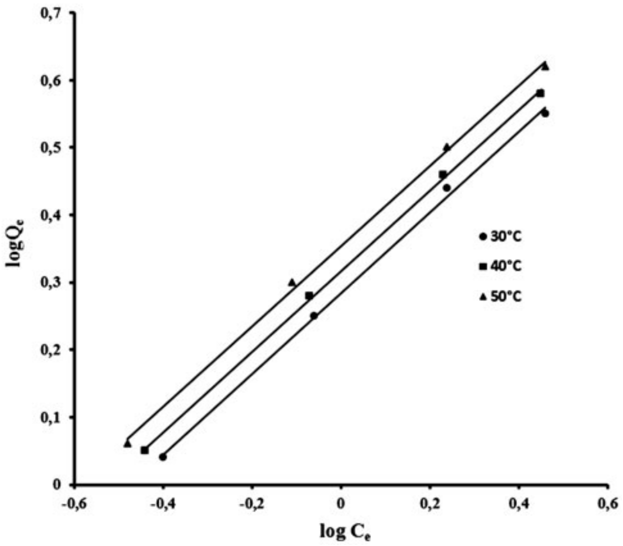

Fig. 5. Freundlich isotherm for the removal of fluoride by Purolite A-520E resin.

Table 6
Equilibrium constants and thermodynamic parameters for the removal of fluoride by Purolite A520E resin

	k_0			ΔG° (kJ mol^{-1})				
$[F^-]_i$	30°C	40°C	50°C	30°C	40°C	50°C	ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1} k^{-1})
2.5	2.62	2.97	3.30	−2.43	−2.83	−3.20	9.36	39
5.0	2.36	2.47	2.70	−2.16	−2.35	−2.57	3.96	20.2
7.5	1.64	1.70	1.74	−1.25	−1.38	−1.49	2.41	12.1
10	1.23	1.26	1.32	−0.52	−0.60	−0.75	2.89	11.3

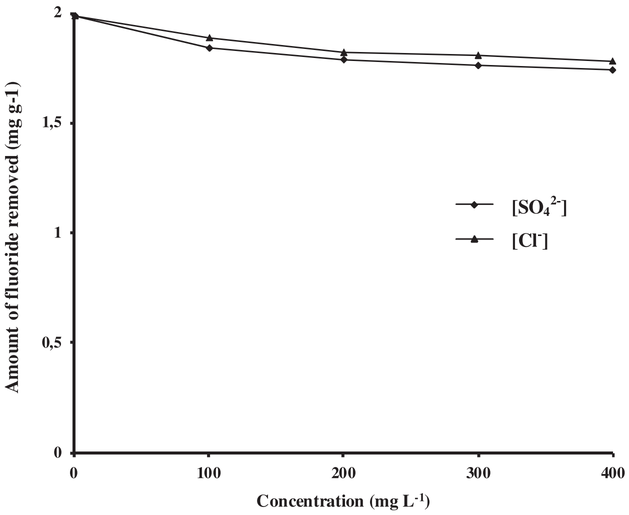

Fig. 6. Effect of co-ions (SO_4^{2-} and HCO_3^{2-}) on the adsorption of fluoride by the Purolite A520E resin.

ΔH° and ΔS° were determined from the slope and intercept of the plot of ln k_0 vs. $1/T$.

The standard free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) with equilibrium constants are given in Table 6. The values of enthalpy are positive indicating the endothermic nature of the process. The negative ΔG° values indicate that the process is spontaneous. The low values of ΔS° reveal that during the doping of fluoride ions onto the Purolite A520E resin, the degree of the internal freedom of the system is decreased [28].

3.6. Effect of different anions

Drinking water contains many anions. Therefore, the effect of sulfate and hydrogenocarbonate on the adsorption of fluoride on the Purolite A520E resin was also examined. The initial fluoride concentration was fixed at 5 mg L^{-1} while the initial concentration of other anions varied from 100 to 400 mg L^{-1}. The results of these studies are given in Fig. 6. It is seen that the addition of the common co-ions does not have any significant effect on the sorption ability of resin for fluoride ion. From these observations, we conclude that it may be due to the nature of fluoride which has been demonstrated to be a hard anion [29].

3.7. Test with field samples

The Purolite A520E resin has been tested by treating water samples collected from the groundwater Louza 2 source located in Gafsa region (south of Tunisia). A volume of 100 mL of aliquot sample was taken and then agitated with 0.2 g of Purolite A520E resin for 30 min. Some relevant chemical parameters of the raw (Louza 2) and the treated waters are given in Table 7. The fluoride content was reduced to 1.20 from 3.39 mg L^{-1} by treating with the Purolite A520E resin. It was observed that all the water parameters were lower than the standards.

3.8. Economic evaluation

The cost of the produced cubic meter of water depends on the chemical cost as the feedwater quality is very determinant. In our case where the feedwater quality is good, the major chemical used for defluoridation is Purolite A520E resin. For the regeneration of

Table 7
Chemical parameters of the raw and the treated waters

	Concentration (mg L^{-1})	
	Raw water	Treated water
Na^+	225	225
Ca^{2+}	95	95
Mg^{2+}	28	28
HCO_3^-	189	175
Cl^-	210	289
SO_4^{2-}	320	186
F^-	3.39	1.20

the resin, the used chemical is sodium chloride NaCl. The cost of chemical is estimated to 0.25 €/m^3. If the regeneration of the resin is integrated, the cost of the treatment is certain to decrease. Concerning the chemical cost, the estimated one in this case is comparable to the cost evaluated by Elazhar et al. [30].

4. Conclusion

The following conclusions can be drawn from our investigations:

(1) The removal of fluoride from aqueous solutions depends on the shaking time and Purolite A520E resin dose.

(2) The fluoride ion can be effectively adsorbed using Purolite A520E resin. The resin is a suitable adsorbent and can be regenerated several times with sodium chloride solution (6%).

(3) Linear plots of C_e/Q_e vs. C_e and log Q_e against log C_e indicate the applicability of the Langmuir and Freundlich isotherms, respectively. The values of $R_L < 1$ and the adsorption intensity of the Freundlich constant n between 1 and 10 indicate favorable adsorption.

(4) The values of enthalpy are positive, indicating the endothermic nature of the process. The negative ΔG° values indicate that the process is spontaneous. The low values of ΔS° reveal that during the doping of fluoride ions onto the Purolite A520E resin, the degree of the internal freedom of the system is decreased.

(5) The cost of the produced cubic meter of water is estimated to be 0.25€/m^3. If the regeneration of the resin is integrated, the cost of the treatment is certain to decrease.

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