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Effect of metal ion loaded in a resin towards fluoride retention

Natrayasamy Viswanathan, S. Meenakshi *

Department of Chemistry, Gandhigram Rural University, Gandhigram 624302, Tamil Nadu, India

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ABSTRACT

Indion FR 10 is a commercially available ion exchange resin with sulphonic acid functionality named as H^+ form, has appreciable defluoridation capacity (DC). It has been chemically modified to La^{3+}, Fe^{3+}, Ce^{3+} and Zr^{4+} forms by incorporating respective metal ions into the resin in order to know their fluoride selectivity by measuring the DC of the respective resin. The maximum DC of these chemically modified ion exchange resins namely La^{3+}, Fe^{3+}, Ce^{3+} and Zr^{4+} forms were found to be 469.7, 467.5, 456.3 and 470.9 mg F^-/kg respectively suggests their higher selectivity towards fluoride than H^+ form which has the DC of only 275 mg F^-/kg at 11 mg/L initial fluoride concentration. The higher DC of the modified resins was explained by electrostatic adsorption and complexation whereas H^+ form retains fluoride by hydrogen bond. The functional groups present in the sorbents were identified by FTIR and the existence of fluoride onto the resins was confirmed by EDAX analysis. The experimental data was fitted with both Freundlich and Langmuir isotherms. Thermodynamic parameters such as ΔG°, ΔH° and ΔS° indicate that the nature of sorption is spontaneous and endothermic. The applicability of reaction-based and diffusion-based kinetic models was investigated. A field trial was carried out with fluoride water collected from a nearby fluoride-endemic village to test the suitability of these sorbents at field conditions.

1. Introduction

Fluorosis, an irreversible disease, is a crippling disorder known to occur due to the entry of fluoride into the body. Drinking water is reported to be the major source of fluoride intake [1]. The World Health Organisation has specified the tolerance limit for fluoride content in drinking water as 1.5 mg/L [2]. The excessive intake of fluoride through drinking water causes three forms of fluorosis namely dental, skeletal and non-skeletal fluorosis [1]. The preferred option for the preventive measure is to find a supply of drinking water with safe fluoride levels and one such option is defluoridation.

Several methods have been suggested for removing excessive fluoride in water and they are chemical precipitation [3,4], ion exchange [5,6], adsorption [7–9] and electrolysis [10]. Among the methods reported adsorption seems to be the most attractive and selective technique for fluoride removal. Many adsorbents have been successfully used for the removal of fluoride which includes activated alumina [1,8,9], activated carbon [11], hydroxyapatite [12], bone charcoal [13], clay [14], etc.

Recently, considerable work has been conducted in developing new adsorbents loaded with metal ions for the purpose of fluoride removal [15]. The metal ion adsorbed onto the porous adsorbents or carrier materials have shown promising results. It has been reported that the adsorption capacity of fluoride on aluminium-impregnated carbon is 3–5 times higher than that of plain activated carbon [16]. In addition, the adsorbents that use rare earth elements are attracting more and more attention because of their selective affinity to fluoride, high adsorption capacity, minimum pollution and easy operation [17]. Different loaded metal ions have different influence on the fluoride removal due to differences in their properties [15,18–21].

In our present investigation, different multivalent metal ions incorporated cation exchanger was examined for its selectivity towards fluoride so as to suggest a best sorbent for fluoride sorption. A comparison was made with the original resin which is in H^+ form with the modified forms of resins, based on their DC under various equilibrating conditions like contact time, dosage, different initial fluoride concentrations, pH and in the presence of competitor co-anions. The reasonable mechanism of fluoride removal by these resins was also suggested. The experimental data were fitted with isotherms and the kinetic models. The modified resins were tested with a field sample collected from a nearby fluoride-endemic village for their suitability under field conditions.

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* Corresponding author. Tel.: +91 451 2452371; fax: +91 451 2454466.
E-mail addresses: natrayasamy_viswanathan@rediffmail.com (N. Viswanathan), drs_meena@yahoo.co.in, drs_meena@rediffmail.com (S. Meenakshi).

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Table 1
Physical and chemical properties of Indion FR 10

Constituents	Indion FR 10[a]
Particle size (mesh)	16–50
Physical state	Solid
Odour	No odour
Ionic form	Chelating type resin with sulphonic acid functionality
Matrix	Crosslinked polystyrene (44–50% of styrene/divinylbenzene)
Appearance	Golden yellow coloured spherical beads
Operating pH range	4–9
% Moisture content (w/w)	46–50
Specific gravity (in water)	1.14–1.16
Maximum operating temperature (°C)	80

[a] Specifications as per the manufacture.

Table 2
Metal chelating characteristics of Indion FR 10

Resins	Ion exchange capacity of the resin (mmol/g)	Colour of the metal loaded resin
H^+ form	0.75	Yellow
La^{3+} form	1.28	Yellowish orange
Fe^{3+} form	1.27	Brown
Ce^{3+} form	1.25	Yellowish orange
Zr^{4+} form	1.29	Yellowish orange

2. Results and discussion

2.1. Characterisation of the sorbents

Indion FR 10 is a crosslinked polystyrene resin with sulphonic acid functional group. The specifications of Indion FR 10 as per manufacturer are given in Table 1. The ion exchange capacity and chelating characteristics of Indion FR 10 with metal ions viz., La^{3+}, Fe^{3+}, Ce^{3+} and Zr^{4+} are presented in Table 2. Fig. 1a and b depicts the FTIR spectra of H^+ form of resin before and after fluoride sorption respectively. The band of untreated resin at 3466 cm^{-1} is due to –OH stretching vibration [7,22,23]. The bands at 1179 and 1036 cm^{-1} (not shown in Fig. 1) are assigned to the sulphonic group [7,23,24]. The slight widening of the broad OH band at 3466 cm^{-1} in the fluoride treated resin may be taken as an indicative of the formation of hydrogen bonding (H-bonding) between the acid hydrogen ($-SO_3H$) and fluoride. This is because H-bonding has a significant influence on the peak shape and intensity, generally causing peak broadening [7,22]. Fig. 1c–j shows the FTIR spectra of the before and after fluoride-sorbed Fe^{3+}, La^{3+}, Ce^{3+} and Zr^{4+} forms. Due to exchange of metal ions, the wavenumber at 3466 cm^{-1} of –OH band of H^+ form was slightly shifted to lower frequencies 3442, 3434, 3438 and 3444 cm^{-1} for the exchange of Fe^{3+}, La^{3+}, Ce^{3+} and Ce^{4+} respectively. The shift to lower frequencies is due to the higher molecular weight of exchanged cations [25] which confirms the presence of loaded metal ions in the respective modified resins. Similar results were observed by Rodriguez-Fuentes et al. [26].

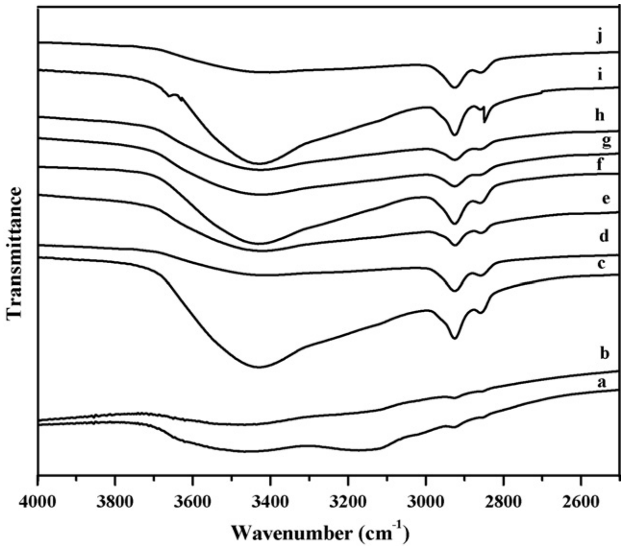

Fig. 1. FTIR spectra of (a) H^+, (c) Fe^{3+}, (e) La^{3+}, (g) Ce^{3+} and (i) Zr^{4+}forms; fluoride-sorbed (b) H^+, (d) Fe^{3+}, (f) La^{3+}, (h) Ce^{3+} and (j) Zr^{4+}forms.

The qualitative elemental composition of the resins before and after fluoride sorption was found by energy dispersive X-ray analyzer (EDAX). The elements found in the sorbents were oxygen, sulphur, aluminium, lanthanum, iron, cerium, zirconium and carbon, this last element could be from the tape used as sample holder. The EDAX spectra of H^+, La^{3+}, Fe^{3+}, Ce^{3+} and Zr^{4+} forms confirms the presence of respective ions in their corresponding resins (cf. Fig. 2a–e). The fluoride sorption has occurred on all the forms of resins which were confirmed by the presence of fluoride peak in EDAX spectra of respective fluoride-sorbed resins (cf. Fig. 2f–j).

2.2. Effect of contact time

The effect of DC of resins with contact time in the range of 10–60 min was studied using 3 mg/L as initial fluoride concentration with neutral pH at room temperature and is shown in Fig. 3. From the graph it is evident that the DC of all the sorbents increases with increasing time and finally reaches saturation. All the metal loaded resins reached saturation after 30 min and H^+ form needed a minimum contact time of 40 min to attain equilibrium. It is also interesting to note that all the modified resins were found to possess higher DC than H^+ form. For subsequent experiments, 40 min was fixed as the contact time for H^+ form and 30 min for all the modified forms of resins.

2.3. Optimization of resin dosage

To examine the effect of the dosage on the percentage fluoride removal, studies were conducted with a fixed time, 3 mg/L as initial fluoride concentration at neutral pH in room temperature. The effect of percentage fluoride removal on sorbent dosage is shown in Fig. 4 which demonstrates that there is an increase in percentage fluoride removal with the increase of dosage of the resins as expected [27]. This experiment was carried out to optimize the sorbent dosages to bring down the fluoride level to below 1 ppm which is the tolerance limit for fluoride. About 1.0 g of the sorbent was found to be the optimum dosage for all the forms and hence in all subsequent experiments the optimum dosage of all the sorbents was fixed as 1.0 g.

2.4. Effect of initial fluoride concentration

The effect of DC with different initial concentrations of fluoride ions viz., 3, 5, 7, 9 and 11 mg/L with neutral pH at 303 K were studied. Fig. 5 shows the influence of varying the initial fluoride concentration on the fluoride removal by resins. It has been found that the DC of resins increases with increasing fluoride concentration. Similar type of result was observed by Lv et al. [28] while using layered double hydroxides for defluoridation. The results once again confirm that the modified forms of resins have higher

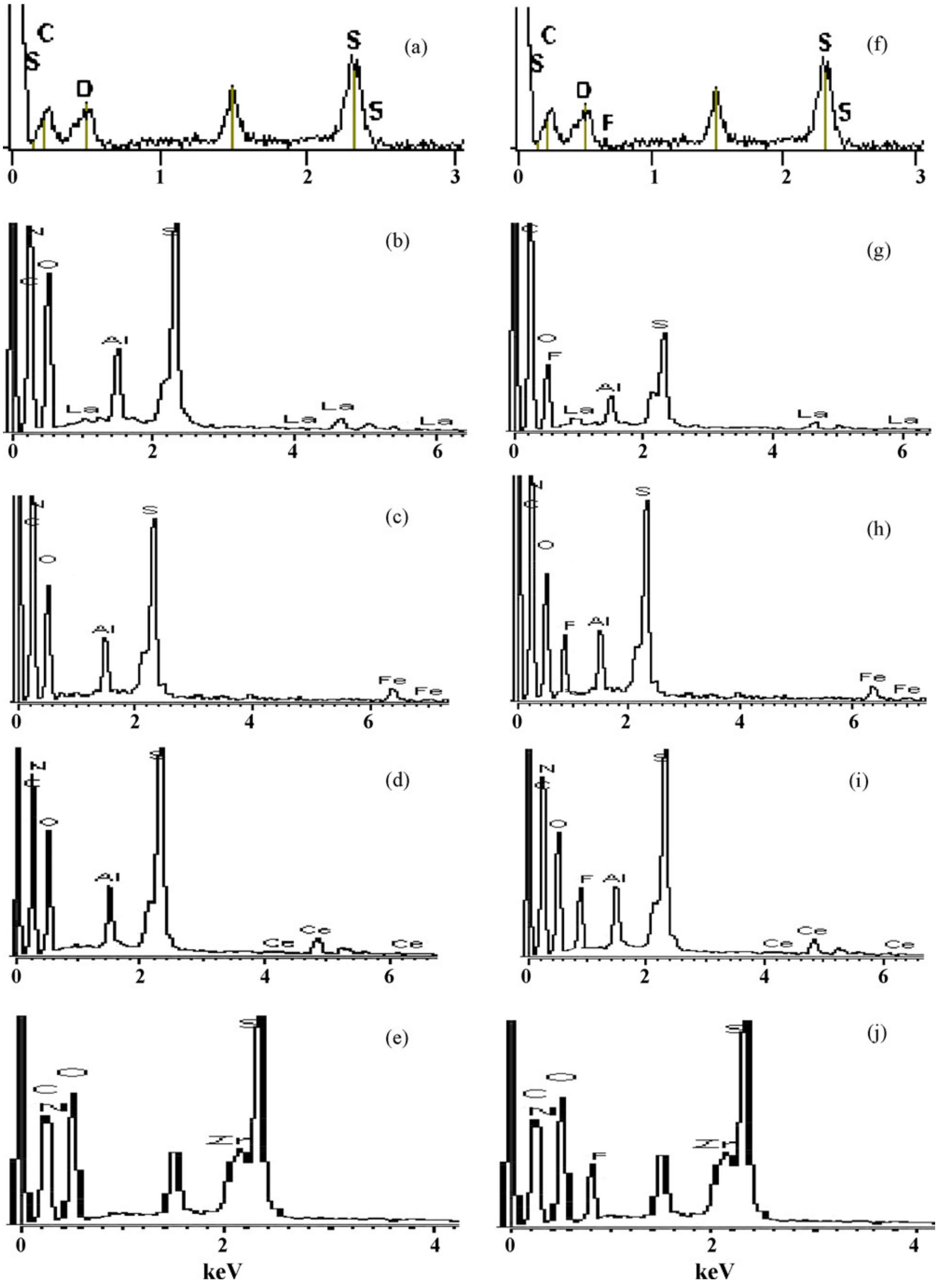

Fig. 2. EDAX spectra of (a) H^+, (b) La^{3+}, (c) Fe^{3+}, (d) Ce^{3+} and (e) Zr^{4+} forms; (f–j) fluoride-sorbed H^+, La^{3+}, Fe^{3+}, Ce^{3+} and Zr^{4+}forms.

DC than the original resin in all the initial concentrations studied. As most of the fluoride-endemic areas, the fluoride level was found to have a maximum of 3 mg F^-/L in drinking water, for further studies the initial fluoride concentration was fixed as 3 mg/L.

2.5. *pH effect on fluoride sorption*

The removal of fluoride from aqueous solution was highly dependent on the solution pH, as it altered the surface charge on the adsorbent. Therefore the removal of fluoride by the resins 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. The pH of the working solution was controlled by adding HCl/NaOH solution. Fig. 6 explains the DC of resins as a function of pH, which indicates that the DC of these sorbents was not influenced by the pH of the environment. Similar type of results was observed when the commercial ion exchangers were used as the sorbent for fluoride removal [7]. In all the pH ranges studied, the DC of the modified forms found to be higher than that of H^+ form. As modified resins possesses higher DC than H^+ form, only modified resins were considered for further studies in order to identify the best sorbent for fluoride among them.

2.6. *Effect of competitor anions*

Fig. 7 explain the dependence of DC of La^{3+} form in the presence of co-anions like Cl^-, SO_4^{2-}, HCO_3^- and NO_3^- with an initial concentration of 100 mg/L and keeping all other parameters such as time, pH, dosage and initial fluoride concentration as constants.

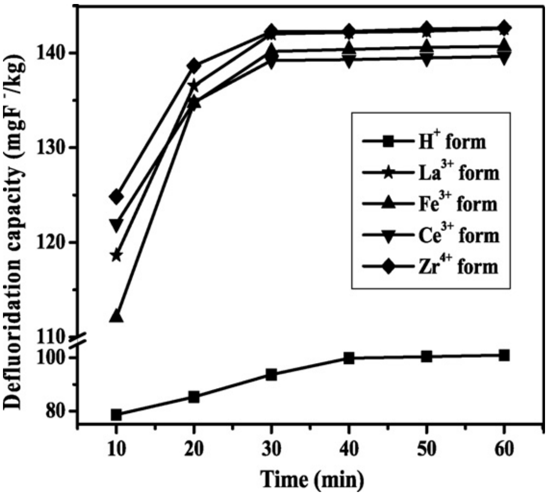

Fig. 3. Effect of contact time on the DC of resins.

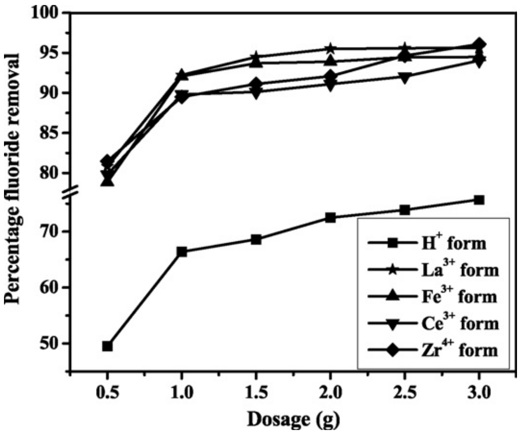

Fig. 4. Effect of dosage on percentage fluoride removal of sorbents.

From the graph it is evident that the overall DC of the resin was slightly influenced by the presence of Cl^-, SO_4^{2-} and NO_3^- ions and it is very interesting to note that the DC is not reduced by the presence of HCO_3^- ion. Similar trend was observed for the other modified forms of resins viz., Fe^{3+}, $Ce^{3+}$and Zr^{4+} also. Even though there is a slight decrease in DC of sorbents in the presence of other anions studied except HCO_3^- ion, they have considerable DC and hence these sorbents could be effectively used as defluoridating agents. This is further supported by the field trial studies of these sorbents.

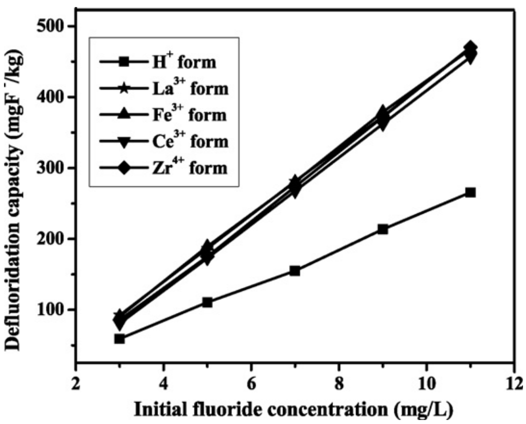

Fig. 5. Effect of DC with different initial fluoride concentrations of sorbents.

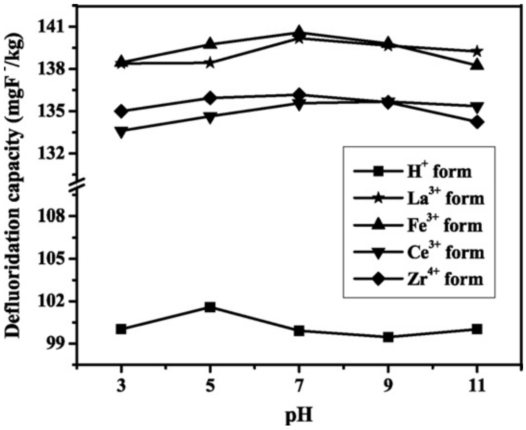

Fig. 6. Effect of pH on the DC of the sorbents.

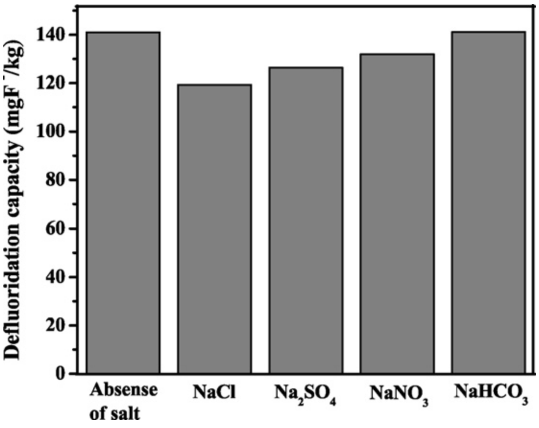

Fig. 7. Effect of other anions on the DC of La^{3+} form.

2.7. Sorption isotherms

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

2.7.1. Freundlich isotherm

The linear form of Freundlich [29] 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 and the values are presented in Table 3. Values of $1/n$ are lying between 0 and 1 and the n value lying in the range of 1–10 confirms the favorable conditions for adsorption [7]. This condition is obeyed by all modified resins suggesting fluoride get sorbed by these resins. The values of k_F remains almost constant for all the sorbents at the temperatures studied. The linear plot of $\log q_e$ vs. $\log C_e$ indicates the applicability of Freundlich isotherm.

Table 3
Freundlich and Langmuir isotherm parameters of the modified sorbents

Modified resins	Temperature (K)	Freundlich isotherm					Langmuir isotherm				
		$1/n$	n	k_F (mg/g)(L/mg)$^{1/n}$	r	χ^2	Q° (mg/g)	b (L/g)	R_L	r	χ^2
La^{3+} form	303	0.813	1.230	0.684	0.999	3.05 E−5	1.931	0.510	0.218	0.999	3.81 E−6
	313	0.789	1.267	0.805	0.999	1.11 E−5	1.748	0.731	0.256	0.993	3.79 E−6
	323	0.743	1.346	0.877	0.998	2.95 E−5	1.441	1.125	0.281	1.00	3.85 E−6
Fe^{3+} form	303	0.784	1.276	0.887	0.999	1.52 E−5	1.704	0.858	0.289	0.999	5.41 E−6
	313	0.769	1.300	0.959	0.999	7.49 E−5	1.608	1.049	0.312	0.998	1.41 E−5
	323	0.701	1.427	0.962	0.998	2.69 E−5	1.258	1.667	0.327	0.998	1.67 E−5
Ce^{3+} form	303	0.798	1.253	0.845	0.998	5.70 E−5	1.799	0.738	0.263	0.999	6.27 E−6
	313	0.787	1.271	0.865	0.998	3.34 E−5	1.721	0.817	0.271	1.00	3.28 E−7
	323	0.741	1.350	0.863	0.999	2.26 E−5	1.431	1.113	0.277	0.998	7.22 E−6
Zr^{4+} form	303	0.875	1.143	0.555	0.998	8.76 E−6	2.825	0.240	0.182	0.999	3.95 E−6
	313	0.869	1.151	0.573	0.999	4.64 E−6	2.710	0.263	0.187	0.998	1.42 E−6
	323	0.829	1.206	0.596	0.997	2.83 E−6	2.101	0.383	0.194	0.997	1.02 E−6

2.7.2. Langmuir isotherm

The linear Langmuir [30] isotherm model can be represented by the equation

$$\frac{C_e}{q_e} = \frac{1}{Q^\circ b} + \frac{C_e}{Q^\circ} \qquad (2)$$

where Q° 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 and the values are given in Table 3. The linear plot of C_e/q_e vs. C_e indicates the applicability of Langmuir isotherm.

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 [31]

$$R_L = \frac{1}{1 + bC_o} \qquad (3)$$

where b is the Langmuir isotherm constant (L/mg) and C_o is the initial concentration of fluoride (mg/L). The R_L values between 0 and 1 for the sorbents indicate favorable adsorption at all the temperatures studied (cf. Table 3).

2.7.3. Chi-square analysis

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

$$\chi^2 = \sum \frac{(q_e - q_{e,m})^2}{q_{e,m}} \qquad (4)$$

where $q_{e,m}$ is equilibrium capacity (mg/g) obtained from the model and q_e is experimental data of the equilibrium capacity (mg/g). The results of chi-square analysis are presented in Table 3. The comparatively lower χ^2 values of Langmuir isotherm indicate that the sorption occurs through a monolayer coverage of the fluoride on the surface of the sorbents.

2.8. Thermodynamic treatment of the sorption process

Thermodynamic parameters associated with the adsorption, viz., standard free energy change (ΔG°), standard enthalpy change (ΔH°) and standard entropy change (ΔS°) were calculated using Khan and Singh method and van't Hoff equation [7,32] and the values are shown in Table 4. The negative values of ΔG° confirm the feasibility and the spontaneous nature of fluoride sorption. The positive value of ΔH° indicates that the sorption reaction is endothermic. The positive value of ΔS° which is a measure of randomness at the solid/liquid interface during fluoride sorption indicates the sorption process is irreversible and stable.

2.9. 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 [33].

2.9.1. 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 [34] is given as.

$$\log(q_e - q_t) = \log\ q_e - \frac{k_{ad}}{2.303} t \qquad (5)$$

where q_t is the amount of fluoride on the surface of the sorbent 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 5.

Table 4
Thermodynamic parameters of modified resins obtained at different temperatures

Thermodynamic parameters		La^{3+} form	Fe^{3+} form	Ce^{3+} form	Zr^{4+} form
ΔG° (kJ mol^{-1})	303 K	−2246.1	−1039.1	−1389.7	−3931.5
	313 K	−1453.7	−596.9	−1202.4	−3847.2
	323 K	−542.7	−358.9	−572.5	−3093.6
ΔH° (kJ mol^{-1})		28.7	22.7	14.1	16.9
ΔS° (kJ mol^{-1} K^{-1})		87.1	71.2	41.6	42.7

Table 5
Pseudo-first-order rate constants for fluoride sorption on modified resins at different temperatures with different initial concentrations

C_o (mg/L)	Mass (g)	Temperature (K)	La^{3+} form		Fe^{3+} form		Ce^{3+} form		Zr^{4+} form	
			k_{ad} (min^{-1})	r	k_{ad} (min^{-1})	r	k_{ad} (min^{-1})	r	k_{ad} (min^{-1})	r
5	1.0	303	0.230	0.987	0.228	0.949	0.233	0.906	0.191	0.946
		313	0.191	0.991	0.131	0.965	0.170	0.942	0.164	0.962
		323	0.210	0.987	0.124	0.990	0.124	0.922	0.147	0.970
7	1.0	303	0.216	0.986	0.182	0.992	0.184	0.977	0.175	0.972
		313	0.182	0.991	0.198	0.993	0.168	0.984	0.160	0.970
		323	0.180	0.990	0.120	0.985	0.166	0.964	0.154	0.973
9	1.0	303	0.233	0.951	0.244	0.981	0.182	0.989	0.205	0.998
		313	0.286	0.957	0.226	0.985	0.181	0.998	0.159	0.979
		323	0.205	0.988	0.115	0.975	0.168	0.985	0.226	0.996
11	1.0	303	0.181	0.972	0.235	0.998	0.205	0.997	0.242	0.980
		313	0.226	0.967	0.177	0.962	0.237	0.988	0.214	0.997
		323	0.187	0.995	0.173	0.973	0.184	0.992	0.182	0.984

Table 6
Pseudo-second-order kinetic parameters of modified resins at different temperatures with different initial concentrations

Modified resins	Parameters	303 K				313 K				323 K			
		5 mg/L	7 mg/L	9 mg/L	11 mg/L	5 mg/L	7 mg/L	9 mg/L	11 mg/L	5 mg/L	7 mg/L	9 mg/L	11 mg/L
La^{3+} form	q_e (mg/g)	0.264	0.388	0.474	0.568	0.266	0.350	0.457	0.582	0.256	0.342	0.449	0.553
	k (g/mg min)	1.161	0.540	0.605	0.569	1.209	2.205	1.143	0.519	2.175	5.734	2.055	1.222
	h (mg/g min)	0.081	0.081	0.136	0.184	0.085	0.270	0.239	0.176	0.143	0.671	0.414	0.374
	r	0.999	0.999	0.999	0.998	0.999	0.999	0.999	1.00	0.999	1.00	0.999	0.999
Fe^{3+} form	q_e (mg/g)	0.265	0.365	0.466	0.582	0.249	0.353	0.452	0.545	0.245	0.341	0.437	0.538
	k (g/mg min)	1.229	1.110	0.928	0.600	4.777	2.150	1.819	2.042	10.853	9.315	7.496	3.589
	h (mg/g min)	0.087	0.148	0.202	0.203	0.295	0.268	0.372	0.606	0.654	1.086	1.431	1.040
	r	0.999	0.999	0.999	0.998	1.00	0.999	0.999	0.999	1.00	1.00	0.999	0.999
Ce^{3+} form	q_e (mg/g)	0.248	0.348	0.467	0.575	0.246	0.345	0.455	0.583	0.243	0.341	0.450	0.546
	k (g/mg min)	3.255	2.298	0.865	0.647	4.562	3.113	1.314	0.561	8.583	6.144	1.816	1.591
	h (mg/g min)	0.200	0.278	0.189	0.214	0.276	0.371	0.272	0.190	0.508	0.713	0.368	0.474
	r	0.999	1.00	0.999	0.999	0.999	1.00	1.00	0.997	1.00	1.00	0.999	0.999
Zr^{4+} form	q_e (mg/g)	0.245	0.348	0.452	0.554	0.242	0.341	0.444	0.541	0.242	0.337	0.445	0.540
	k (g/mg min)	2.373	1.250	0.889	0.685	2.841	1.752	1.119	0.979	3.218	2.648	1.317	1.113
	h (mg/g min)	0.141	0.151	0.182	0.210	0.167	0.204	0.221	0.287	0.189	0.301	0.260	0.325
	r	0.999	1.00	0.999	0.999	1.00	0.999	0.999	0.999	1.00	1.00	0.999	0.999

In addition, the pseudo-second-order model is also widely used. There are four types of linear pseudo-second-order kinetic models [35] and the most popular linear form is

$$\frac{t}{q_t}=\frac{1}{h}+\frac{t}{q_e} \tag{6}$$

where $q_t=(q_e^2kt)/(1+q_ekt)$, amount of fluoride on the surface of the resin 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, $h=kq_e^2$ (mg/g min). The value of q_e (1/slope), k (slope^2/intercept) and h (1/intercept) of the pseudo-second-order equation can be found out experimentally by plotting t/q_t against t and the values obtained for fluoride sorption at different temperatures viz., 303, 313 and 323 K for modified forms are presented in Table 6. The plot of pseudo-second-order model of La^{3+} form at 303 K is shown in Fig. 8. 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.

2.9.2. Diffusion-based models

For a solid/liquid sorption process, the solute transfer is usually characterised either by particle diffusion or pore diffusion control. A simple equation for the particle diffusion controlled sorption process [36] is given as follows,

$$\ln\left(1-\frac{C_t}{C_e}\right)=-k_pt \tag{7}$$

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.

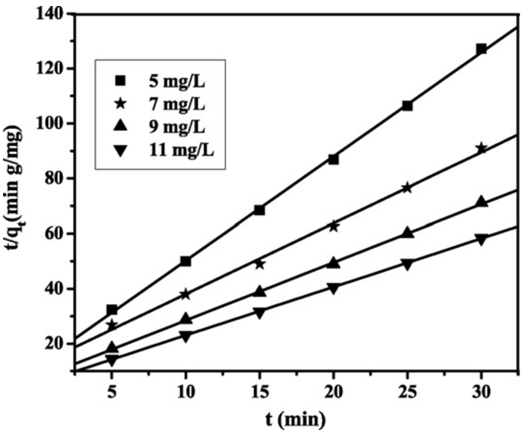

Fig. 8. Pseudo-second-order plot of La^{3+} form at 303 K.

Table 7

Particle and pore diffusion model parameters for fluoride sorption on modified resins at different initial concentrations with different temperatures

C_o (mg/L)	Mass (g)	Modified 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 $\mathrm{min}^{0.5}$)	r	k_p (min^{-1})	r	k_i (mg/g $\mathrm{min}^{0.5}$)	r	k_p (min^{-1})	r	k_i (mg/g $\mathrm{min}^{0.5}$)	r
5	1.0	La^{3+} form	0.199	0.995	0.043	0.948	0.179	0.996	0.043	0.946	0.198	0.992	0.042	0.912
		Fe^{3+} form	0.187	0.981	0.043	0.943	0.147	0.975	0.041	0.875	0.131	0.989	0.040	0.841
		Ce^{3+} form	0.154	0.970	0.040	0.880	0.160	0.951	0.040	0.860	0.129	0.917	0.040	0.837
		Zr^{4+} form	0.156	0.971	0.040	0.908	0.150	0.971	0.039	0.896	0.159	0.960	0.040	0.885
7	1.0	La^{3+} form	0.238	0.972	0.062	0.966	0.194	0.993	0.058	0.896	0.148	0.984	0.057	0.854
		Fe^{3+} form	0.197	0.987	0.060	0.931	0.182	0.990	0.058	0.894	0.128	0.980	0.056	0.833
		Ce^{3+} form	0.160	0.986	0.057	0.888	0.158	0.988	0.057	0.875	0.151	0.975	0.056	0.842
		Zr^{4+} form	0.165	0.978	0.057	0.928	0.164	0.973	0.056	0.906	0.157	0.971	0.056	0.883
9	1.0	La^{3+} form	0.202	0.977	0.077	0.953	0.214	0.992	0.075	0.914	0.205	0.988	0.075	0.887
		Fe^{3+} form	0.225	0.986	0.077	0.928	0.199	0.975	0.075	0.891	0.115	0.975	0.071	0.831
		Ce^{3+} form	0.186	0.989	0.077	0.933	0.196	0.997	0.075	0.908	0.190	0.989	0.075	0.894
		Zr^{4+} form	0.194	0.999	0.075	0.933	0.173	0.972	0.074	0.920	0.195	0.993	0.074	0.913
11	1.0	La^{3+} form	0.213	0.944	0.092	0.945	0.211	0.975	0.094	0.950	0.202	0.997	0.092	0.903
		Fe^{3+} form	0.221	0.999	0.096	0.941	0.183	0.965	0.091	0.880	0.149	0.955	0.089	0.857
		Ce^{3+} form	0.199	0.996	0.095	0.938	0.221	0.989	0.095	0.941	0.176	0.993	0.091	0.890
		Zr^{4+} form	0.193	0.998	0.092	0.935	0.194	1.00	0.089	0.917	0.196	0.988	0.090	0.911

[a] DM—diffusion model.

The pore diffusion model used here refers to the theory proposed by Weber and Morris [37] and its intraparticle equation is

$$q_t = k_i t^{1/2} \tag{8}$$

where k_i is the intraparticle rate constant (mg/g $\mathrm{min}^{0.5}$). The slope of the plot of q_t against $t^{1/2}$ will give the value of intraparticle rate constant.

Both particle and pore diffusion models were used to describe the sorption of fluoride on 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 7. The higher r values obtained for particle diffusion model suggest that the modified resins follow particle diffusion model which is further confirmed by SAE values.

2.9.3. The best fit kinetic models

The assessment of the employed kinetic models for fitting the sorption data was made by calculating the sum of the absolute errors [SAE]. Lower values of SAE show better fit to sorption data [38].

$$\mathrm{SAE} = \sum_{i=1}^{n} \left| q_{t,\mathrm{m}} - q_{t,\mathrm{e}} \right|_i \tag{9}$$

where $q_{t,\mathrm{e}}$ and $q_{t,\mathrm{m}}$ is the experimental sorption capacity of fluoride (mg/g) at time t and the corresponding value which is obtained from the kinetic models. The SAE values of all the kinetic models are summarized in Table 8. Smaller SAE values of pseudo-second-order among the reaction-based models once again confirm the sorption of fluoride follows pseudo-second-order model. Among the diffusion-based kinetic models, particle diffusion model

Table 8

SAE values of kinetic models employed for fluoride sorption on modified resins

Resins	Kinetic models	303 K				313 K				323 K			
		5 mg/L	7 mg/L	9 mg/L	11 mg/L	5 mg/L	7 mg/L	9 mg/L	11 mg/L	5 mg/L	7 mg/L	9 mg/L	11 mg/L
La^{3+} form	Pseudo-first-order	0.032	0.079	0.081	0.024	0.007	0.122	0.039	0.078	0.034	0.182	0.130	0.161
	Pseudo-second-order	0.021	0.051	0.022	0.015	0.001	0.023	0.006	0.028	0.025	0.030	0.062	0.024
	Particle diffusion	0.045	0.048	0.044	0.039	0.052	0.312	0.363	0.470	0.246	0.220	0.290	0.335
	Pore diffusion	0.233	0.230	0.395	0.540	0.250	0.497	0.573	0.523	0.333	0.589	0.659	0.745
Fe^{3+} form	Pseudo-first-order	0.032	0.052	0.022	0.042	0.199	0.097	0.087	0.251	0.247	0.367	0.498	0.307
	Pseudo-second-order	0.015	0.010	0.009	0.017	0.042	0.094	0.064	0.107	0.012	0.012	0.018	0.059
	Particle diffusion	0.056	0.049	0.044	0.045	0.354	0.387	0.334	0.268	0.260	0.206	0.205	0.218
	Pore diffusion	0.254	0.390	0.513	0.543	0.402	0.515	0.657	0.840	0.460	0.643	0.841	0.938
Ce^{3+} form	Pseudo-first-order	0.034	0.117	0.070	0.026	0.121	0.171	0.125	0.060	0.237	0.213	0.197	0.199
	Pseudo-second-order	0.014	0.083	0.050	0.010	0.036	0.059	0.047	0.020	0.012	0.030	0.113	0.131
	Particle diffusion	0.281	0.356	0.351	0.426	0.314	0.308	0.375	0.455	0.257	0.202	0.321	0.301
	Pore diffusion	0.391	0.520	0.491	0.565	0.414	0.547	0.600	0.547	0.441	0.615	0.641	0.793
Zr^{4+} form	Pseudo-first-order	0.048	0.067	0.026	0.041	0.095	0.113	0.148	0.060	0.133	0.181	0.047	0.154
	Pseudo-second-order	0.025	0.008	0.020	0.013	0.059	0.101	0.064	0.040	0.048	0.065	0.021	0.083
	Particle diffusion	0.296	0.324	0.294	0.295	0.284	0.281	0.291	0.248	0.272	0.236	0.247	0.234
	Pore diffusion	0.321	0.395	0.462	0.540	0.361	0.456	0.512	0.677	0.355	0.502	0.558	0.686

possesses lower SAE values suggesting that the sorption of fluoride occurs by external diffusion.

2.10. Mechanism of fluoride retention

During modification of H^+ form by respective metal ions viz., La^{3+}, Fe^{3+}, Ce^{3+} and Zr^{4+}, the H^+ ion gets exchanged by loaded metal ions and the amount of exchanged metal ions is given in terms of metal exchange capacity of resin in Table 2. These loaded metal ions may attract fluoride from aqueous solution due to the electrostatic adsorption and strong Lewis acid–base interaction [39,40]. All the sorbents selectively retains fluoride as it is the hardest Lewis base and the metal ions loaded into the resin are hard Lewis acids. The type of electrostatic adsorption in H^+ form is H-bonding whereas for the modified forms it is ionic. Simultaneously the modified resins may attract fluoride by complexation too, as fluoride act as a chelating agent. Hence the modified resins possesses higher DC than that of H^+ form. The maximum DC of the chemically modified ion exchange resins namely La^{3+}, Fe^{3+}, Ce^{3+} and Zr^{4+} forms were found to be 469.7, 467.5, 456.3 and 470.9 mg F^-/kg respectively suggests their higher selectivity towards fluoride than H^+ form which has only the DC of 275 mg F^-/kg at 11 mg/L initial fluoride concentration. The order of maximum fluoride uptake capacity of different metal ions loaded on Indion FR 10 resin was Zr(IV) > La(III) > Fe(III) > Ce(III) which is further supported by the Q° values of Langmuir isotherm (cf. Table 3). The DCs of all the modified resins are almost comparable and are double than that of original resin in H^+ form as observed in case of their ion exchange capacities (cf. Table 2) and the possible mechanism of fluoride sorption by these sorbents is shown in Fig. 9.

2.11. Field trial

The modified resins used in this study are also tested with field sample taken in a nearby fluoride-endemic village. About 1.0 g of sorbent was added to 50 mL of fluoride water sample and the contents were shaken for 30 min at room temperature and the results obtained are presented in Table 9. There is a significant reduction in the levels of other water quality parameters in addition to fluoride. It is evident from the results that all modified resins can be effectively employed for fluoride removal.

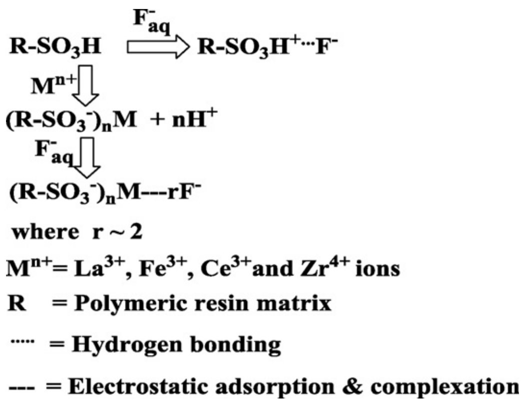

Fig. 9. Mechanism of fluoride removal by the sorbents.

Table 9
Field trial results

Water quality parameters	Before treatment	After treatment			
		La^{3+} form	Fe^{3+} form	Ce^{3+} form	Zr^{4+} form
F^- (mg/L)	4.13	0.29	0.28	0.26	0.23
pH	9.60	8.00	7.96	7.60	7.96
Cl^- (mg/L)	85.20	84.40	78.10	85.20	81.70
Total hardness (mg/L)	140.00	60.00	50.00	50.00	60.00
Total dissolved solids (mg/L)	1350.00	1190.00	1170.00	1200.00	930.00
Na^+ (mg/L)	173.00	116.00	127.00	130.00	123.00
K^+ (mg/L)	23.00	6.00	5.00	6.00	5.00

3. Conclusions

In conclusion, all modified resins possess higher DC which in turn indicates their affinity to fluoride than the original resin. The DC of these sorbents is not influenced by pH of the medium and is slightly influenced in the presence of co-anions except bicarbonate. The sorption process follows Langmuir isotherm. The values of thermodynamic parameters indicate that the fluoride removal process is spontaneous and endothermic in nature. The kinetics of the modified resins follows pseudo-second-order and particle diffusion models. The results of field trial indicate that the modified forms of resins could be effectively employed as promising defluoridating agents.

4. Experimental

4.1. 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, washed with distilled water and kept in an oven at 120 °C till to attain constant weight and has been modified into La^{3+}, Fe^{3+}, Ce^{3+} and Zr^{4+} forms as follows. The La^{3+}, Fe^{3+}, Ce^{3+} and Zr^{4+} forms of resins were prepared by treating H^+ form with respective 5% (w/v) of $LaCl_3 \cdot 7H_2O$, $FeCl_3 \cdot 6H_2O$, $Ce(NO_3)_3 \cdot 6H_2O$ and $ZrOCl_2 \cdot 8H_2O$ solutions for 24 h and the treated resins were washed with distilled water to neutral pH and kept in an oven at 120 °C till to attain constant weight [15]. The dried resin samples were used for the sorption studies. All other chemicals employed were of analytical reagent grade and used without further purification. For the field study, fluoride containing water was collected from a nearby fluoride-endemic village.

4.2. 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 kinetic studies were carried out in a temperature controlled batch sorption system. The effect of initial fluoride concentration with different temperatures at 303, 313 and 323 K on sorption rate was studied with different initial fluoride concentrations viz., 5, 7, 9 and 11 mg/L by keeping the mass of sorbent as 1 g and volume of solution as 50 mL at neutral pH. The solution was then filtered and the residual fluoride ion concentration was measured. 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 carried out with the same instrument with pH electrode. All other water quality parameters were analyzed by using standard methods [41]. The ion exchange capacity of the resin was calculated using standard procedure [42,43].

4.3. Analysis

FTIR spectra of the resin were recorded with JASCO-460 plus model using KBr pellets prepared by mixing resin with KBr. The results of FTIR were used to confirm the functional groups present in the resins. The elemental composition of the sorbents were analyzed by EDAX (HITACHI-S-3400 model) which confirm the presence of elements 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 SAE analysis.

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