



Role of metal ion incorporation in ion exchange resin on the selectivity of fluoride

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ABSTRACT

Indion FR 10 resin has sulphonic acid functional group (H^+ form) possesses appreciable defluoridation capacity (DC) and its DC has been enhanced by chemical modification into Na^+ and Al^{3+} forms by loading respective metal ions in H^+ form of resin. The DCs of Na^+ and Al^{3+} forms were found to be 445 and 478 $mg F^-/kg$, respectively, whereas the DC of H^+ form is 265 $mg F^-/kg$ at 10 mg/L initial fluoride concentration. The nature and morphology of sorbents are characterized using FTIR and SEM analysis. The fluoride sorption was explained using the Freundlich, Langmuir and Redlich–Peterson isotherms and kinetic models. The calculated thermodynamic parameters such as ΔG° , ΔH° , ΔS° and sticking probability (S^*) explains the nature of sorption. Comparison was also made by the elution capacity of these resins in order to select a cost effective material. A field trial was carried out to test the suitability of the resins with fluoride water collected from a nearby fluoride-endemic area.

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1. Introduction

Fluoride pollution of water can occur due to anthropogenic activities or geochemical processes [1]. The removal of fluoride from water is one of the most important issues due to the effect on human health and environment. Fluoride in drinking water may be beneficial or detrimental depending on its concentration [2]. The optimum fluoride level in drinking water for general good health set by World Health Organization is 1.5 mg/L [3]. Drinking water is a major source of fluoride intake. There is no treatment for fluorosis but it can be easily prevented. One such preventive measure is defluoridation of water. Available techniques for the removal of fluoride belong to the following three major categories viz., adsorption [4,5], chemical precipitation [6] and ion exchange [7]. Membrane processes such as reverse osmosis [8], nano filtration [9], electro dialysis [10] and Donnan dialysis [11] were investigated to reduce fluoride concentration from water. Among the methods, adsorption technology is economical and efficient method for producing high quality of water. In recent years, a variety of adsorbents like metal loaded adsorbents [1], activated alumina [4], chitosan beads [12], composites [13], activated carbon [14], clay [15], hydroxyapatite [16], etc., have been identified as the promising defluoridating agents.

Though defluoridation capacity (DC) of the material is an important criterion, it is also necessary to consider the other factors like flow rate, acceptability by the users, ease of operation, etc., while designing the column for the success of technology. Ion exchangers are proved to be most promising materials in the domain of water treatment. With reference to fluoride, most of the ion exchangers remove them by adsorption rather than ion exchange process, as the concentration of fluoride is lesser than other anions present in water [5]. Meenakshi and Viswanathan [5] proposed that cationic type resins were more selective for fluoride removal than the anion exchange resins. However, the DC and selectivity for fluoride of the cation type resins depends upon the type of the metal ion in the resin. Different loaded metal ions have different influence on the fluoride removal due to differences in their properties [17–19]. Hence the fundamental challenge of our present investigation is to maximize the DC of cation exchange resins by increasing the fluoride selectivity. In the present study a commercial cation exchanger with sulphonic acid group namely Indion FR 10 which removes fluoride by means of adsorption have been modified into Na^+ and Al^{3+} forms in order to enhance the DC.

The comparison of the original resin which is in H^+ form with that of Na^+ and Al^{3+} forms of resins was made based on their DC under various equilibrating conditions like contact time, initial fluoride concentrations, pH, temperature and in presence of competitor co-anions. The fluoride removal by these resins was explained using equilibrium isotherms and kinetic models. The resins were tested with a field sample collected

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in a nearby fluoride-endemic village for their suitability under field conditions. Best regenerant was also suggested for the continuous use of these sorbents. These fundamental data were useful in selecting the most suitable material for field application.

2. Materials and methods

2.1. Materials

Indion FR 10 is an ion exchange resin with sulphonic acid group (H^+ form) was supplied by Ion Exchange (India) Ltd., Mumbai. This resin having H^+ as an ion exchanger was washed with distilled water and dried at oven at $120^\circ C$ and has been modified into Na^+ and Al^{3+} forms as follows. The Na^+ form was prepared by treating H^+ form with 5% (w/v) $NaHCO_3$ solution for 24 h, washed with distilled water to pH 7 and kept in an oven at $120^\circ C$ for 12 h. Al^{3+} form of resin was prepared by treating H^+ form with 5% (w/v) $NaHCO_3$ solution for 24 h, washed with distilled water till it reaches neutral pH and immersed in 5% (w/v) $Al_2(SO_4)_3$ for 24 h, then the resin was washed with distilled water till it attains neutral pH and dried at $120^\circ C$ for 12 h. The dried resin samples were used for the sorption studies. All other chemicals employed were of analytical reagent grade and were used without purification. Double distilled water was used for preparing all the solutions. For the field study, fluoride-containing water was collected from a nearby fluoride-endemic village.

2.2. Sorption experiments

Defluoridation experiments were carried out by batch equilibration method in duplicate. In a typical case, 1 g of the sorbent was added to 50 ml of NaF solution of initial concentration 3 mg/L. The contents were shaken thoroughly using a thermostated shaker rotating at a speed of 200 rpm. The solution was then filtered and the residual fluoride concentration was measured. Kinetic studies were carried out in a temperature controlled water bath shaker. The effect of initial fluoride concentration with different temperatures at 303, 313 and 323 K on sorption rate was studied at the following initial fluoride concentrations viz., 2, 4, 6, 8 and 10 mg/L by keeping the mass of sorbent as 1 g and volume of fluoride solution as 50 ml at pH 7.

2.3. Analysis

The concentration of fluoride was measured using expandable ion analyzer EA 940 with the fluoride ion selective electrode BN 9609 (Orion, USA). The pH measurements were done with the same instrument with pH electrode. All other water quality parameters were analyzed by using standard methods [20]. The pH at zero point of charge (pH_{zpc}) of resins was measured using the pH drift method [21].

The surface morphology of the resins was visualized by SEM with HITACHI-S-3000H model. The SEM enables the direct observation of the surface microstructures of the fresh and fluoride-sorbed resins. FTIR spectra of the resins were recorded with JASCO-460 plus model by mixing resin with KBr. The results of FTIR were used to confirm the functional groups present in the resins.

Computations were made using Microcal Origin (Version 6.0) software. The goodness of fit was discussed using regression correlation coefficient (r), chi-square analysis and squared sum of errors (SSE) analysis.

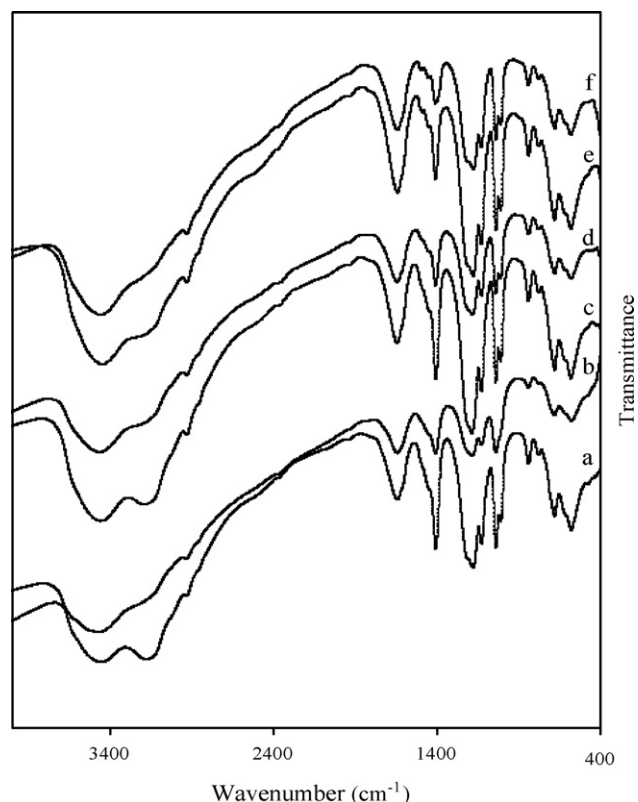


Fig. 1. FTIR spectra of (a) H^+ form, (b) fluoride-treated H^+ form, (c) Na^+ form, (d) fluoride-treated Na^+ form, (e) Al^{3+} form and (f) fluoride-treated Al^{3+} form.

3. Results and discussion

3.1. Characterization of sorbents

Indion FR 10 resin is a cationic resin with sulphonic acid functional group as per the specifications of the manufacturer [5]. Fig. 1 a and b depicts the FTIR spectra of H^+ form resin before and after fluoride sorption, respectively. The band of H^+ form at 3466 cm^{-1} is due to $-OH$ stretching vibration [5,22,23]. The bands at 1179 and 1036 cm^{-1} are assigned to the sulphonic group [5,23,24]. The slight widening of the broad $-OH$ band at 3466 cm^{-1} in the fluoride-treated resin may be taken as indicative of the formation of hydrogen bonding (H-bonding) between the acid hydrogen ($-SO_3H$) and the fluoride [5,22]. Fig. 1c and d depicts the FTIR spectra of Na^+ form and fluoride-treated Na^+ form, respectively. The stretching frequency at 1135 and 1055 cm^{-1} corresponds to $-SO-Na$ stretching and confirms the presence of Na in Na^+ form [25]. The FTIR spectra of the fresh Al^{3+} form and fluoride-sorbed Al^{3+} form is shown in Fig. 1e and f, respectively. The stretching frequency at 1121 and 1045 cm^{-1} corresponds to the presence of $-SO-Al$ stretching and the stretching frequency at 775 cm^{-1} indicates the presence of $Al-O$ stretching in Al^{3+} form [25]. The difference in the $-SO-$ stretching frequencies of H^+ , Na^+ , Al^{3+} forms also confirm their change during modification. This is also further confirmed by pH_{zpc} values in which the structural changes were indicated by the shifting of pH_{zpc} values [26,27]. For H^+ form it is observed as 3.5, 5.6 for Na^+ form and for Al^{3+} form it is 6.7.

SEM images of the resins before and after fluoride sorption of H^+ form are shown in Fig. 2a and b, respectively. The respective SEM pictures of Na^+ form before and after treatment with fluoride are shown in Fig. 2c and d. Similarly SEM images of Al^{3+} form and fluoride-sorbed Al^{3+} form are shown in Fig. 2e and f, respectively.

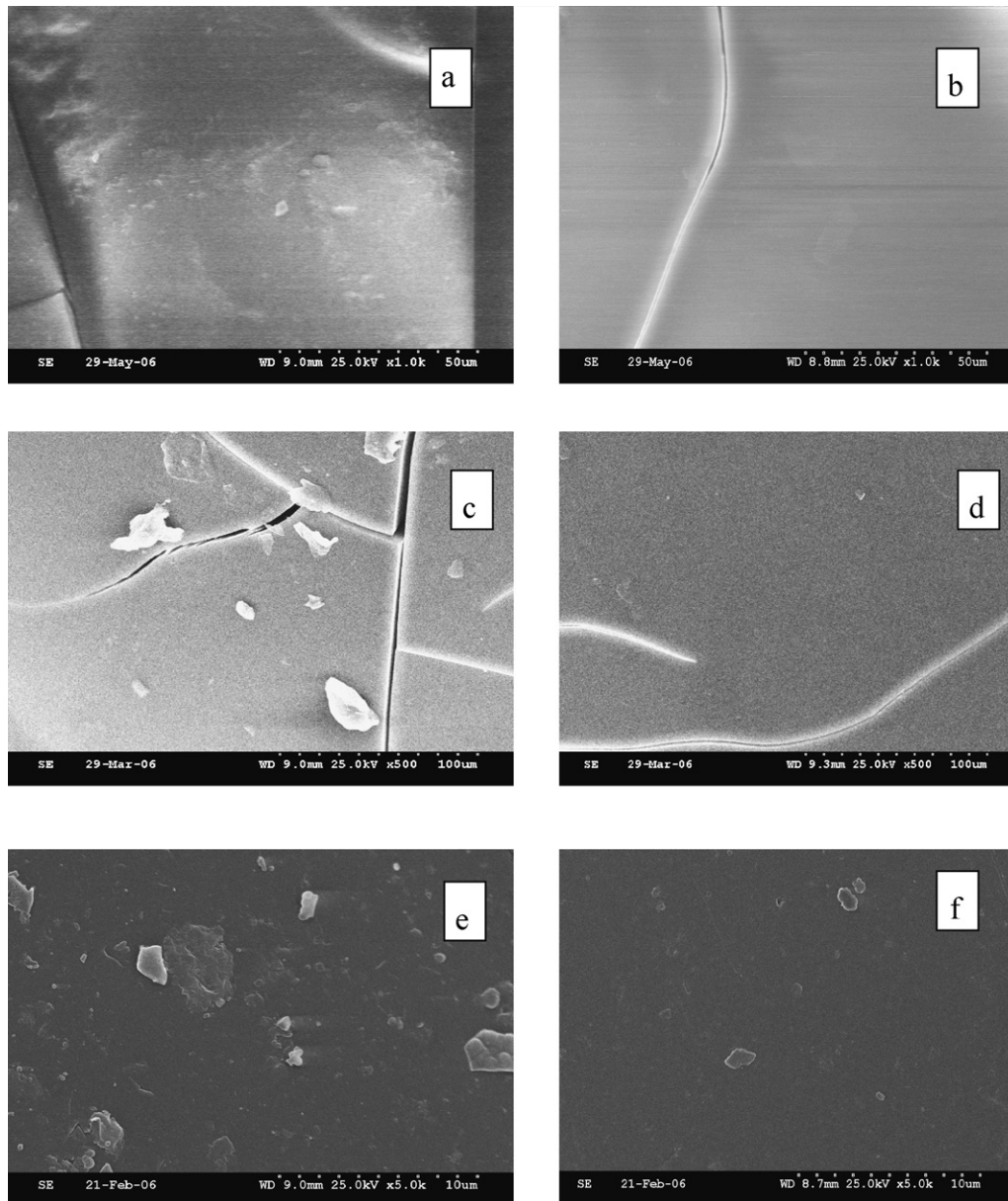


Fig. 2. SEM micrographs of (a) H^+ form, (b) fluoride-sorbed H^+ form, (c) Na^+ form, (d) fluoride-sorbed Na^+ form, (e) Al^{3+} form and (f) fluoride-sorbed Al^{3+} form.

The alteration of the surface morphology in the fluoride-sorbed resins indicates the sorption of fluoride occurs onto the sorbents.

3.2. Effect of contact time

The effect of DC of sorbents with contact time was studied using 3 mg/L as initial fluoride concentration with neutral pH at room temperature to find out a minimum time of contact needed to attain maximum DC. The sorption of fluoride has been investigated as a function of time in the range of 5–50 min. Fig. 3a shows the variation of DC with time. It is evident that the DC of all the sorbents increases sharply with increasing time and reach saturation after 40 min in the case of H^+ form and 30 min in the case of both Na^+ and Al^{3+} forms. Therefore, 40 min shaking time for H^+ form and 30 min in case of Na^+ and Al^{3+} forms were found to be appropriate for maximum adsorption and was used in all subsequent measurements.

appropriate for maximum adsorption and was used in all subsequent measurements.

3.3. Influence of pH

The pH of the medium is an important variable for the adsorption of fluoride on the adsorbents [28]. The effect of pH on fluoride adsorption by the sorbents was studied at five different pH levels viz., 3, 5, 7, 9 and 11 by keeping other parameters like contact time, dosage and initial fluoride concentration as constant at 303 K. Various pH of the working solution were controlled by adding HCl/NaOH solution. Fig. 3b explains the variation of DC as a function of pH and it is observed that the DC of all the resins studied is not influenced by the pH of the medium and hence it is decided that the pH has no significant role. Similar type of results was observed when the modified chitosan beads were used as the sorbent for

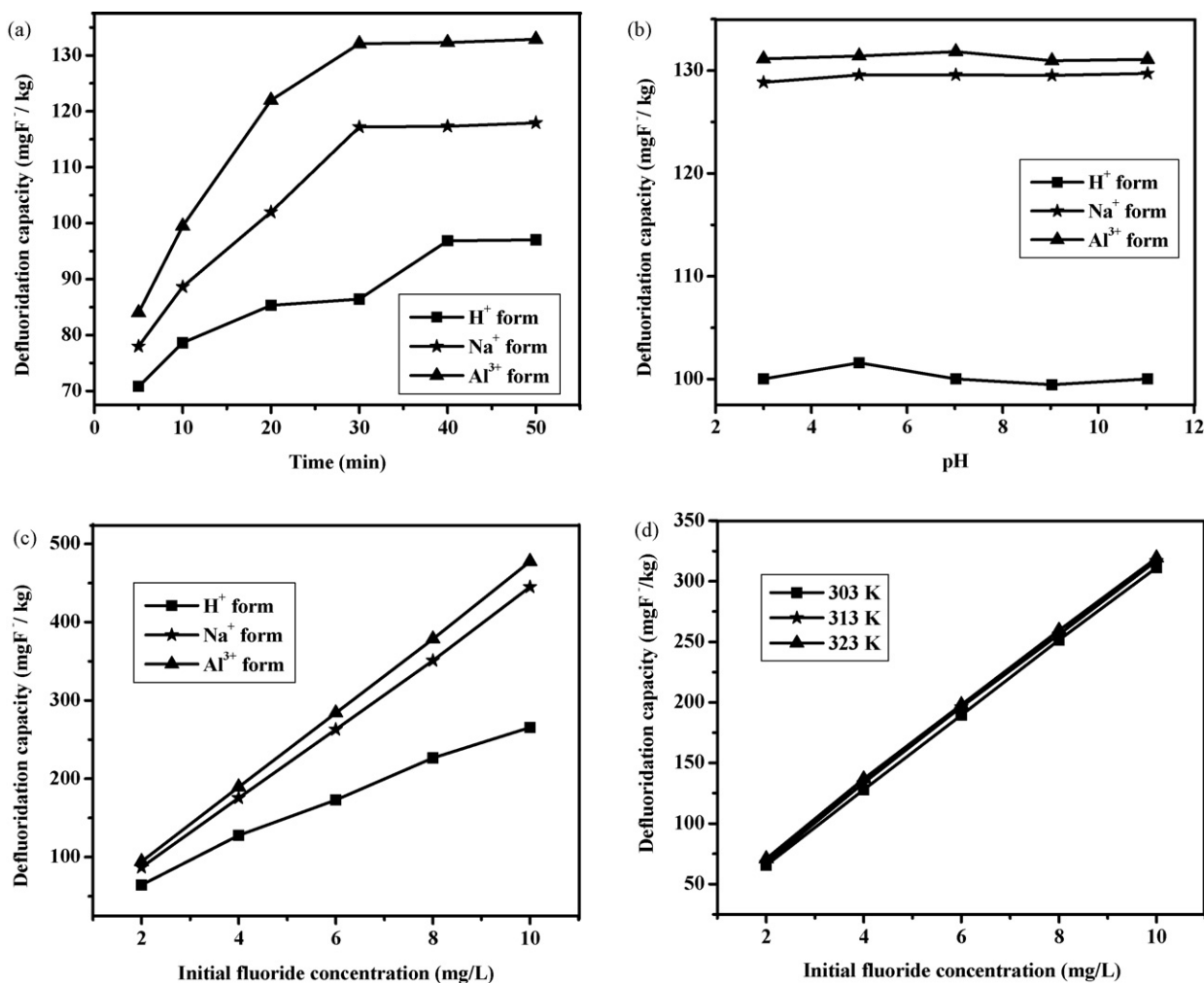


Fig. 3. Effect of (a) contact time, (b) pH, (c) initial fluoride concentration and (d) temperature.

defluoridation [12]. For further experiments neutral pH was maintained for sorption studies.

3.4. Influence of the sorbate concentration

The effect of DC on different initial fluoride concentrations viz., 2, 4, 6, 8 and 10 mg/L with neutral pH at 303 K were studied and are shown in Fig. 3c. The DC of the sorbents increases with increase in the initial fluoride concentration. It is evident from Fig. 3c that the modified forms of resins have higher DC than the original resin. Among the modified forms of resins Al³⁺ form has higher DC than Na⁺ form which in turn possesses higher DC than H⁺ form. In most of the fluoride-endemic areas, the fluoride level in drinking water found to have a maximum of 3 mg F⁻/L. Hence, for further studies the initial concentration of fluoride was fixed as 3 mg/L.

3.5. Effect of temperature

Sorption studies were carried out at three different temperatures viz., 303, 313 and 323 K with different initial fluoride concentrations viz., 2, 4, 6, 8 and 10 mg/L by keeping all other factors as constant. The effect of temperature for Al³⁺ form is shown in Fig. 3d. It has been observed that the DC of Al³⁺ form is not much influenced by the temperature indicates its temperature indepen-

dent nature. Similar types of results were observed for H⁺ and Na⁺ forms also.

3.6. Effect of competitor anions

Fig. 4 explains the DC of Al³⁺ form in the presence of coexisting anions. For measuring the effect of concentration of chloride ion on the DC of sorbent, the experiment was carried out by varying the initial chloride concentrations viz., 100, 200, 300, 400, 500 and 600 mg/L and keeping all other parameters such as time, pH, dosage and initial fluoride concentration as constants. Similar experiments were carried out with other anions as variable. From the graph it is evident that the overall DC of Al³⁺ form was not much altered by the presence of other anions which suggest the fact that the sorbent is selective for fluoride removal and same results were observed for H⁺ and Na⁺ forms also. Parallel types of results were reported by Chubar et al. [29] and Onyango et al. [30].

3.7. Sorption isotherms

To quantify the sorption capacity of the resins studied for the removal of fluoride, three isotherms namely Freundlich, Langmuir and Redlich–Peterson isotherms have been adopted.

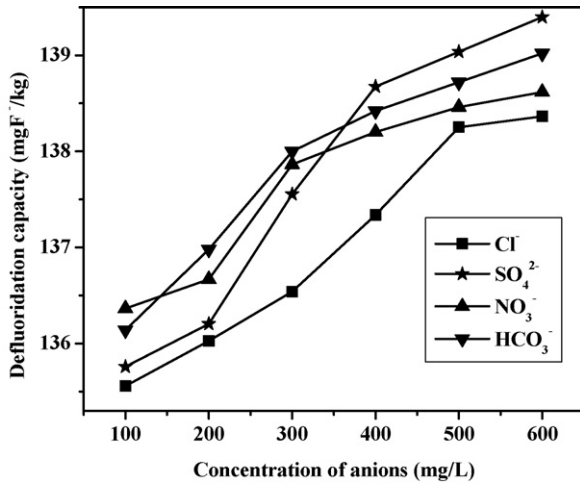


Fig. 4. Effect of common anions in DC of Al³⁺ form at 303 K.

3.7.1. Freundlich isotherm

The linear form of Freundlich [31] isotherm is represented by the equation,

$$\log q_e = \log k_F + \frac{1}{n} \log C_e \tag{1}$$

where q_e is the amount of fluoride adsorbed per unit weight of the sorbent (mg/g), C_e is the equilibrium concentration of fluoride in solution (mg/L), k_F is a measure of adsorption capacity and $1/n$ is the adsorption intensity. The plot of $\log q_e$ vs. $\log C_e$ is linear which indicates the applicability of Freundlich isotherm. The constants k_F and $1/n$ of Freundlich isotherm for all the types of sorbents are given in Table 1. Adsorption process is favorable when the value of $1/n$ lies between 0.1 and 1, the value of n lies between 1 and 10. This condition is obeyed by all the types of resins suggesting fluoride gets sorbed by these resins. The values of k_F were found to be almost constant in all the temperatures studied for all the resins.

3.7.2. Langmuir isotherm

Langmuir [32] isotherm model can be represented by the equation

$$\frac{C_e}{q_e} = \frac{1}{Q^0 b} + \frac{C_e}{Q^0} \tag{2}$$

where Q^0 is the amount of adsorbate at complete monolayer coverage (mg/g), which gives the maximum sorption capacity of sorbent and b (L/mg) is the Langmuir isotherm constant that relates to the energy of adsorption were calculated from the slope and intercept of the plot C_e/q_e vs. C_e and the values are given in Table 1. The value of 'b' increases with increasing temperature confirms that fluoride sorption takes place more readily with increase in temperature. Langmuir model effectively described the sorption data with r^2 values >0.99.

In order to find out the feasibility of the isotherm, the essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L [33]

$$R_L = \frac{1}{1 + bC_0} \tag{3}$$

where b is the Langmuir isotherm constant and C_0 is the initial concentration of fluoride (mg/L). The R_L values between 0 and 1 indicate favorable adsorption for all temperatures studied (cf. Table 1).

Table 1 Isotherm parameters with r and chi-square values

Resins	Temperature (K)	Freundlich isotherm				Langmuir isotherm				Redlich–Peterson isotherm					
		1/n	n	k_F (mg/g)	$(L/mg)^{1/n}$	Q^0 (mg/g)	b (L/g)	R_L	r	χ^2	A (L/mg)	g	B (L/mg) ^g	r	χ^2
H ⁺ form	303	0.792	1.26	1.032	1.032	1.308	0.139	0.026	0.994	4.3E-2	1.00	0.226	9.76	0.999	3.8E-4
	313	0.779	1.28	0.994	1.356	1.356	0.162	0.029	0.995	3.8E-2	1.53	0.235	14.09	0.996	1.4E-3
	323	0.783	1.28	0.962	1.305	1.305	0.170	0.032	0.991	6.3E-3	15.60	0.218	141.6	0.992	3.2E-3
Na ⁺ form	303	0.938	1.07	0.074	2.346	2.346	0.033	0.755	0.962	1.7E-3	1.00	0.067	12.52	0.960	1.8E-3
	313	0.909	1.10	0.079	1.590	1.590	0.052	0.657	1.00	5.5E-7	1.53	0.096	18.44	0.999	4.1E-5
	323	0.888	1.13	0.094	1.468	1.468	0.069	0.593	0.999	2.4E-6	15.60	0.113	164.56	1.00	2.2E-6
Al ³⁺ form	303	0.921	1.09	0.092	2.112	2.112	0.045	0.688	0.990	4.9E-4	1.00	0.087	9.90	0.987	6.3E-4
	313	0.889	1.13	0.101	1.457	1.457	0.075	0.571	1.00	1.7E-5	1.53	0.119	14.14	0.999	3.6E-5
	323	0.821	1.22	0.111	0.981	0.981	0.129	0.436	0.997	1.0E-4	15.60	0.180	139.28	1.00	7.5E-6

3.7.3. Redlich–Peterson isotherm

It is a modified three-parameter isotherm which incorporates features of both Langmuir and Freundlich equation. The linear form of Redlich–Peterson isotherm [34] is given in the equation,

$$\ln \left(A \frac{C_e}{q_e} - 1 \right) = g \ln C_e + \ln B \quad (4)$$

Three isotherm constants A , B and g can be evaluated from the linear plot represented by Eq. (4) using a trial and error optimization method. A general trial and error procedure which is applicable to computer operation was developed to determine the value of r for a series of values of A for the linear regression of $\ln[A(C_e/q_e) - 1]$ vs. $\ln C_e$ and to obtain the best value of A which yields a maximum 'optimized' value of r and the respective values of g and B were determined from the slope and intercept of the plot $\ln[A(C_e/q_e) - 1]$ vs. $\ln C_e$.

The calculated Redlich–Peterson constants and their corresponding linear correlation coefficient (r) are shown in Table 1. The r values for Redlich–Peterson isotherm for all the materials were found to be very nearer to both Langmuir and Freundlich isotherms. This shows that all the isotherms viz., Langmuir, Freundlich and Redlich–Peterson isotherm can be used to represent the experimental data of the sorption of fluoride onto the modified resins. The plot of q_e vs. C_e for all the three isotherms of Al^{3+} form at 323 K is shown in Fig. 5.

3.7.4. Chi-square analysis

To identify a suitable isotherm model for the sorption of fluoride on the resins, this analysis has been carried out. The equivalent mathematical statement is

$$\chi^2 = \sum \frac{(q_e - q_{e,m})^2}{q_{e,m}} \quad (5)$$

where $q_{e,m}$ is equilibrium capacity obtained by calculating from the model (mg/g) and q_e is experimental data of the equilibrium capacity (mg/g). The results of chi-square analysis are shown in Table 1. The values of χ^2 for all the isotherms studied were very low indicating that all the three types of isotherms can be considered as best fitting models.

3.8. Thermodynamic treatment of the sorption process

Thermodynamic parameters associated with the adsorption viz., standard free energy change (ΔG°), standard enthalpy change

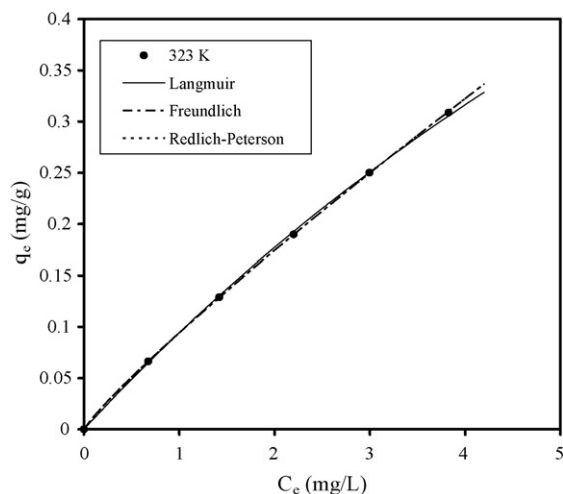


Fig. 5. Plot of q_e vs. C_e for the isotherms of fluoride sorption on Al^{3+} form at 323 K.

(ΔH°), standard entropy change (ΔS°) and sticking probability (S^*) were calculated using Khan and Singh method, van't Hoff equation and Horsfall and Spiff method [5,35,36]. The negative values of ΔG° confirm the feasibility of the process and the spontaneous nature of sorption with a high preference for fluoride sorption onto resins. The positive value of ΔH° indicates the reaction is endothermic in nature. The positive value of ΔS° which is a measure of randomness at the solid/liquid interface during fluoride sorption indicates the adsorption process is irreversible and stable. The values of S^* for all the forms are very close to zero indicating that the nature of adsorption is electrostatic attraction in which for Na^+ and Al^{3+} forms it is ionic and for H^+ form it is H-bonding [36].

3.9. Sorption kinetic models

The two main types of sorption kinetic models namely reaction-based and diffusion-based models were adopted to fit the experimental data [37]. The study of sorption dynamics describes the solute uptake rate and evidently this rate controls the residence time of adsorbate uptake at the solid/solution interface. A relatively higher r values indicates that the model successfully describes the kinetics of fluoride sorption.

3.9.1. Reaction-based models

The most commonly used pseudo-first-order and pseudo-second-order models were employed to explain the solid/liquid adsorption.

A simple pseudo-first-order kinetic model [38] is given as:

$$\log(q_e - q_t) = \log q_e - \frac{k_{ad}}{2.303} t \quad (6)$$

where q_t is the amount of fluoride on the surface of the resin at time t (mg/g) and k_{ad} is the equilibrium rate constant of pseudo-first-order sorption (min^{-1}). The slope of the straight-line plot of $\log(q_e - q_t)$ against t for different experimental conditions will give the value of the rate constants (k_{ad}) and are given in Table 2. The pseudo-first-order plot of Al^{3+} form at 323 K is shown in Fig. 6a, similar type of plots was obtained for other forms of resins.

A pseudo-second-order model is also widely used to describe the kinetics of the sorption when the initial concentration of the solute was low. Though there are four types of linear pseudo-second-order kinetic models [39], the most popular linear form is

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e} \quad (7)$$

where $q_t = q_e^2 kt / (1 + q_e kt)$, amount of fluoride on the surface of the bead at any time, t (mg/g), k is the pseudo-second-order rate constant (g/mg min), q_e is the amount of fluoride sorbed at equilibrium (mg/g) and the initial sorption rate, $h = k q_e^2$ (mg/g min). The value of q_e (1/slope), k (slope²/intercept) and h (1/intercept) of the pseudo-second-order equation can be found out experimentally by plotting t/q_t against t .

The fitness of the data and the values of q_e , k and h were obtained from the plots of t/q_t vs. t for fluoride sorption at different temperatures viz., 303, 313 and 323 K for H^+ , Na^+ and Al^{3+} forms are presented in Table 3. The pseudo-second-order plot of Al^{3+} form at 323 K is shown in Fig. 6b, similar type of plots was obtained for other forms of resins. The plot of t/q_t vs. t gives a straight line with higher correlation coefficient r values which is higher than that observed with pseudo-first-order model indicating the applicability of the pseudo-second-order model.

Table 2
Pseudo-first-order rate constants for the sorption of fluoride on resins at different temperatures with different initial fluoride concentrations

C_0 (mg/L)	Temperature (K)	H^+ form		Na^+ form		Al^{3+} form	
		k_{ad} (min^{-1})	r	k_{ad} (min^{-1})	r	k_{ad} (min^{-1})	r
2	303	0.035	0.978	0.080	0.843	0.060	0.945
	313	0.022	0.952	0.130	0.988	0.102	0.982
	323	0.021	0.972	0.107	0.912	0.065	0.961
4	303	0.055	0.950	0.117	0.981	0.102	0.970
	313	0.046	0.974	0.090	0.914	0.103	0.926
	323	0.017	0.966	0.121	0.987	0.064	0.999
6	303	0.031	0.936	0.096	0.952	0.088	0.940
	313	0.033	0.985	0.107	0.959	0.095	0.946
	323	0.036	0.977	0.128	0.928	0.068	0.976
8	303	0.032	0.976	0.126	0.945	0.121	0.939
	313	0.028	0.969	0.117	0.919	0.121	0.983
	323	0.018	0.937	0.117	0.964	0.065	0.994
10	303	0.052	0.955	0.119	0.965	0.113	0.987
	313	0.022	0.941	0.108	0.883	0.097	0.894
	323	0.014	0.894	0.121	0.949	0.085	0.971

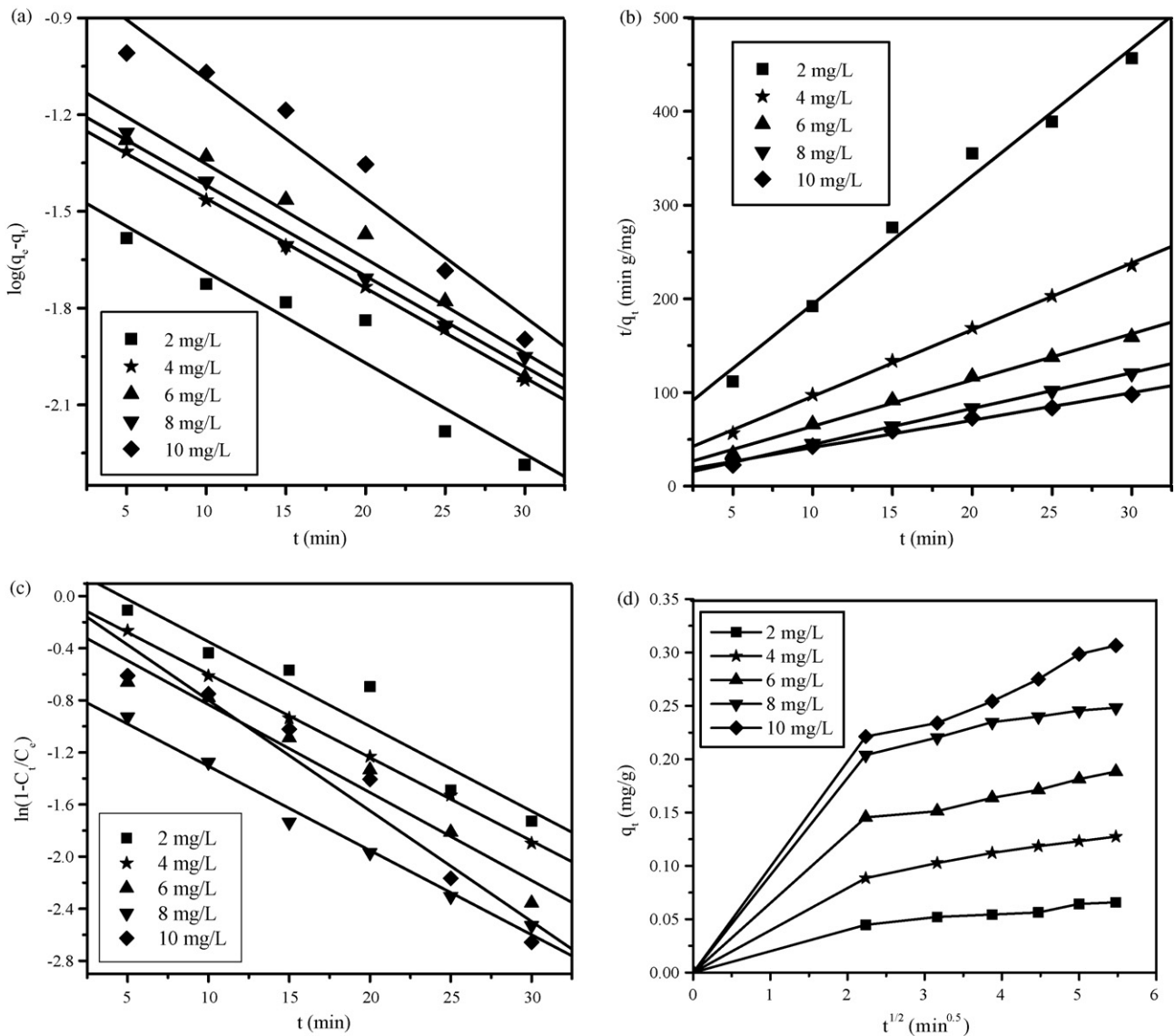


Fig. 6. Kinetic model plots of Al^{3+} form at 323 K (a) pseudo-first-order, (b) pseudo-second-order, (c) particle diffusion and (d) intraparticle diffusion.

3.9.2. Diffusion-based models

For a solid–liquid sorption process, the solute transfer is usually characterized either by particle diffusion or pore diffusion control.

A simple equation for the particle diffusion controlled sorption process [5,40] is given as follows,

$$\ln \left(1 - \frac{C_t}{C_e} \right) = -k_p t \tag{8}$$

where k_p is the particle rate constant (min^{-1}). The value of particle rate constant is obtained by the slope of the plot $\ln(1 - C_t/C_e)$ against t . The particle diffusion plot of Al^{3+} form at 323 K is shown in Fig. 6c, similar type of plots was obtained for other forms of resins.

The pore diffusion model used here refers to the theory proposed by Weber and Morris [41] and its equation is

$$q_t = k_i t^{1/2} \tag{9}$$

where k_i is the intraparticle rate constant ($\text{mg/g min}^{0.5}$). The slope of the plot of q_t against $t^{1/2}$ will give the value of intraparticle rate constant. The intraparticle diffusion plot of Al^{3+} form at 323 K is shown in Fig. 6d, similar type of plots was obtained for other forms of resins.

The straight-line plots of $\ln(1 - C_t/C_e)$ vs. t and q_t vs. $t^{0.5}$ indicates the applicability of both particle and pore diffusion models. The k_p , k_i and r values of particle and pore diffusion models are illustrated in Table 4. The higher r values obtained for both particle and pore diffusion models suggest that all the materials follow both the models.

3.9.3. The best-fit kinetic model

The assessment of the employed kinetic models for fitting the sorption data was made by calculating the squared sum of errors (SSE). Lower values of SSE show better fit to sorption data [5,37].

$$\text{SSE} = \sum \frac{(q_{t,e} - q_{t,m})^2}{q_{t,e}^2} \tag{10}$$

where $q_{t,e}$ and $q_{t,m}$ is the experimental sorption capacity of fluoride (mg/g) at time t and the corresponding value which is obtained from the kinetic models. The SSE values of all the kinetic models are summarized in Table 5. Smaller SSE values were observed for pseudo-second-order and particle diffusion models suggesting that these two models are significant in defining the fluoride sorption process.

3.10. Mechanism of fluoride removal by the sorbents

The fluoride removal capacity of these sorbents may be controlled by adsorption mechanism rather than ion exchange as they are cationic resins. When H^+ form is in contact with Na^+ and Al^{3+} solutions, the respective metal ions gets exchanged for H^+ ion by ion exchange mechanism. The metal ions in the matrix will attract fluoride by means of electrostatic adsorption and strong Lewis acid–base interaction [42,43]. All the sorbents selectively retains fluoride as it is the hardest Lewis base and the ions loaded into the resin are hard Lewis acids. The possible mechanism of fluoride removal by H^+ , Na^+ and Al^{3+} forms is shown in Fig. 7. The type of electrostatic adsorption in H^+ form is H-bonding whereas for Na^+ and Al^{3+} forms it is ionic. Among the sorbents, Al^{3+} form possesses slightly higher DC than the other two forms since it removes fluoride by complexation mechanism also, in addition to electrostatic adsorption because it is a

Table 3 Pseudo-second-order kinetic parameters of sorbents at different temperatures with different initial fluoride concentrations

Resins	Parameters	303 K					313 K					323 K				
		2 mg/L	4 mg/L	6 mg/L	8 mg/L	10 mg/L	2 mg/L	4 mg/L	6 mg/L	8 mg/L	10 mg/L	2 mg/L	4 mg/L	6 mg/L	8 mg/L	10 mg/L
H^+ form	q_e (mg/g)	0.073	0.146	0.208	0.242	0.367	0.068	0.127	0.202	0.248	0.282	0.071	0.127	0.186	0.253	0.273
	k (g/mg min)	3.122	1.214	1.146	2.824	0.588	5.687	4.007	1.791	7.908	6.343	3.139	4.306	4.380	3.575	4.950
	h (mg/g min)	0.016	0.026	0.050	0.166	0.079	0.026	0.065	0.073	0.485	0.504	0.016	0.070	0.152	0.229	0.370
	r	0.999	0.996	0.996	1.00	0.994	0.998	0.999	0.999	1.00	1.00	0.995	0.999	1.00	0.999	1.00
Na^+ form	q_e (mg/g)	0.080	0.141	0.189	0.250	0.292	0.078	0.126	0.189	0.241	0.292	0.084	0.146	0.207	0.259	0.349
	k (g/mg min)	6.631	1.030	1.398	1.188	3.750	1.657	2.613	1.945	2.880	3.727	1.052	1.507	1.313	2.419	3.552
	h (mg/g min)	0.004	0.020	0.050	0.074	0.321	0.010	0.042	0.069	0.167	0.317	0.008	0.032	0.056	0.163	0.067
	r	0.885	0.992	0.996	0.996	1.00	0.993	0.995	0.999	0.999	0.999	0.987	0.999	0.998	1.00	0.996
Al^{3+} form	q_e (mg/g)	0.073	0.140	0.195	0.291	0.329	0.087	0.141	0.204	0.272	0.320	0.073	0.140	0.202	0.261	0.341
	k (g/mg min)	1.284	1.687	2.297	0.537	1.296	1.093	2.323	2.139	1.595	3.230	3.263	2.069	1.682	2.340	0.727
	h (mg/g min)	0.007	0.033	0.088	0.046	0.140	0.008	0.046	0.089	0.118	0.332	0.017	0.041	0.069	0.160	0.085
	r	0.954	0.997	0.998	0.988	0.999	0.997	0.998	0.998	0.999	1.00	0.993	0.999	0.997	1.00	0.995

Table 4
Particle and pore diffusion model parameters for fluoride sorption on sorbents with different initial fluoride concentrations at different temperatures

C ₀ (mg/L)	Resins	303 K				313 K				323 K			
		Particle DM ^a		Pore DM ^a		Particle DM ^a		Pore DM ^a		Particle DM ^a		Pore DM ^a	
		k _p (min ⁻¹)	r	k _i (mg/g min ^{0.5})	r	k _p (min ⁻¹)	r	k _i (mg/g min ^{0.5})	r	k _p (min ⁻¹)	r	k _i (mg/g min ^{0.5})	r
2	H ⁺	0.0808	0.978	0.0057	0.955	0.0421	0.980	0.0047	0.948	0.0441	0.959	0.0054	0.967
	Na ⁺	0.0797	0.843	0.0097	0.928	0.1303	0.988	0.0099	0.937	0.1068	0.912	0.0106	0.995
	Al ³⁺	0.0598	0.945	0.0084	0.957	0.1017	0.982	0.0112	0.976	0.0650	0.961	0.0064	0.978
4	H ⁺	0.1077	0.955	0.0124	0.987	0.0337	0.973	0.0052	0.970	0.0300	0.960	0.0057	0.954
	Na ⁺	0.1172	0.981	0.0160	0.984	0.0904	0.913	0.0083	0.972	0.1209	0.987	0.0151	0.971
	Al ³⁺	0.1019	0.970	0.0126	0.994	0.1032	0.926	0.0106	0.994	0.0640	0.999	0.0119	0.993
6	H ⁺	0.0834	0.914	0.0148	0.955	0.1054	0.991	0.0194	0.981	0.0240	0.957	0.0057	0.967
	Na ⁺	0.0961	0.952	0.0153	0.993	0.1066	0.959	0.0131	1.00	0.1284	0.928	0.0175	0.997
	Al ³⁺	0.0877	0.940	0.0111	0.992	0.0953	0.946	0.0114	0.983	0.0675	0.976	0.0138	0.989
8	H ⁺	0.0734	0.976	0.0086	0.928	0.0573	0.963	0.0038	0.952	0.0411	0.981	0.0086	0.957
	Na ⁺	0.1001	0.977	0.0185	0.975	0.1166	0.919	0.0106	0.994	0.1165	0.964	0.0139	0.958
	Al ³⁺	0.1205	0.939	0.0301	0.983	0.1209	0.983	0.0173	0.956	0.0647	0.994	0.0139	0.982
10	H ⁺	0.1123	0.958	0.0252	0.958	0.0227	0.884	0.0055	0.888	0.0143	0.843	0.0063	0.852
	Na ⁺	0.1192	0.964	0.0087	0.999	0.1084	0.883	0.0078	0.983	0.1209	0.949	0.0350	0.999
	Al ³⁺	0.1128	0.987	0.0211	0.991	0.0974	0.894	0.0096	0.986	0.0849	0.971	0.0283	0.985

^a DM - diffusion model.

Table 5
SSE values of kinetic models employed for fluoride sorption onto sorbents

Resins	Kinetic models	303 K					313 K					323 K				
		2 mg/L	4 mg/L	6 mg/L	8 mg/L	10 mg/L	2 mg/L	4 mg/L	6 mg/L	8 mg/L	10 mg/L	2 mg/L	4 mg/L	6 mg/L	8 mg/L	10 mg/L
H ⁺ form	Pseudo-first-order	0.384	0.253	0.301	0.669	0.185	0.313	0.137	0.312	0.232	0.113	0.309	0.426	0.190	0.592	0.529
	Pseudo-second-order	0.012	0.035	0.025	0.001	0.119	1.0E-4	0.002	0.006	5.7E-6	0.002	7.3E-5	0.004	1.0E-4	1.0E-4	0.011
	Particle diffusion	0.165	0.126	0.155	0.107	0.111	0.323	0.369	0.082	0.024	0.434	0.311	0.420	0.470	0.256	0.613
Na ⁺ form	Pore diffusion	0.299	0.237	0.355	0.678	0.365	0.423	0.626	0.266	0.861	0.824	0.322	0.597	0.722	0.699	0.792
	Pseudo-first order	0.030	0.078	0.013	0.024	0.026	0.059	0.023	0.015	0.020	0.033	0.086	0.053	0.022	0.019	0.001
	Pseudo-second-order	0.015	0.068	0.008	0.010	4.6E-4	0.039	0.003	0.004	0.001	2.0E-4	0.064	0.027	0.012	0.002	0.028
Al ³⁺ form	Particle diffusion	0.327	0.103	0.153	0.089	0.060	0.128	0.162	0.117	0.077	0.075	0.001	0.136	0.116	0.086	0.139
	Pore diffusion	0.412	0.121	0.340	0.396	0.760	0.144	0.459	0.441	0.645	0.783	0.024	0.196	0.322	0.574	0.198
	Pseudo-first order	0.036	0.018	0.036	0.055	0.016	0.095	0.013	0.027	0.013	0.042	0.044	0.057	0.058	0.090	0.021
Al ³⁺ form	Pseudo-second-order	0.029	0.013	0.001	0.045	0.004	0.088	0.005	0.002	0.005	1.0E-4	0.002	9.0E-4	7.0E-4	4.5E-5	0.007
	Particle diffusion	0.405	0.167	0.159	0.160	0.105	0.247	0.174	0.071	0.096	0.102	0.339	0.306	0.260	0.226	0.207
	Pore diffusion	0.443	0.276	0.538	0.187	0.485	0.313	0.396	0.542	0.489	0.757	0.361	0.326	0.444	0.575	0.324

Table 6
Field trial results of the sorbents

Water quality parameters	Before treatment	After treatment		
		H ⁺ form	Na ⁺ form	Al ³⁺ form
F ⁻ (mg/L)	2.79	0.83	0.18	0.24
pH	8.44	7.68	7.82	7.90
Electrical conductivity (ms/cm)	0.98	0.61	0.12	0.35
Cl ⁻ (mg/L)	56.80	49.70	46.20	49.70
Total hardness (mg/L)	120.00	60.42	58.12	56.07
Total dissolved solids (mg/L)	500.00	460.00	350.00	300.00
Na ⁺ (mg/L)	85.70	70.20	79.20	77.70
K ⁺ (mg/L)	2.20	0.90	0.10	0.20

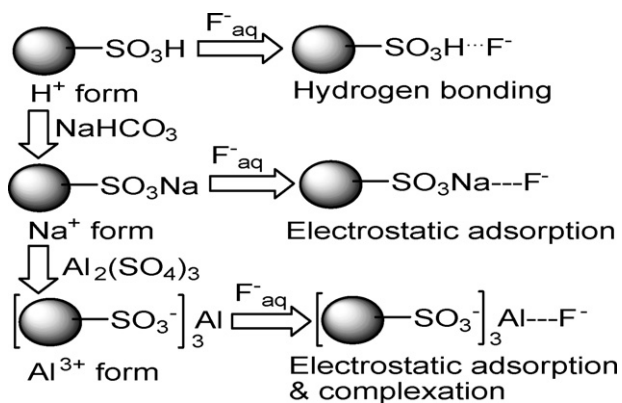


Fig. 7. Mechanism of fluoride removal by the sorbents.

strong Lewis acid, possesses higher valency and chelating efficiency.

3.11. Field studies

Various forms of resins used in our study are also tested with field sample taken from a nearby fluoride-endemic area. The results of these trials are presented in Table 6. It is evident from the result that all the sorbents can be effectively employed for removing the fluoride. There is no significant change in the levels of other water quality parameters. In fact, the levels of most of the water quality parameters have been reduced by these resins, in addition to fluoride. The modified forms of resins give better results than H⁺ form.

3.12. Regeneration of exhausted sorbents

The exhausted resins were eluted using eluents viz., HCl, H₂SO₄ and NaOH. Mineral acids elute fluoride as HF and NaOH as NaF. All the regeneration experiments were carried out at room temperature. The elution capacities of these forms of resins were studied using 0.1 M HCl, 0.1 M H₂SO₄ and 0.1 M NaOH. Out of these three eluents, HCl has been identified as the best eluent as it has 90% elution capacity while H₂SO₄ and NaOH have 80% and 75% elution capacities, respectively. After regeneration, the sorbents can be reused for fluoride removal.

4. Conclusions

In general all the forms of resins possess reasonably good defluorination efficiency. The DC of these sorbents is independent of pH of the medium and unaltered in the presence of co-anions present in the medium. Al³⁺ form has higher DC among the sorbents studied. The mechanism of fluoride removal by the sorbents

is mainly controlled by chemisorption. The sorption process follows Freundlich, Langmuir and Redlich–Peterson isotherms. The values of thermodynamic parameters indicate that the fluoride removal is spontaneous and endothermic in nature. The rate of the reaction of all the forms is controlled by pseudo-second-order and particle diffusion kinetic models. Field trial results indicate that these sorbents can be effectively used to remove the fluoride from water. 0.1 M HCl has been identified as the best eluent for the regeneration of the sorbents. This type of result could definitely throw more light in selecting best sorbent for fluoride removal.

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