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Selective sorption of fluoride using Fe(III) loaded carboxylated chitosan beads

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Chitosan beads (CB) as such have very low defluoridation capacity (DC) of 52 mgF$^-$/kg have been suitably modified by carboxylation followed by chelation with Fe^{3+} ion (Fe-CCB), in order to effectively utilize both hydroxyl and amine groups for defluoridation. The modified beads showed enhanced DC to a very significant level of 4230 mgF$^-$/kg. The fluoride removal process is governed by both adsorption and complexation mechanism. The sorbent was characterized using Fourier transform infrared spectrometer (FTIR) and scanning electron microscope (SEM) analysis. The experimental data have been analysed using isotherm and kinetic models. Thermodynamic parameters such as ΔG°, ΔH° and ΔS° were calculated to predict the nature of sorption. A field trial was carried out with fluoride water collected from a nearby fluoride-endemic village.

1. Introduction

Fluorosis caused by excess intake of fluoride, is a slow, progressive disorder, known to affect predominantly the skeletal systems, teeth, the structure and function of the skeletal muscle, brain and spinal cord [1]. Recent studies have shown accumulation of fluoride in the hippocampus of the brain causing the degeneration of neurons and decreased aerobic metabolism [2] and altered free-radical metabolism in the liver, kidney and heart [3]. The World Health Organisation has specified the tolerance limit for fluoride content in drinking water as 1.5 mg/L [4]. Drinking water is reported to be the major source of fluoride intake. The preferred option for the preventive measure is to find a supply of safe drinking water with safe fluoride levels and one such option is defluoridation.

Several methods have been suggested for removing excessive fluoride in water viz., chemical precipitation [5], ion exchange [6], adsorption [7] and electrolysis [8]. Among the methods reported adsorption seems to be the most attractive technique for fluoride removal. Many adsorbents have been successfully used for the removal of fluoride which includes activated alumina [9], activated carbon [10], zeolite [11], clay [12], etc. Recently, considerable work has been conducted in developing new adsorbents loaded with metal ions for the purpose of fluoride removal [13]. The metal ion adsorbed onto the porous adsorbents or carrier materials have shown promising results.

Chitosan, a derivative from *N*-deacetylation of chitin, is a well-known sorbent and effective in the uptake of metals since the amine groups of chitosan chain can serve as chelation sites for metals [14]. With regards to defluoridation, the fluoride removal capacity of natural chitosan is minimal which indicates that the hydroxyl and amine groups of chitosan have not been effectively involved in fluoride removal. Hence in order to exploit these groups of chitosan, chemical modifications were carried out.

The main goal of our present investigation is to maximize the defluoridation capacity (DC) of chitosan beads (CB) by the substitution of functional groups such as organic acids onto hydroxyl groups and chelation of amine groups with Fe^{3+} ion. The DC of Fe^{3+} loaded carboxylated chitosan beads (Fe-CCB) was calculated 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 Fe-CCB was also investigated. The experimental data were fitted with isotherms and the kinetic models.

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Fe-CCB was tested with a field sample collected from a nearby fluoride-endemic village for its suitability under field conditions.

2. Experimental

2.1. Materials

Chitosan was supplied by Pelican Biotech and Chemicals Labs, Kerala (India). Its deacetylation degree is 85%. The viscosity of the chitosan solution was determined to be 700 (mPa s) by Brookfield Dial Reading Viscometer using electronic drive-RVT model (USA make). The chitosan solution was maintained at a constant viscosity for the beads preparation in order to maintain uniform molecular weight. NaF, NaOH, HCl, glacial acetic acid, glutaraldehyde, chloroacetic acid, $FeCl_3 \cdot 6H_2O$ and all other chemicals and reagents were of analytical grade. For the field study, water containing fluoride was collected from a nearby fluoride-endemic village.

2.2. Preparation of Fe(III) incorporated carboxylated chitosan beads (Fe-CCB)

Chitosan beads (CB) were prepared, cross-linked with glutaraldehyde and hydroxyl groups were carboxylated using chloroacetic acid as suggested by Jeon and Höll [15]. Then, the amine groups of carboxylated chitosan beads (CCB) were chelated with Fe^{3+} ion by treating CCB with 5% $FeCl_3 \cdot 6H_2O$ solution for 24 h, washed with distilled water to neutralize the pH, dried at room temperature and used for sorption studies.

2.3. Sorption experiments

Defluoridation experiments were carried out by batch equilibration method. In a typical case, 0.1 g of the sorbent was added to 50 ml of NaF solution of initial concentration 10 mg/L. The contents were shaken thoroughly using a thermostated shaker rotating at a speed of 200 rpm. 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., 11, 13, 15 and 17 mg/L by keeping the mass of sorbent as 0.1 g and volume of solution as 50 mL at neutral pH. The solution was then filtered and the residual fluoride concentration was measured.

2.4. 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 carried out with the same instrument with pH electrode. All other water quality parameters were analysed by using standard methods [16]. pH at zero point of charge (pH_{zpc}) of beads was measured using the pH drift method [17].

SEM images were obtained with HITACHI-S-3400H model. FTIR spectra of the bead were recorded with JASCO-460 plus model using KBr pellets prepared by mixing the sorbent with KBr. The results of FTIR were used to confirm the functional groups present in the beads before and after fluoride sorption. The specific surface area of the beads was analysed using BET isotherm method with NOVA 1000 model.

Computations were made using Microcal Origin (Version 6.0) software. The significance of data trends and goodness of fit was discussed using error bar plot, regression correlation coefficient (r), chi-square analysis and SAE error analysis.

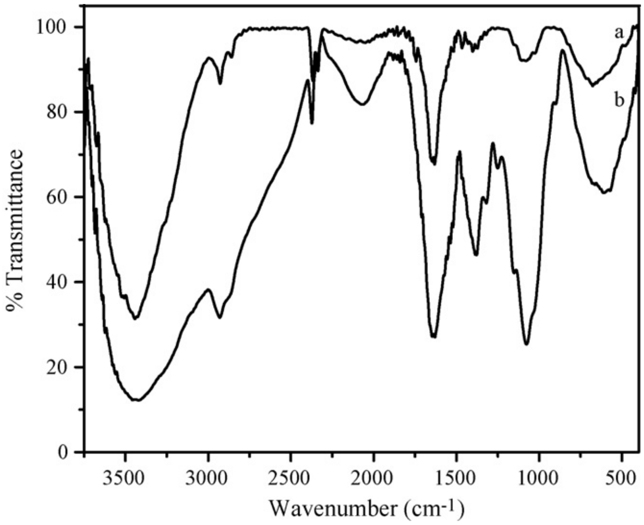

Fig. 1. FTIR spectra of (a) Fe-CCB and (b) fluoride-treated Fe-CCB.

3. Results and discussion

3.1. Characterisation of sorbent

The specific surface area of the Fe-CCB is found to be 2.09 m^2/g. Fig. 1a and b represent the FTIR spectra of Fe-CCB and fluoride-sorbed Fe-CCB. The sharp band at 1630 cm^{-1} confirms the presence of carbonyl group in Fe-CCB. The presence of –OH group is confirmed by having a band at 3420 cm^{-1} [18]. A slight broadening of band at 3420 cm^{-1} in the fluoride-sorbed Fe-CCB may be taken as an indicative of electrostatic adsorption between the sorbent and the fluoride [19,20].

SEM pictures of before and after fluoride sorption of Fe-CCB are shown in Fig. 2a and b, respectively. The change in the SEM micrographs of the sorbent before and after fluoride treatment indicates the structural changes in the sorbent.

pH_{zpc} is an indicator of the net surface charge of the adsorbent and its preference for ionic species. The surface morphological changes of the chitosan beads with that of Fe-CCB were also confirmed by the shifting of pH_{zpc} values. The pH_{zpc} of CB is 7.88 where as for Fe-CCB it was shifted to 3.22 which clearly indicates the occurrence of structural changes in Fe-CCB. Parallel results of shifting of pH_{zpc} values are reported by Al-Degs et al. [21] during the modification of surfaces of sorbent.

3.2. Effect of contact time

The effect of DC of raw and modified chitosan beads with contact time was studied using 10 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 fluoride sorption has been investigated as a function of time in the range of 10–60 min. Fig. 3a shows the variation of DC of sorbents with contact time. From the graph it is evident that the DC of both the sorbents increases with increasing time and finally reaches saturation. Both CB and Fe-CCB reached saturation after 40 min. Hence for further studies, 40 min was fixed as the contact time for fluoride removal. It is very interesting to note that the Fe-CCB was found to possess an extremely higher DC of 4230 mg F^-/kg than raw chitosan bead which has only 52 mg F^-/kg. As the raw chitosan possess negligible DC, for subsequent studies only Fe-CCB was considered.

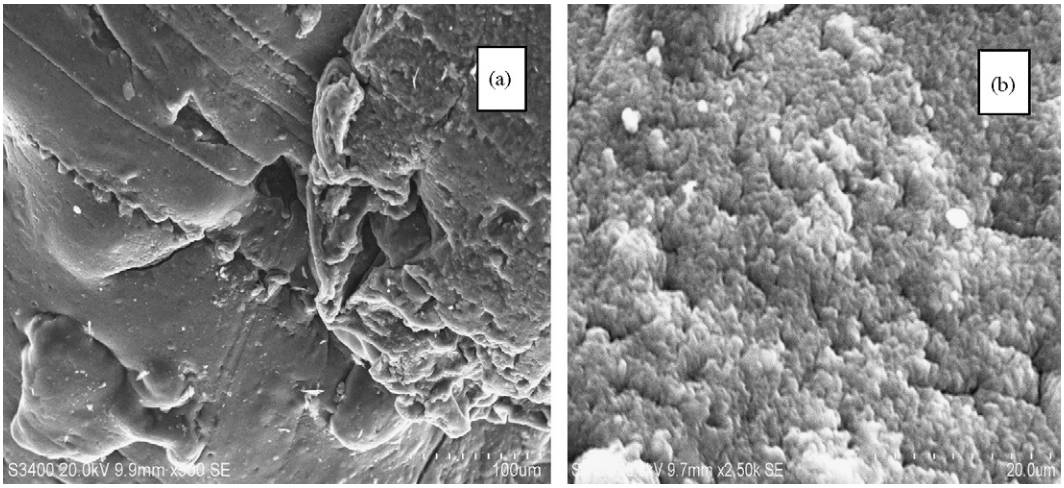

Fig. 2. SEM images of (a) Fe-CCB and (b) fluoride-sorbed Fe-CCB.

3.3. Optimization of sorbent dosage

In order to examine the effect of the dosage on the percentage fluoride removal, studies were conducted with a fixed time, 10 mg/L as initial fluoride concentration at pH 7 in room temperature. The effect of percentage fluoride removal on sorbent dosage is shown in Fig. 3b which demonstrates that there is an increase in percentage fluoride removal with the increase of the dosage of the sorbent as expected [22]. This experiment was carried out to optimize the sorbent dosage to bring down the fluoride level to below 1 ppm

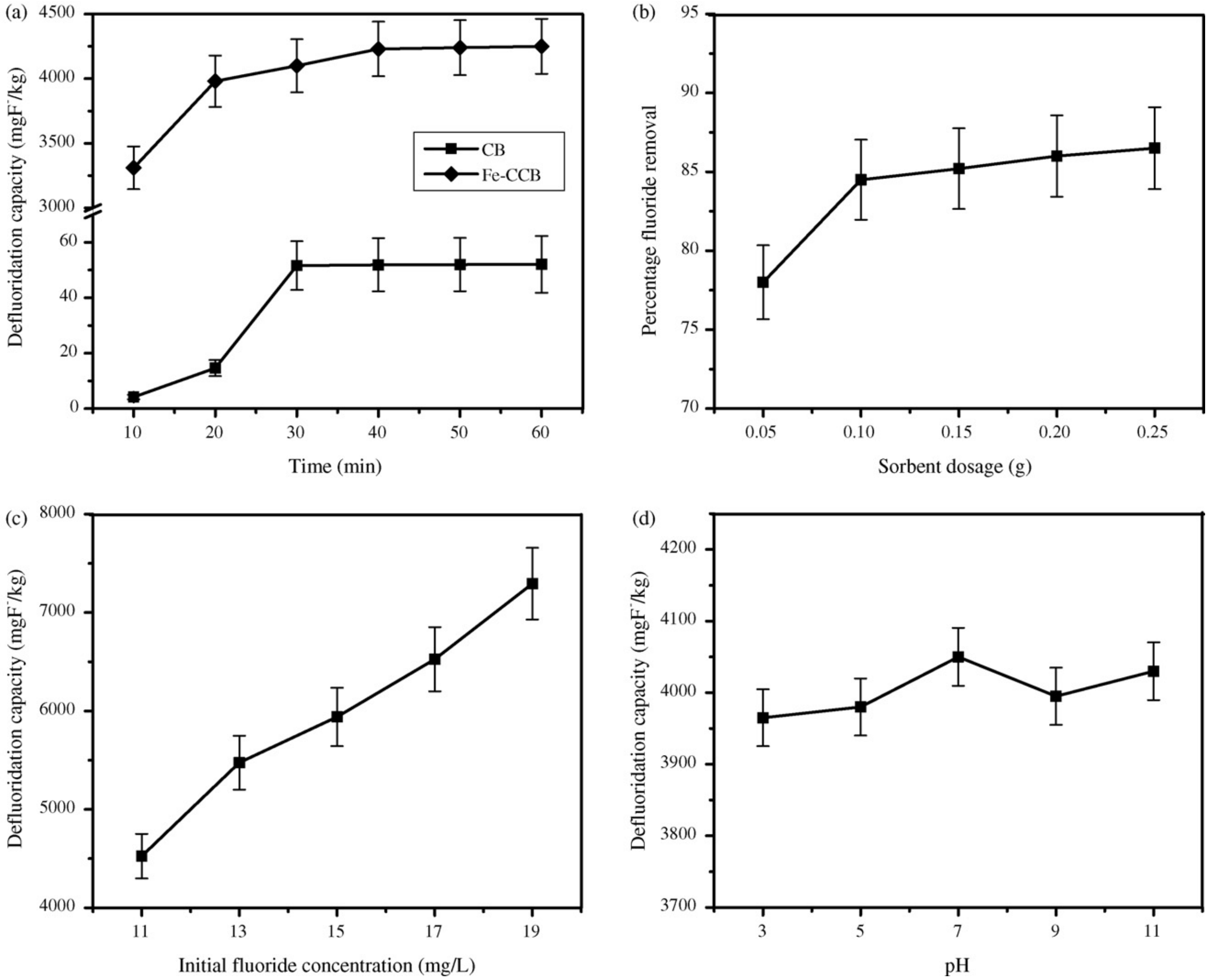

Fig. 3. (a) Effect of contact time on DC of CB and Fe-CCB. (b) Effect of dosage of sorbent on percentage fluoride removal of Fe-CCB. (c) Effect of DC of Fe-CCB with different initial fluoride concentrations. (d) Influence of pH medium on the DC of Fe-CCB.

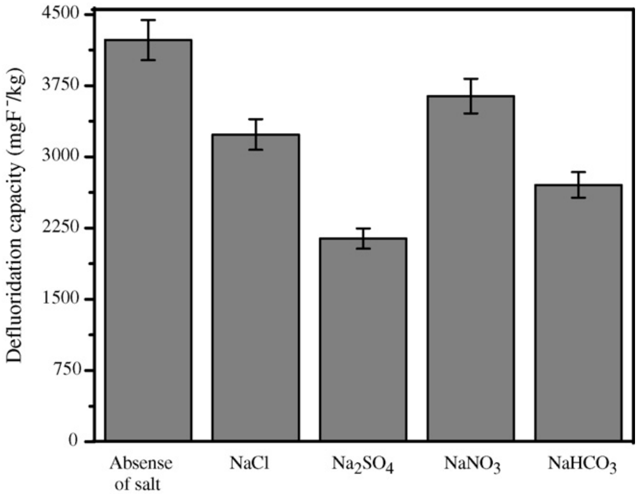

Fig. 4. Effect of coexisting anions on the DC of Fe-CCB.

which is the tolerance limit for fluoride. 0.1 g dosage of the sorbent was found to be the optimum dose and hence in all subsequent experiments the dosage of the sorbent was fixed as 0.1 g.

3.4. *Effect of initial sorbate concentration*

The effect of different initial fluoride concentrations, viz., 11, 13, 15, 17 and 19 mg/L, on DC with neutral pH at 303 K was studied. Fig. 3c shows the influence of varying the initial fluoride concentration on the fluoride removal by the sorbent. It has been found that the DC of beads increases with increasing fluoride concentration. Similar type of result was observed by Lv et al. [23] while using layered double hydroxides for fluoride removal.

3.5. *Influence of pH medium*

The pH is an important variable affecting defluoridation at water–adsorbent interfaces. Therefore the removal of fluoride by the sorbent 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. 3d explains the DC of Fe-CCB as a function of pH. Though it appears that the DC of the sorbent was slightly influenced by pH of the medium, the differences are not so significant and hence it can be concluded that there is no dependence on DC of the sorbent by pH of the medium studied. Hence for further experiments, neutral pH was fixed as the optimum pH.

3.6. *Effect of foreign anions*

Fig. 4 shows the dependence of DC of Fe-CCB in the presence of co-anions like Cl^-, SO_4^{2-}, HCO_3^- and NO_3^- with a fixed initial concentration of 200 mg/L and keeping all other parameters such as time, pH, dosage and initial fluoride concentration as constants. From the graph it is evident that the overall DC of the sorbent was altered by the presence of Cl^-, SO_4^{2-} NO_3^- and HCO_3^- ions and hence a significant reduction in DC was observed and it is obvious that the other ions may also compete with F^- ion during sorption.

3.7. *Sorption isotherms*

To quantify the sorption capacity of Fe-CCB for the removal of fluoride, two commonly used isotherms namely Freundlich and Langmuir have been adopted.

3.7.1. *Freundlich isotherm*

The linear form of Freundlich [24] isotherm is represented by the following equation

$$\log q_e = \log k_F + \frac{1}{n}\log C_e \qquad (1)$$

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 linear plot of $\log q_e$ vs. $\log C_e$ indicates the applicability of Freundlich isotherm. The values of $1/n$ and k_F for the sorbent were calculated from the slope and the intercept of the linear plot of $\log q_e$ vs. $\log C_e$ and are listed in Table 1. The 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. With rise in temperature, the k_F values get increases indicates that the fluoride uptake by Fe-CCB is an endothermic process.

3.7.2. *Langmuir isotherm*

Langmuir [25] isotherm model can be represented in the form of equation

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

where Q^o 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. A linear plot is obtained for the sorbent when C_e/q_e is plotted against C_e which gives Q^o and b values from the slope and intercept, respectively, and the calculated values are listed in Table 1.

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 [26]:

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

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

Table 1
Isotherm and thermodynamic parameters of Fe-CCB

Temperature (K)	Freundlich isotherm					Langmuir isotherm					Thermodynamic parameters		
	$1/n$	n	k_F (mg/g) (L/mg)$^{1/n}$	r	χ^2	Q^o (mg/g)	b (L/g)	R_L	r	χ^2	ΔG^o (kJ mol^{-1})	ΔH^o (kJ mol^{-1})	ΔS^o (kJ mol^{-1} K^{-1})
303	0.648	1.543	2.588	0.998	3.27E−4	15.385	0.175	0.342	0.990	7.16 E−4	−5470.46	17.09	38.43
313	0.591	1.692	2.958	0.998	2.75E−4	13.699	0.239	0.276	0.993	8.20 E−4	−5061.21		
323	0.543	1.842	3.296	0.999	1.73E−5	12.346	0.318	0.223	0.998	3.32 E−4	−4727.04		

Table 2
The parameters of various kinetic models with r and SAE values

Kinetic models	Parameters	303 K				313 K				323 K			
		11 mg/L	13 mg/L	15 mg/L	17 mg/L	11 mg/L	13 mg/L	15 mg/L	17 mg/L	11 mg/L	13 mg/L	15 mg/L	17 mg/L
Pseudo-first-order	k_{ad} (min^{-1})	0.140	0.136	0.145	0.154	0.131	0.127	0.129	0.140	0.147	0.126	0.120	0.122
	r	0.925	0.950	0.979	0.976	0.973	0.940	0.962	0.978	0.975	0.899	0.965	0.961
	SAE	1.05	1.24	1.47	2.31	1.78	1.01	0.73	0.90	1.21	0.91	1.71	1.12
Pseudo-second-order	q_e (mg/g)	6.369	6.623	7.092	7.634	5.525	6.024	6.667	7.407	5.618	5.988	6.536	7.354
	k (g/mg min)	0.009	0.013	0.016	0.019	0.020	0.024	0.027	0.026	0.021	0.029	0.039	0.030
	h (mg/g min)	0.366	0.559	0.825	1.122	0.606	0.875	1.196	1.464	0.648	1.029	1.661	1.647
	r	0.984	0.992	0.996	0.998	0.99	0.993	0.997	0.998	0.992	0.996	0.998	0.999
	SAE	0.54	0.87	0.81	0.58	0.82	0.53	0.41	0.39	0.78	0.42	0.29	0.33
Particle diffusion	k_p (min^{-1})	0.140	0.136	0.152	0.154	0.138	0.128	0.129	0.145	0.155	0.126	0.126	0.127
	r	0.925	0.950	0.976	0.976	0.967	0.940	0.962	0.975	0.970	0.899	0.957	0.956
	SAE	1.82	1.98	1.87	1.92	1.52	1.65	1.72	2.09	1.43	1.58	1.44	1.75
Intraparticle diffusion	k_i (mg/g min$^{0.5}$)	0.737	0.748	0.755	0.746	0.579	0.568	0.565	0.631	0.586	0.525	0.483	0.593
	r	0.972	0.976	0.970	0.978	0.973	0.970	0.991	0.982	0.974	0.974	0.973	0.972
	SAE	0.50	0.96	0.87	0.89	0.77	0.86	0.72	0.77	0.48	0.96	0.84	0.86

3.7.3. Chi-square analysis

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

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

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). If data from the model are similar to the experimental data, χ^2 will be a small number, while if they differ, χ^2 will be a bigger number. Therefore, it is also necessary to analyse the data set using the non-linear chi-square test to confirm the best-fit isotherm for the sorption system [27]. The results of chi-square analysis are presented in Table 1. The lower χ^2 values of Freundlich isotherm can be considered as best fitting model for the sorption of fluoride on Fe-CCB.

3.8. 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 according to Khan and Singh method [28]. The values of thermodynamic parameters are shown in Table 1. The negative values of ΔG° confirm the spontaneous nature of fluoride sorption. The value of ΔH° is positive indicating that the sorption process is endothermic. The positive value of ΔS° which is a measure of randomness at the solid–liquid interface indicates the fluoride sorption is irreversible and stable.

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 [29]. 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 regression correlation coefficient (r) value indicates that the model successfully describes the kinetics of fluoride removal.

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 [30] is given as.

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

where q_t is the amount of fluoride on the surface of the sorbent beads 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. Linear plots of log ($q_e - q_t$) against t gives straight line indicate the applicability of Lagergren equation. The pseudo-first-order model seems to be liable because of the higher correlation coefficient (r).

In addition, the pseudo-second-order model is also widely used. There are four types of linear pseudo-second-order kinetic models [31] the most popular linear form is

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

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 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. 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 of Fe-CCB are presented in Table 2. 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.

3.9.2. Diffusion-based models

For a solid–liquid sorption process, the solute transfer is usually characterized either by particle diffusion or intraparticle diffusion control. Both particle and intraparticle diffusion models were used to describe the fluoride removal by Fe-CCB.

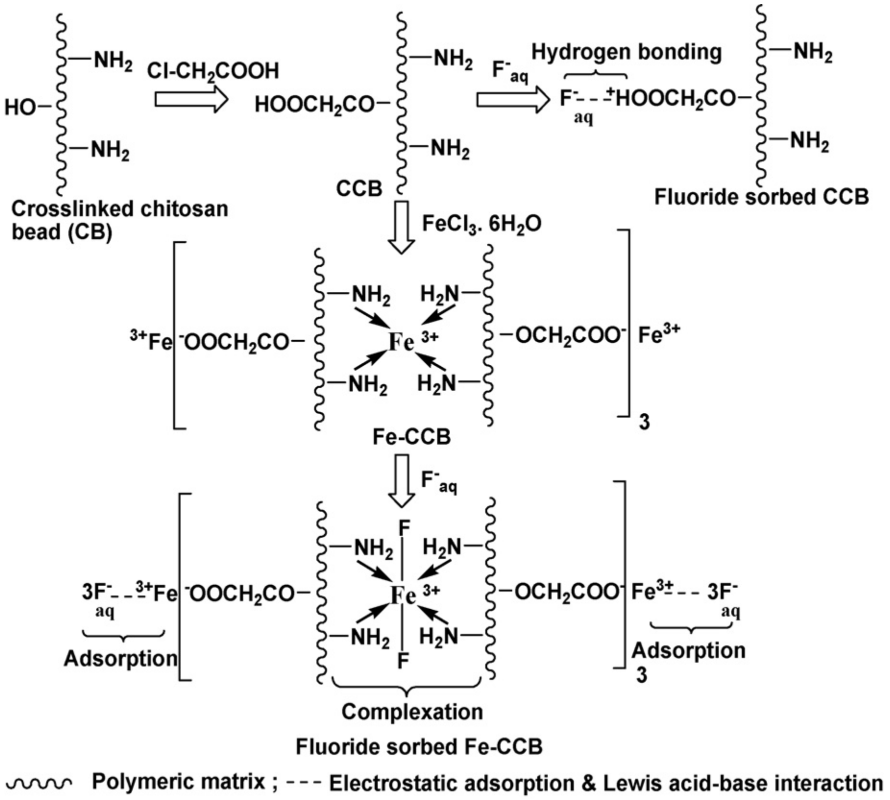

Fig. 5. Mechanism of fluoride sorption by Fe-CCB.

A simple equation for the particle diffusion controlled sorption process [7,32] is given as follows:

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

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.

The intraparticle diffusion model used here refers to the theory proposed by Weber and Morris [33] and its equation is

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

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

The straight line plots of $\ln(1-C_t/C_e)$ vs. t and q_t vs. $t^{1/2}$ indicate the applicability of both particle and intraparticle diffusion models. The k_p, k_i and r values of both particle and intraparticle diffusion models are illustrated in Table 2. The higher r values obtained for both particle and intraparticle diffusion models suggest that the fluoride diffusion on Fe-CCB follows both the models.

3.9.3. The best-fit model

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 [34].

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

where $q_{t,\text{e}}$ and $q_{t,\text{m}}$ are 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 Fe-CCB for all the kinetic models are summarized in Table 2. Smaller SAE values were observed for pseudo-second-order and intraparticle diffusion models indicate that these two models are significant in defining the fluoride sorption process suggesting that the sorption of fluoride onto bead pores of Fe-CCB.

3.10. Sorption mechanism

During carboxylation of cross-linked chitosan bead (CCB), the –COOH group has been introduced in the place of hydroxyl group of the chitosan. Then the amino groups of chitosan have formed a chelated complex with the added Fe^{3+} ion similar to that of Fe^{3+} in hemoglobin, simultaneously there is a possibility of exchange of Fe^{3+} ion for H^+ ion in carboxyl group of CCB also, which contains oxygen atom that can act as an electron pair donor to the Lewis acid (Fe^{3+}). The mechanism of fluoride removal by Fe-CCB is shown in Fig. 5. Both CCB and Fe-CCB remove fluoride by means of electrostatic adsorption. In Fe-CCB, F^- ion is trapped from the solution due to the electrostatic adsorption and strong Lewis acid–base interaction [35]

Table 3
Field trial results of Fe-CCB

Water quality parameters	Before treatment	After treatment
F^- (mg/L)	4.13	1.08
pH	9.60	8.69
Cl^- (mg/L)	85.20	81.20
Total hardness (mg/L)	140.00	120.00
Total dissolved solids (mg/L)	1350.00	1125.00
Na^+ (mg/L)	173.00	171.00
K^+ (mg/L)	23.00	22.00

whereas CCB removes fluoride by H-bonding and thus both the sorbents remove fluoride by means of electrostatic adsorption. Simultaneously, the Fe(III)-chelated amino groups (Fe-CCB) also form a complex with fluoride. Therefore Fe-CCB removes fluoride by complexation in addition to adsorption and hence it shows an enhanced DC than the CCB which in turn higher than raw chitosan bead. Though the presence of co-ions alters the overall DC of the sorbent, fluoride seems to be selective as it is the hardest Lewis base among all other anions.

3.11. Field trial

The sorbent used in this study was also tested with field sample taken in a nearby fluoride-endemic village. About 0.25 g of sorbent was added to 50 ml of fluoride water sample and the contents were shaken with constant time at room temperature. These results are presented in Table 3. There is also a significant reduction in the levels of other water quality parameters in addition to fluoride. It is noted from the result that the sorbent can be effectively employed for fluoride removal.

4. Conclusions

In conclusion, Fe-CCB possesses extremely higher DC than raw chitosan. The DC of the sorbent is independent of pH of the medium and is slightly affected in the presence of co-anions. The sorption process follows Freundlich isotherm. The values of thermodynamic parameters indicate that the nature of fluoride removal process is spontaneous and endothermic. The kinetics of Fe-CCB follows pseudo-second-order and intraparticle diffusion models. The results of field trial indicate that the sorbent can be effectively used to remove the fluoride from water.

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References

[1] M. Lakshmi Vani, K.R. Pratap, Fluoride 33 (2000) 17–26.
[2] B. Spittle, Fluoride 31 (1998) 89–90.
[3] A. Sharma, N.J. Chinoy, Fluoride 31 (1998) S26.
[4] WHO Report, Fluoride and Fluorides: Environmental Health Criteria, World Health Organisation, 1984.
[5] C.J. Huang, J.C. Liu, Water Res. 33 (1999) 3403–3412.
[6] K.M. Popat, P.S. Anand, B.D. Dasare, React. Polym. 23 (1994) 23–32.
[7] S. Meenakshi, N. Viswanathan, J. Colloid Interface Sci. 308 (2007) 438–450.
[8] Z. Amor, B. Bariou, N. Mameri, M. Taky, S. Nicolas, A. Elmidaoui, Desalination 133 (2001) 215–223.
[9] S. Meenakshi, Ph.D. Thesis, Gandhigram, Tamilnadu, India, 1992.
[10] Y.H. Li, S. Wang, X. Zhang, J. Wei, C. Xu, Z. Luan, D. Wu, Mater. Res. Bull. 38 (2003) 469–476.
[11] M.S. Onyango, Y. Kojima, O. Aoyi, E.C. Bernardo, H. Matsuda, J. Colloid Interface Sci. 279 (2004) 341–350.
[12] S. Meenakshi, C. Sairam Sundaram, Rugmini Sukumar, J. Hazard. Mater. 153 (2008) 164–172.
[13] F. Luo, K. Inoue, Solvent Extr. Ion Exc. 22 (2004) 305–322.
[14] E. Guibal, I. Saucedo, M. Jansson-Charrier, B. Delanghe, P. Le Cloirec, Water Sci. Technol. 30 (1994) 183–190.
[15] C. Jeon, W.H. Höll, Water Res. 37 (2003) 4770–4780.
[16] APHA, Standard Methods for the Examination of Water and Waste Water, American Public Health Association, Washington, DC, 2005.
[17] M.V. Lopez-Ramon, F. Stoeckli, C. Moreno-Castilla, F. Carrasco-Marin, Carbon 37 (1999) 1215–1221.
[18] R.B. Hernandez, A.P. Franco, O.R. Yola, A. Lopez-Delgado, J. Felcman, M.A.L. Recio, A.L.R. Merce, J. Mol. Struct. 877 (2008) 89–99.
[19] Y. Nakano, K. Takeshita, T. Tsutsumi, Water Res. 35 (2001) 496–500.
[20] D. Zhou, L. Zhang, S. Guo, Water Res. 39 (2005) 3755–3762.
[21] Y.S. Al-Degs, M.I. El-Barghouthi, A.A. Issa, M.A. Khraisheh, G.M. Walker, Water Res. 40 (2006) 2645–2658.
[22] A. Mellah, S. Chegrouche, Water Res. 31 (1997) 621–629.
[23] L. Lv, J. He, M. Wei, D.G. Evans, Z. Zhou, Water Res. 41 (2007) 1534–1542.
[24] H.M.F. Freundlich, Z. Phys. Chem. 57A (1906) 385–470.
[25] I. Langmuir, J. Am. Chem. Soc. 38 (1916) 2221–2295.
[26] T.W. Weber, R.K. Chakravorti, J. Am. Inst. Chem. Eng. 20 (1974) 228–238.
[27] Y.S. Ho, Carbon 42 (2004) 2115–2116.
[28] A.A. Khan, R.P. Singh, Colloid Surf. 24 (1987) 33–42.
[29] Y.S. Ho, J.C.Y. Ng, G. McKay, Sep. Purif. Methods 29 (2000) 189–232.
[30] S. Lagergren, K. Sven, Vetenskapsakad. Handl. 24 (1898) 1–39.
[31] Y.S. Ho, Water Res. 40 (2006) 119–125.
[32] M. Chanda, K.F. O'Driscoll, G.L. Rempel, React. Polym. 1 (1983) 281–293.
[33] W.J. Weber, J.C. Morris, J. Sanitary Eng. Div. 90 (1964) 79–91.
[34] S. Kundu, A.K. Gupta, Chem. Eng. J. 122 (2006) 93–106.
[35] A. Dabrowski, Z. Hubicki, P. Podkoscielny, E. Robens, Chemosphere 56 (2004) 91–106.