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Effect of metal ions loaded onto iminodiacetic acid functionalized cation exchange resin for selective fluoride removal

Subbaiah Muthu Prabhu, S. Meenakshi*

Department of Chemistry, The Gandhigram Rural Institute (Deemed University), Gandhigram, Tamil Nadu
624 302, India
Tel. +91 451 2452371; Fax: +91 451 2454466; email: drs_meena@rediffmail.com

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ABSTRACT

In the present work, Duolite (DLE) C 466 (Sodium form of iminodiacetic acid functionalized macroporous cross-linked polystyrene), a commercially available resin has been modified by loading various metal ions like Fe^{3+}, Al^{3+}, Ce^{3+}, and La^{3+} to enhance the fluoride removal capacity of the resin. The effect of pH, dose of adsorbent, contact time, co-ions, and temperature on fluoride removal efficiency was studied. In order to establish the structural modifications, metals loaded DLE resins were characterized by FTIR and SEM−EDAX studies. The sorption data were subjected to Langmuir and Freundlich isotherms, and the sorption process follows Freundlich isotherm. Thermodynamic parameters such as ΔG°, ΔH°, and ΔS° indicated that the nature of fluoride sorption is spontaneous and endothermic. Dynamic adsorption data indicated that the pseudo-second-order rate equation is the suitable model for the sorption reaction.

Keywords: Adsorption; Fluoride; Resin; Isotherm; Thermodynamics; Kinetic model

1. Introduction

Fluoride is an essential constituent for both humans and animals depending on the total amount ingested or its concentration in drinking water. Fluoride (F^-) contamination in groundwater has been recognized as one of the serious problems worldwide [1]. Fluorosis is a chronic disease that occurs due to the consumption of excess fluoride, mainly through drinking water. The World Health Organization has set a guideline value of 1.5 mg/L as the maximum permissible level of fluoride for drinking water [2]. However, the fluoride concentration of the ground water in many parts around the world is very high, and hence fluorosis among human being is a worldwide problem [3]. Different methods have been adopted to abate excess fluoride from aqueous solution, such as precipitation [4], electrolysis [5], nanofiltration [6], ion exchange [7], and adsorption [8] are proposed to control the concentration of fluoride in aqueous environment. Among these techniques, adsorption is the most widely used for defluoridation, because of its ease of operation and cost-effectiveness, especially for individual homes and small community systems in rural area. Many adsorbents have been successfully used for the removal of fluoride which includes activated alumina [9–11], activated carbon [12], hydroxyapatite [13], bone charcoal [14], clay [15], Chitosan [16–18] etc.

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*Corresponding author.

Ion exchangers are proved to be the most promising materials in the domain of water treatment. In the present study, a commercial cation exchanger resin (Duolite C 466), namely sodium form of iminodiacetic acid functionalized macroporous cross-linked polystyrene has been modified as exchanging Na^+ with various metal ions like Fe^{3+}, Al^{3+}, Ce^{3+}, and La^{3+} in order to increase the defluoridation capacity (DC). Nevertheless, the selectivity of the fluoride removal and its DC of the cation type chelating resins depend upon the type of the metal ion introduced in the resin [19,20] as the metal ions have different influence on the fluoride removal due to differences in their properties [21,22]. The effect of pH, initial concentration of fluoride solution, shaking time, and adsorbent doses on the removal of fluoride were investigated in this study. These fundamental data were useful in selecting the most suitable material for field application.

2. Materials and methods

2.1. Materials

The ion-exchange resins, namely Duolite C 466, a chelating resin was supplied by Auchtel products Ltd, Ratnagiri. The physical and chemical properties of the resin are given in Table 1. NaF, NaOH, $FeCl_3.6H_2O$, $Al_2(SO_4)_3$, $Ce(NO_3)_3.6H_2O$, and $LaCl_3.7H_2O$ were purchased from Central Drug House, New Delhi, and all the other chemicals and reagents used were of analytical grade. All the solutions were prepared using double distilled water.

2.2. Preparation of metal-loaded adsorbent

The Duolite C 466 Na^+ ion exchange resin with iminodiacetic acid group (Na^+ form) having Na^+ as an ion exchanger, washed with distilled water and kept in an oven at 120˚C till it attained constant weight and has been modified into Fe^{3+}, Al^{3+}, Ce^{3+}, and La^{3+} by treating Na^+ form with respective 5% (w/v) of $FeCl_3.6H_2O$, $Al_2(SO_4)_3$, $Ce(NO_3)_3.6H_2O$, and $LaCl_3.7H_2O$ solution 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 [17,18].

Table 1
Physical and chemical properties of the resin

Constituents	Duolite C 466
Particle size (mesh)	16–50
Matrix	Macroporous Cross-linked polystyrene
Appearance	Beige color opaque Beads
Shipping/Ionic form	Sodium
Bulk density (gm/lit)	680–730
Operating pH range	0–14
Effective size (mm)	0.45–0.60
% Moisture content (w/w)	55–60
Maximum operating temperature, °C	Upto 80

2.3. Sorption experiments

Batch adsorption tests were carried out to study the effect of various parameters on the adsorption efficiency of various metal ions loaded on resin. In a typical case, 0.1 g of fixed sorbent dose was added to 50 mL of NaF solution whose initial concentration was fixed as 10 mg/L with a desired pH 7 at room temperature. The pH of the medium was adjusted with 0.1M HCl or 0.1M NaOH. The contents were shaken thoroughly using a thermostated shaker rotating at a speed of 200 rpm. The kinetic and thermodynamic parameters of adsorption were established by conducting the experiments at 303, 313, and 323 K in a temperature controlled mechanical shaker. The DC of the sorbents was studied at different conditions like various mass of sorbents, contact time of the sorbent for maximum defluoridation, pH of the medium, and the effect of co-anions on defluoridation. After shaking, the suspension was filtered and then the filtrate was analyzed for residual ion concentration. All other water quality parameters were analyzed by using standard methods [23].

2.4. Analysis

Expandable ion analyzer EA 940 (Orion, USA) with ion selective fluoride electrode BN 9609 (Orion, USA) was used for the quantitative analysis of

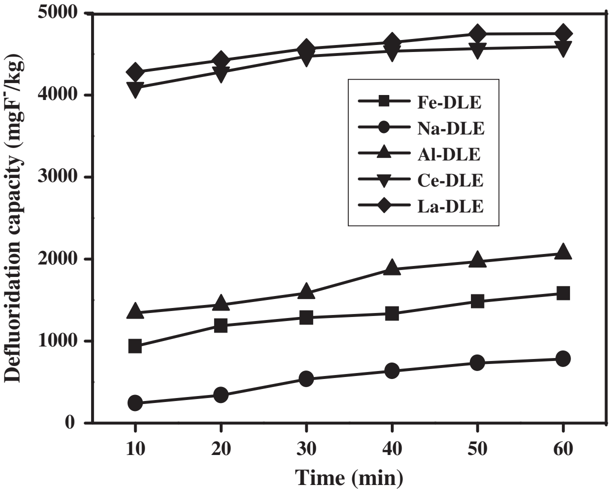


Fig. 1. Effect of contact time on DC of the modified resins.

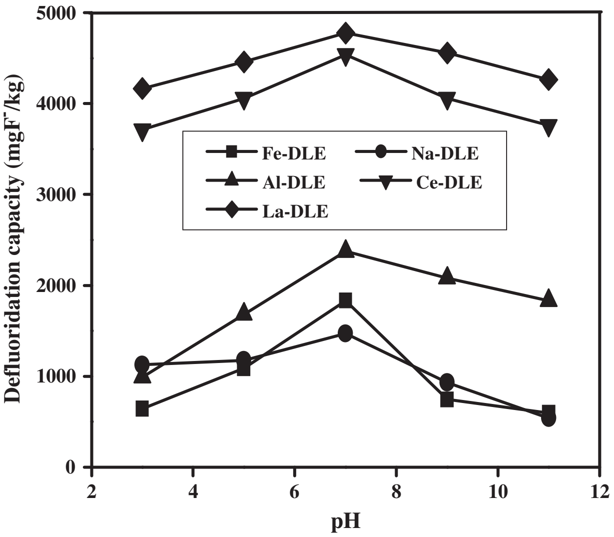


Fig. 2. Influence of pH on DC of the modified resins.

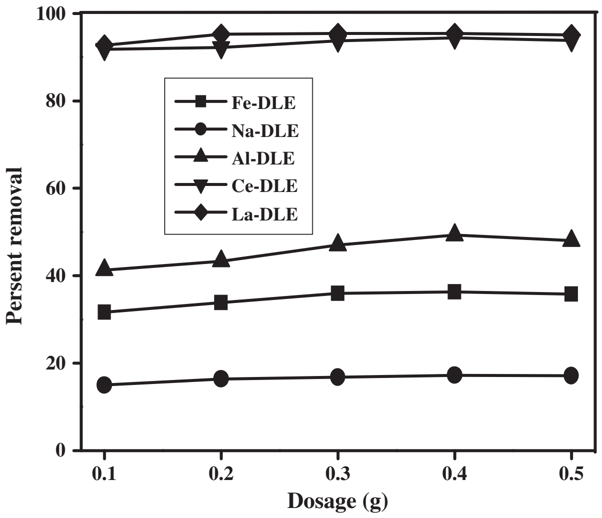


Fig. 3. Effect of dose on DC of the modified resins.

fluoride. The pH measurements were done with the same instrument with pH electrode. IR spectra were recorded on a JASCO-460 FT-IR spectrometer as KBr pellets. The scanning electron microscope (SEM) images were taken using Vega3 Tescan model and EDAX spectra were taken by Bruker Nano GMBH, Germany. Computations were made using Microcal Origin (Version 6.0) software.

3. Results and discussion

3.1. Effect of contact time

Fig. 1 illustrates the effect of DC of all the resins as a function of contact time with 10 mg/L as initial fluoride concentration. About 50 ml solution of desired fluoride concentration was taken into conical flask containing known weight of adsorbent and was shaken for 24 h on rotary shaker to attain the equilibrium. Adsorbent was then separated using filter paper and the filtrate was analyzed for residual fluoride using ion selective electrode. All adsorption experiments were carried out at room temperature (303 K). All the metal loaded Duolite (DLE) resins reached saturation after 60 min. Hence, in the subsequent experiments the shaking time was fixed as 60 min for all metal loaded DLE resin. The DC of La-DLE was found to be higher than all other metal loaded resin. The DC of the La, Ce, Al, Na, and Fe loaded resins were found to be 4,760, 4,519, 1875, 1,759, and 784 mgF$^-$/kg, respectively.

3.2. Influence of pH of the medium

The fluoride sorptive effect at different pH environments was experimentally verified for all the resins by varying the pH ranges from 3 to 11 with 10 mg/L as initial fluoride concentration at 303 K. Fig. 2 shows the DC of all the resins was slightly influenced by the pH of the medium. Though the degree of variation differs with various metal loaded resins, the maximum DC for all the resins was observed at pH 7. As the maximum DC was observed at pH 7, further experiments were carried out at pH 7.

3.3. Optimization of sorbent dosage

The percent removal varies with different dosages of sorbent, viz., 0.1, 0.2, 0.3, 0.4, and 0.5 g was studied to ascertain the effect of dosages and to optimize the minimum dosages required for bringing down the

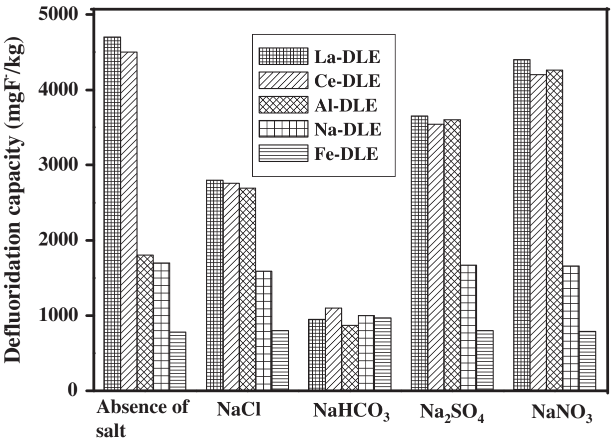


Fig. 4. Effect of competitor ions on DC of the modified resins.

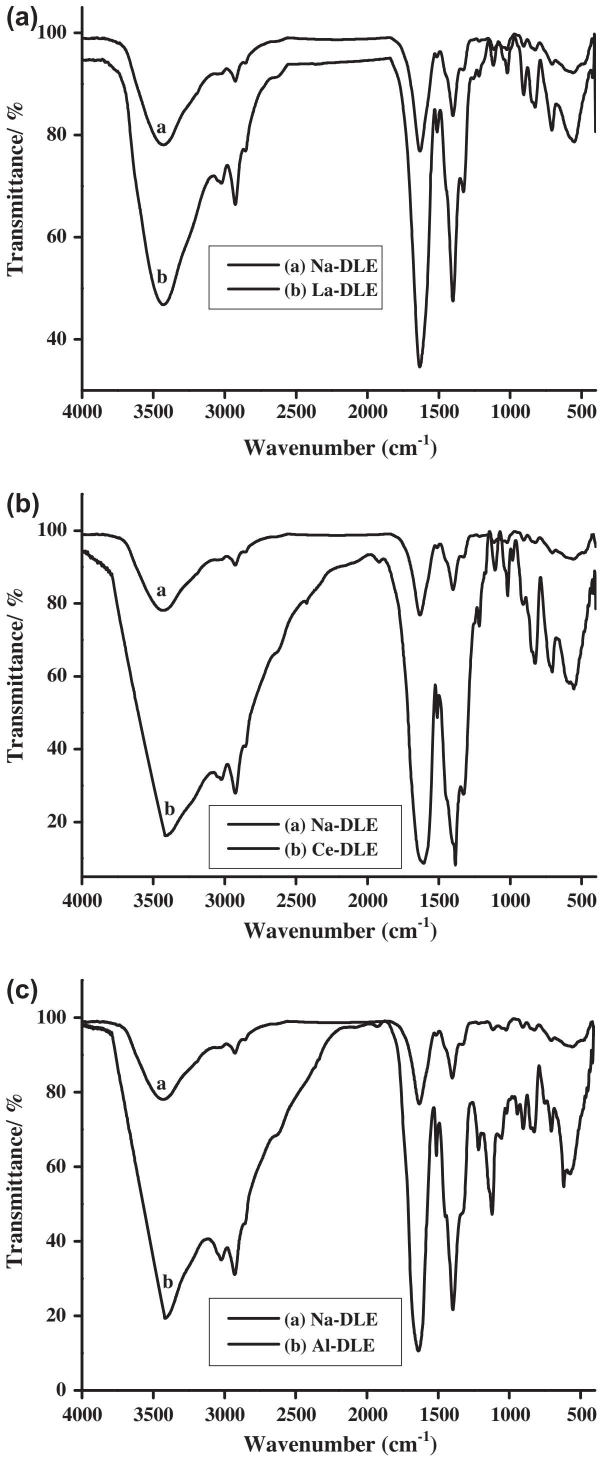


Fig. 5. FTIR spectra of (a) La-DLE resin, (b) Ce-DLE resin, and (c) Al-DLE resin.

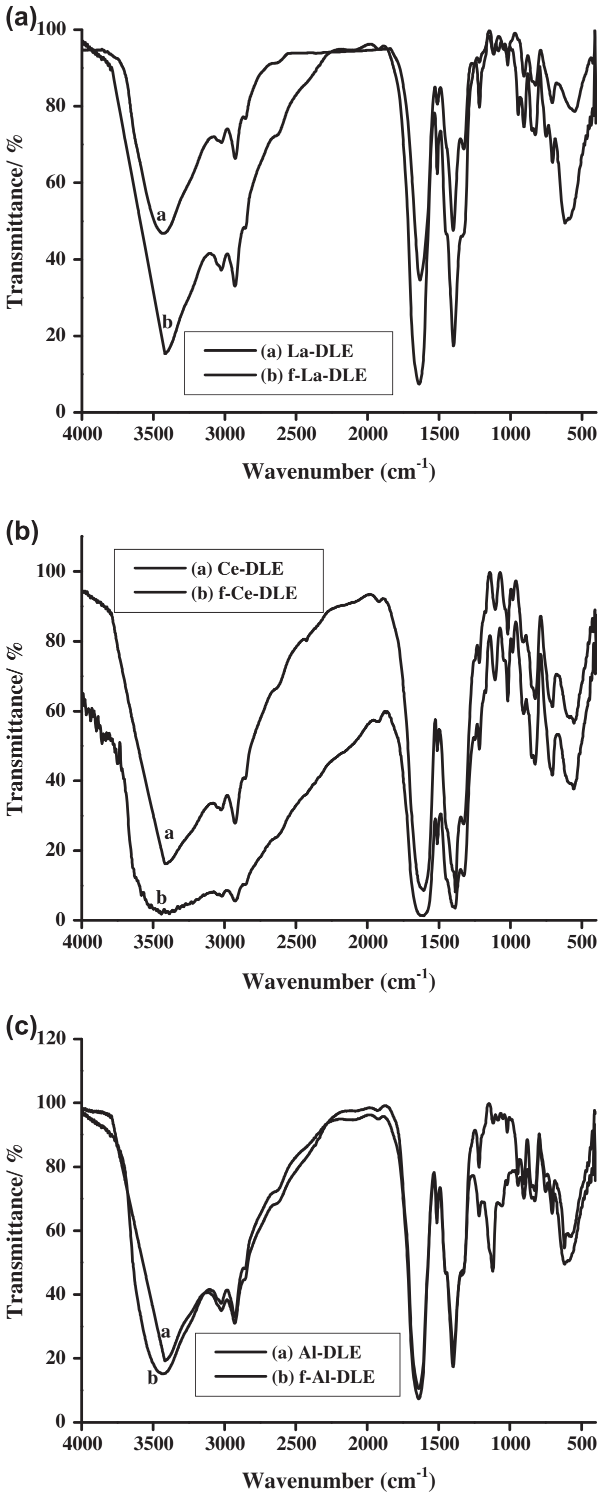


Fig. 6. FTIR spectra of fluoride sorbed (a) f-La-DLE resin, (b) f-Ce-DLE resin, and (c) f-Al-DLE resin.

fluoride level to the tolerance limit. It was observed as shown in Fig. 3 that the percent removal increases by increasing sorbent dosages [24] from 0.1 to 0.5 g and stayed almost constant after 0.5 g of all the sorbents. 0.1 g of the sorbent was found to be the optimum dose and hence, in all subsequent experiments the dosage of all the sorbents was fixed as 0.1 g.

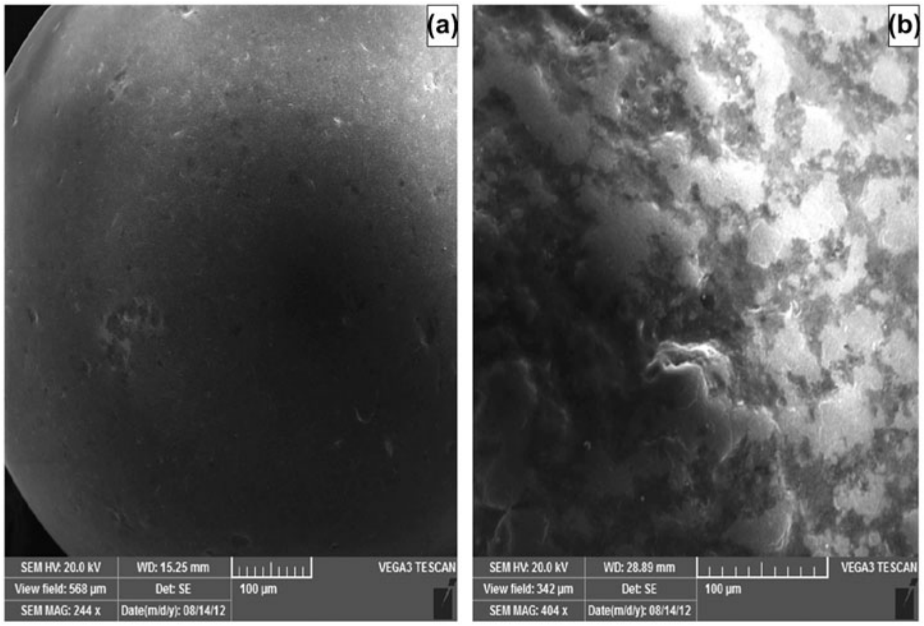


Fig. 7. SEM micrographs of (a) La-DLE resin and (b) fluoride sorbed f-La-DLE resin.

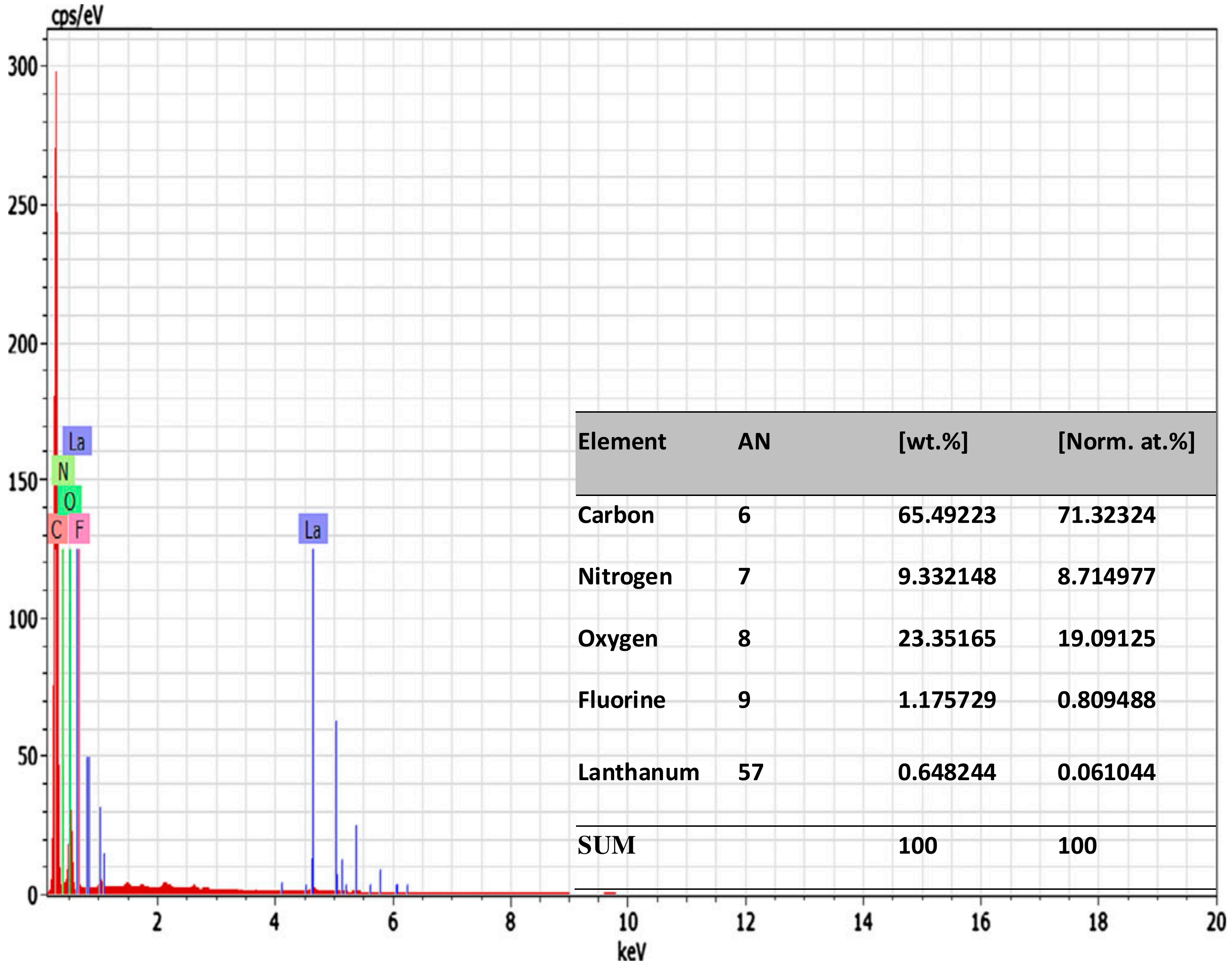
3.4. Effect of competitor anions

The fluoride-contaminated drinking water contains several common other anions, viz., Cl^-, SO_4^{2-}, HCO_3^-, and NO_3^- which can compete with the DC of all the metal loaded resins and hence, the dependence of DC on all the resins was investigated in the presence of co-anions with an initial concentration of 200 mg/L of these ions by keeping 10 mg/L as the initial fluoride concentration with neutral pH at 303 K. Fig. 4 shows that there is a slight decrease in the DC of all the resins in the presence of Cl^-, SO_4^{2-}, and NO_3^- ions, but the presence of HCO_3^- ions results in the decrease of DC. This is due to the competition of bicarbonate ions with fluoride ions in the sorption process due to its size and charge of the anions. Even though there is a slight decrease in DC of sorbent in presence of other anions, the metal loaded resins has significant DC suggesting its selectivity towards fluoride and hence it could be used as a promising defluoridating agent. Parallel interference of bicarbonate ions on the DC of the sorbent Alumina has been cited earlier by Karthikeyan et al. [25]. As the metal loaded resin showed higher DC, further experiments were restricted to La-DLE resin.

3.5. Instrumental analysis

FTIR spectrum is a useful tool to identify functional groups in a molecule, as each specific chemical bond often has a unique energy absorption band and can obtain structure, bond information, and study of strength and fraction of hydrogen bonding. DLE resin, virgin adsorbents (La-DLE, Ce-DLE and Al-DLE), and fluoride sorbed (f-La-DLE, f-Ce-DLE and f-Al-DLE) sorbents were analyzed by FTIR spectroscopy. As shown in Fig. 5(a), FTIR spectroscopy revealed that after impregnation, a sharp band appeared between 1,500 and 1,650 cm^{-1} confirms the presence of La-DLE. Fig. 6(a), the fluoride sorbed La-DLE indicating a broad band in the range of 3,400–3,510 cm^{-1} is due to the stretching mode of structural –OH groups of the resin. The band at 2,921 cm^{-1} indicates the –CH stretching vibration in –CH and $–CH_2$ [26]. A sharp band at 1,640 cm^{-1} confirms the presence of carbonyl group in La-DLE. The slight broadening of band at 3,050 cm^{-1} in the fluoride sorbed La-DLE may be taken as indicative of electrostatic adsorption between the resin and the fluoride [27,28]. Similar results were obtained in Ce-DLE in Figs. 5(b) and 6(b) and Al-DLE in Figs. 5(c) and 6(c), implying that they have adsorption mechanism analogous to that of f-La-DLE.

Surface morphology is an important factor in adsorbent–adsorbate interactions. The surface morphologies of La-DLE resin before and after fluoride sorption is shown in Fig. 7(a) and (b). Before sorption of fluoride the La-DLE resin surface was found to be smooth and after sorption of fluoride, a reduction in the pore size was observed which may be due to sorption of fluoride onto the sorbents. This is further supported by EDAX analysis in Fig. 8. The EDAX spectra of La-DLE confirm the presence of respective ions in their corresponding



Element	AN	[wt.%]	[Norm. at.%]
Carbon	6	65.49223	71.32324
Nitrogen	7	9.332148	8.714977
Oxygen	8	23.35165	19.09125
Fluorine	9	1.175729	0.809488
Lanthanum	57	0.648244	0.061044
SUM		100	100

Fig. 8. EDAX spectra of f-La-DLE resin.

Table 2
Freundlich and Langmuir isotherms of the resin

Temp (*K*)	Freundlich isotherm					Langmuir isotherm			
	$1/n$	K_f (mg/g) (mg/L) $^{1/n}$	r	sd	Q^0 (mg/g)	b (mg/L)	R_L	r	sd
303	0.551	3.081	0.999	0.002	9.967	0.424	0.205	0.997	0.007
313	0.541	3.537	0.998	0.006	10.060	0.533	0.189	0.999	0.006
323	0.607	3.753	0.998	0.005	12.139	0.444	0.201	0.998	0.008

resin. The fluoride sorption on La-DLE was confirmed by the presence of fluoride peak in EDAX spectra of fluoride-treated La-DLE resin.

3.6. Sorption isotherms

Two commonly used isotherms, namely Freundlich and Langmuir have been adopted to quantify the sorption capacity of La-DLE for the removal of fluoride.

The linear form of Freundlich [29] isotherm is represented by the following equation

$$\log q_e = \log K_F + 1/n \log C_e \tag{1}$$

Langmuir [30] isotherm model can be represented in the form of equation

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

Table 3
Thermodynamic parameters of the resin

Thermodynamic parameters		La-DLE
ΔG° (kJ mol^{-1})	303 K	−3.69
	313 K	−3.41
	323 K	−3.37
ΔH° (kJ mol^{-1})		8.57
ΔS° (kJ K^{-1} mol^{-1})		0.02

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 the measure of adsorption capacity and $1/n$ is the adsorption intensity. The linear plot of log q_e vs. log C_e indicates the applicability of Freundlich isotherm. The values of $1/n$ are lying between 0 and 1 and the n value lying in the range of 1–10 confirms the conditions favorable for adsorption. With increase in temperature, the k_F values get increases, indicates that the fluoride removal by La-DLE is an endothermic process. The Freundlich constants of the sorbent are shown in Table 2.

The linear plot of C_e/q_e vs. C_e indicates the applicability of Langmuir isotherm. The values of Q^0 and b are given in Table 2. The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L.

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

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

3.7. Thermodynamic treatment of fluoride sorption process

The feasibility of the fluoride sorption process was assessed by the thermodynamic parameters, viz. standard enthalpy change (ΔH^0), standard free energy change (ΔG^0), and standard entropy change (ΔS^0), calculated by Khan and Singh method and van't Hoff equation [18,31].

The lower values of ΔG^0 confirm the spontaneous nature of the sorption of the fluoride ion by La-DLE. The positive value of ΔS^0 which is a measure of randomness at the solid/liquid interface during fluoride sorption, indicates the sorption process is irreversible and stable. The positive value of ΔH^0 confirms the endothermic nature of the sorption process (Table 3).

3.8. Sorption kinetics

The two types of kinetic models, viz. reaction-based and diffusion-based models, were applied to test the fitness of the experimental data.

3.8.1. Reaction-based models

The most commonly used pseudo-first-order [32] and pseudo-second-order [33] models were employed to explain the solid–liquid adsorption. The slope of the straight-line plot of log $(q_e - q_t)$ against t for different experimental conditions gives the value of the rate constant (k_{ad}) of pseudo-first-order model and is given in Table 4. The pseudo-second-order parameters 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 4. 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.

3.8.2. Diffusion-based models

In a solid–liquid sorption process, the transfer of solute was characterized by particle diffusion [34] or intraparticle diffusion [35] control. Both particle and intra particle diffusion models were applied to describe the fluoride removal by La-DLE resin. The values of rate constants k_i, k_p, and r values at different temperatures viz., 303, 313, and 323 K for both particle diffusion and intraparticle diffusion models of La-DLE resin are presented in Table 4. The higher r values in both the cases indicated the possibility of sorption process being controlled by particle diffusion model.

4. Mechanism of fluoride sorption

The fluoride removal capacity of these sorbents may be controlled by adsorption mechanism. When Na^+ form is in contact with Fe^{3+}, Al^{3+}, Ce^{3+}, and La^{3+} solutions, the respective metal ions gets exchanged for Na^+ 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 [19,36,37]. From fluoride solution, the F^- ions get adsorbed onto the resin surface. In acidic medium, where the La-DLE resin surface acquires positive charges which in turn attracts more fluoride ions by means of electrostatic attraction.

The comparison of DCs of other common resins available such as Aluminum complexed amino phosphonic

Table 4
Kinetic models of La-DLE resin

Kinetic models	Parameters	303 K				313 K				323 K			
		8 mg/L	10 mg/L	12 mg/L	14 mg/L	8 mg/L	10 mg/L	12 mg/L	14 mg/L	8 mg/L	10 mg/L	12 mg/L	14 mg/L
Pseudo-first-order	k_{ad} (min^{-1})	0.060	0.071	0.088	0.026	0.063	0.064	0.055	0.024	0.072	0.067	0.059	0.028
	r	0.988	0.980	0.980	0.895	0.942	0.996	0.994	0.977	0.996	0.899	0.963	0.985
	sd	0.083	0.128	0.159	0.117	0.203	0.046	0.057	0.048	0.056	0.292	0.147	0.044
Pseudo-second-order	q_{e} (mg/g)	3.738	4.798	8.542	6.520	3.814	4.792	5.118	5.516	3.859	4.769	5.740	6.558
	k (g/mg min)	0.152	0.115	0.052	0.035	0.175	0.219	0.068	0.057	0.186	0.260	0.264	0.377
	h (mg/g min)	2.213	2.655	3.837	1.494	2.543	5.046	1.805	1.745	2.767	5.919	8.706	1.620
	r	0.999	0.999	0.999	0.999	0.999	0.998	0.999	0.999	1.000	0.999	0.999	0.998
	sd	0.030	0.096	0.020	0.138	0.058	0.015	0.070	0.103	0.015	0.041	0.016	0.150
Particle diffusion	k_{p} (min^{-1})	0.091	0.061	0.104	0.025	0.063	0.070	0.055	0.024	0.072	0.066	0.058	0.027
	r	0.990	0.977	0.973	0.893	0.943	0.999	0.994	0.977	0.996	0.899	0.963	0.985
	sd	0.272	0.280	0.516	0.264	0.467	0.074	0.130	0.110	0.129	0.673	0.338	0.100
Intraparticle diffusion	k_{i} (mg/g min$^{0.5}$)	0.098	0.111	0.127	0.352	0.078	0.068	0.173	0.199	0.079	0.053	0.066	0.265
	r	0.922	0.931	0.929	0.862	0.957	0.955	0.985	0.977	0.950	0.950	0.898	0.987
	sd	0.078	0.083	0.096	0.393	0.045	0.040	0.058	0.083	0.049	0.033	0.061	0.081

acid type resins [38], Metal(III)-Loaded Amberlite Resins [21], calix[4]arene-based resins [39], Zr(IV) surface-immobilized resin [36], Indion FR chelating resin [3], Metal loaded Indion FR chelating resin [40], and Modified Amberlite resin [37] for fluoride removal with that of La-DLE was made and the La-DLE shows a higher DC which confirms its selectivity towards fluoride.

5. Conclusions

The results suggested that La-DLE resin was an effective material to remove excess fluoride from aqueous solution. At low pH, the La-DLE resin could remove fluoride efficiently and adsorb fluoride rapidly. The pseudo-second-order model could describe kinetic data well, and the adsorption process fitted better into the linearly transformed Freundlich than Langmuir model. DLE is a low-cost material and has high mechanical stability in chemical treatment methods; no considerable leakage of metal ions was observed during usage of DLE and caused no pollution into the solution, and it was demonstrated that La-DLE can be effectively utilized as a promising defluoridation agent.

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