Enhanced and Selective Fluoride Sorption on Ce(III) Encapsulated Chitosan Polymeric Matrix

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ABSTRACT: Chitosan beads (CB) possesses low defluoridation capacity (DC) have been suitably modified by carboxylation followed by chelation with Ce(III) to enhance its DC. The carboxylated chitosan beads (CCB), which has a desirable DC of 1385 mgF$^-$/kg, has been further chemically modified by incorporating Ce^{3+} ion into CCB (Ce-CCB) and its DC was found to be 4798 mgF$^-$/kg, whereas raw chitosan beads (CB) possesses 52 mgF$^-$/kg only. The maximum DC of Ce-CCB was observed at pH 7 and showed selectivity toward fluoride in presence of other coanions. The sorbent was characterized using FTIR and SEM with EDAX analysis. The sorption data was fitted with Freundlich and Langmuir isotherms and kinetic models. The calculated thermodynamic parameters, viz., $\Delta G°$, $\Delta H°$ and $\Delta S°$ indicate the nature of fluoride sorption. A field trial was carried out with fluoride water collected from a nearby fluoride-endemic village to test the suitability of Ce-CCB at field conditions. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 1114–1121, 2009

Key words: adsorption; chitosan; fluoride; isotherms; kinetics

INTRODUCTION

Fluoride, a potent toxic ion, enters the soil and so as to water by natural as well as anthropogenic sources. An excess amount of fluoride ion in drinking water has been known to cause adverse effects on human health.[1] The World Health Organization has specified the tolerance limit for fluoride content in drinking water as 1.5 mg/L.[2] Fluorosis is a chronic disease manifested by mottling of teeth in mild cases and softening of bones, ossification of tendons and ligaments, and neurological damage in severe cases. Fluorosis is prevalent in the areas where people are mostly dependent on naturally occurring groundwater for potable use. 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.

Many methods have been successfully proposed for removing excessive fluoride in water which includes chemical precipitation, ion exchange, adsorption, and electrolysis.[3–6] Among the methods reported, adsorption seems to be the most attractive, selective, and promising technique for fluoride removal. So far,

many adsorbents have been successfully used for the removal of fluoride which includes activated alumina,[1] magnesia,[7] cotton cellulose,[8] hydroxyapatite,[9] zeolite,[10] composite,[11] clay,[12] etc. Recently, considerable work has been conducted in developing new adsorbents loaded with metal ions especially with rare earth metals, viz., La^{3+}, Ce^{3+} ions, etc., for the purpose of fluoride removal.[13] Chitosan is a biopolymer produced from the deacetylation of chitin. The high proportion of amine groups in chitosan has novel binding properties for metal ions and has been extensively studied for heavy metal removal.[14,15] Only few reports are available about its capacity to remove anions.[16,17] To increase its defluoridation capacity (DC), it has been suitably modified by introducing selective functional groups in the chitosan polymeric matrix.

In this study to enhance the DC of chitosan, it was treated with chloroacetic acid, to introduce carboxyl groups in hydroxyl groups of chitosan beads, followed by Ce (III) incorporation by chelating the reactive amine groups of chitosan. A comparison of DC of Ce (III)-loaded carboxylated chitosan beads (Ce-CCB) with that of CCB and CB was made. Defluoridation study was carried out under various equilibrating conditions like contact time, pH, and in the presence of competitor coanions. The reasonable mechanism of fluoride removal by this sorbent was also suggested. The experimental data were fitted with isotherms and the kinetic models. The sorbent was tested with a field sample collected from a nearby fluoride-endemic village for its suitability under field conditions.

EXPERIMENTAL

Materials

Chitosan (85% deacetylated) was supplied by Pelican Biotech and Chemicals Labs, Kerala (India). The viscosity of the chitosan solution was determined to be 700 (mPa·s) by Brookfield Dial Reading Viscometer using electronic drive-RVT model (USA) and this viscosity of chitosan solution was maintained as constant for the beads preparation. NaF, NaOH, HCl, glacial acetic acid, glutaraldehyde, chloroacetic acid, $Ce(NO_3)_3.6H_2O$, and all other chemicals and reagents used were of analytical grade. All the solutions were prepared using double distilled water. For the field study, water containing fluoride was collected from a nearby fluoride endemic village.

Synthesis of Ce (III)-loaded carboxylated chitosan beads

Chitosan beads (CB) were prepared and cross-linked with glutaraldehyde as suggested by Jeon and Holl.[14] The CCB was prepared by treating the wet CB with aqueous $0.5M$ chloroacetic acid maintained at pH 8.0 using $0.1M$ NaOH for 10 h at room temperature to convert hydroxyl groups of chitosan to carboxyl groups. The CCB was washed with distilled water to pH 7 and then dried at room temperature. To effectively utilize the reactive amino groups of chitosan beads for fluoride sorption, the amine groups in CCB were chelated using Ce(III) by treating CCB with 5% (w/v) $Ce(NO_3)_3.6H_2O$ solution for 24 h and then washed in distilled water to pH 7 and then dried at room temperature. The dried beads were used for sorption studies.

Sorption experiments

Defluoridation experiments were carried out by batch equilibration method in duplicate. 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 at room temperature. 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 different temperatures, viz., 303, 313, and 323 K on sorption 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 pH 7. The solution was then filtered and the residual fluoride ion concentration was measured.

Analysis

The concentration of fluoride was measured using expandable ion analyzer EA 940 and the fluoride ion selective electrode BN 9609 with the relative accuracy of ±1 significant digit (Orion, MI). Most of the cations and anions do not interfere with the response of the fluoride electrode to fluoride.[18] The pH measurements were carried out with the same instrument with pH electrode. All other water quality parameters were analyzed by using standard methods.[19] The pH at zero point charge (pH_{zpc}) of the sorbent was measured using the pH drift method.[20]

Scanning electron microscope (SEM) images were recorded with HITACHI-S-3400 model fitted with an energy dispersive X-ray analyzer (EDAX) allows a qualitative detection and localization of elements in the beads. The X-ray elemental mapping represents the distribution of a specific element on a micrograph.

FTIR spectra of the beads were recorded with JASCO-460 plus model using KBr pellets prepared by mixing beads with KBr. The results of FTIR were used to confirm the functional groups present in the beads.

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

RESULTS AND DISCUSSION

Effect of contact time

The effect of contact time of sorbents was studied in the range of 10–60 min with 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. Figure 1 shows the variation of DC of sorbents with time and indicates that the DC of
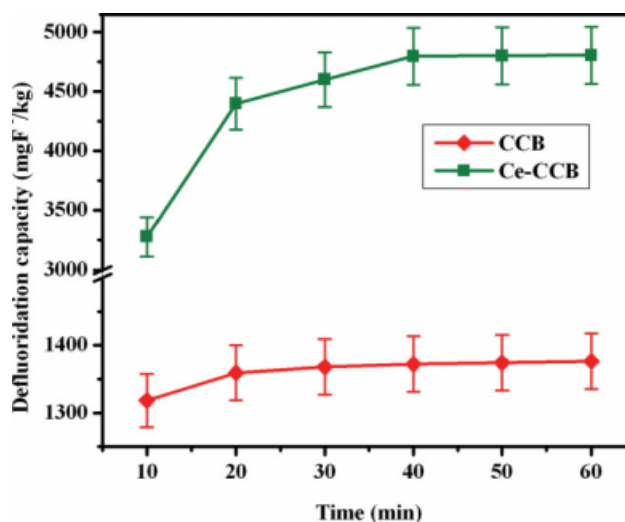

Figure 1 Effect of contact time on the DC of sorbents. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

both CCB and Ce-CCB increases with increasing time and finally reached saturation. All the sorbents reached saturation after 40 min and hence, it was fixed as contact time for subsequent measurements. The DC of Ce-CCB was found to be 4798 mgF^-/kg, whereas for CCB and raw CB it was 1385 and 52 mgF^-/kg (not shown in Fig. 1), respectively. Therefore, further studies were limited to Ce-CCB only.

Effect of pH

The fluoride removal by Ce-CCB was studied at five different pH levels, viz., 3, 5, 7, 9, and 11 by keeping other parameters as constant. The DC of sorbent as a function of pH was shown in Figure 2. 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.

Influence of coexisting anions

The contaminated water may contain the other anions like Cl^-, SO_4^{2-}, HCO_3^-, and NO_3^- in addition to fluoride. To study the interfering role of other common anions, the sorption studies were carried out in the presence of Cl^-, SO_4^{2-}, HCO_3^-, and NO_3^- separately with a fixed initial concentration of 200 mg/L by keeping all other parameters as constant. Figure 3 shows the effect of DC of Ce-CCB in the presence of coanions. It is evident from the graph that the overall DC of the sorbent was not significantly altered by the
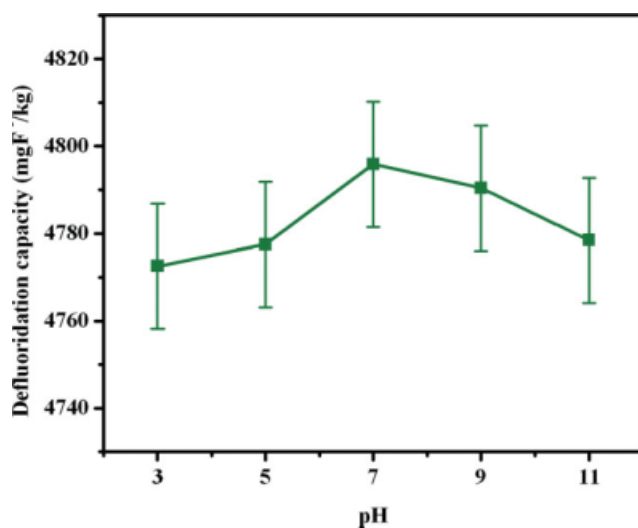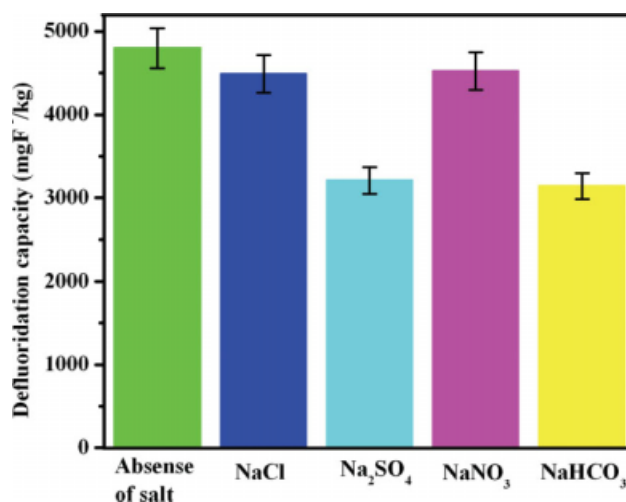

Figure 3 Effect of foreign anions on DC of Ce-CCB. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

presence of coexisting anions which indicates the selectivity of fluoride by the sorbent.

Characterization of sorbents

Figure 4(a,b) represent the FTIR spectra of Ce-CCB and fluoride-sorbed Ce-CCB. A sharp band at 1630 cm^{-1} confirms the presence of carbonyl group in Ce-CCB. The presence of —OH group is confirmed by having a band at 3420 cm^{-1}. The slight broadening of band at 3420 cm^{-1} in the fluoride-sorbed Ce-CCB may be taken as an indicative of electrostatic adsorption between the sorbent and the fluoride.[21,22]

Figure 2 Influence of pH on DC of Ce-CCB. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
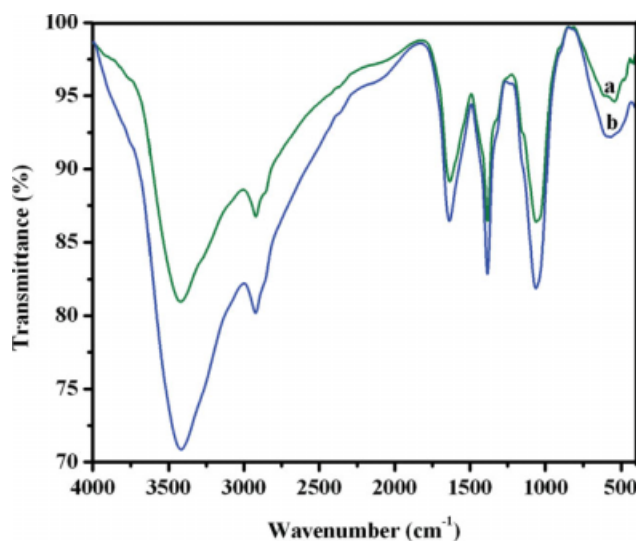

Figure 4 FTIR spectra of (a) Ce-CCB and (b) Fluoride treated Ce-CCB. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
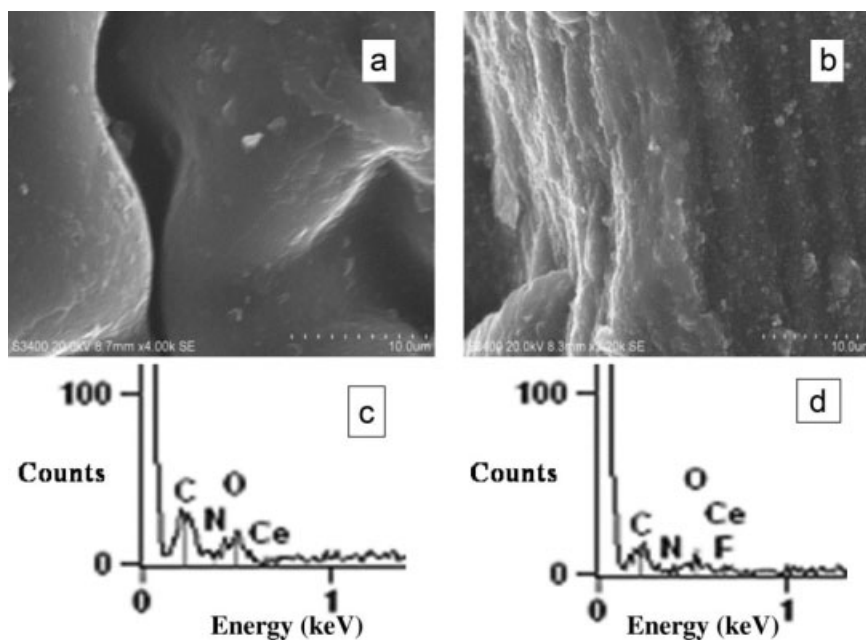
Figure 5 SEM pictures of (a) Fresh Ce-CCB and (b) Fluoride-sorbed Ce-CCB. EDAX spectra of (c) Fresh Ce-CCB and (d) Fluoride-sorbed Ce-CCB.

SEM images of Ce-CCB and fluoride-sorbed CCB are shown in Figure 5(a,b), respectively. Fresh Ce-CCB has many pores on the surface of the bead. Figure 5(b) shows that there is a mass transfer of fluoride ions onto the sorbent surface of fluoride-sorbed Ce-CCB. It means reduction of pores which was thought as mainly due to sorption of fluoride onto the sorbent. This is further supported by EDAX analysis. The EDAX spectra of Ce-CCB confirm the presence of respective ions in their corresponding beads [cf. Fig. 5(c)]. The fluoride sorption on Ce-CCB was confirmed by the presence of fluoride peak in EDAX spectra of fluoride-treated Ce-CCB [cf. Fig. 5(d)].

The surface morphological change of chitosan beads was confirmed by the shifting of pH_{zpc} values.[23] The pH_{zpc} of CB is 7.88 was shifted to 3.90 for Ce-CCB which clearly indicates the occurrence of structural changes in Ce-CCB.

Sorption isotherms

To quantify the sorption capacity of Ce-CCB studied for the removal of fluoride, two common isotherms, viz., Freundlich and Langmuir have been adopted.

Freundlich isotherm

The linear form of Freundlich isotherm[24] 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 sorption capacity, and $1/n$ is the sorption intensity are listed in Table I. The linear plot of $\log q_e$ versus $\log C_e$ 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 favorable conditions for sorption. With rise in temperature, the k_F values get increases indicates that the fluoride uptake by Ce-CCB is an endothermic process.

TABLE I
Isotherm Parameters of Ce-CCB

| Temp (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
303	0.306	3.268	5.224	0.972	6.22 E-3	9.009	1.306	0.065	0.985	1.29 E-2
313	0.272	3.676	5.768	0.981	3.81 E-3	8.850	1.915	0.045	0.992	1.14 E-2
323	0.279	3.584	6.383	0.999	2.92 E-5	9.091	2.558	0.034	0.998	2.21 E-3

Langmuir isotherm

Langmuir isotherm[25] 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 sorbate 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 sorption. A linear plot is obtained for the sorbent when C_e/q_e is plotted against C_e which gives Q° and b values from the slope and intercept, respectively, and the calculated results are listed in Table I. There is no significant increase in the values of Q° with increase in temperature which estimates that sorption capacity of the sorbent is high at lower temperature.[5]

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,[26] R_L

$$R_L = \frac{1}{1 + bC_0} \qquad (3)$$

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

Chi-square analysis

To identify a suitable isotherm model for the sorption of fluoride on Ce-CCB, this analysis has been carried out.[5,9] The equivalent mathematical statement is given as follows,

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

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, whereas if they differ, χ^2 will be a bigger number. The results of chi-square analysis are presented in Table I. The lower χ^2 values of Freundlich isotherm indicate that it is the best fitting isotherm for the sorption of fluoride onto Ce-CCB.

Thermodynamic treatment of the sorption process

Thermodynamic parameters associated with the sorption, viz., standard free energy change (ΔG°), standard enthalpy change (ΔH°), and standard entropy change (ΔS°) were calculated as follows.

The free energy change of sorption process, considering the sorption equilibrium coefficient K_o, is given by the equation,

$$\Delta G^\circ = -RT \ln K_o \qquad (5)$$

where, ΔG° is the standard free energy of sorption (kJ/mol), T is the temperature in Kelvin, and R is the universal gas constant (8.314 J mol^{-1} K^{-1}). The sorption distribution coefficient K_o, was determined from the slope of the plot ln (q_e/C_e) against C_e at different temperatures and extrapolating to zero C_e according to the method suggested by Khan and Singh.[27]

Other thermodynamic parameters such as ΔH° and ΔS° are evaluated using van't Hoff equation,[5,9]

$$\ln K_o = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \qquad (6)$$

where, ΔH° is the standard enthalpy change (kJ/mol) and ΔS° is standard entropy change (kJ/mol. K). The values of ΔH° and ΔS° can be obtained from the slope and intercept of a plot of ln K_o against $1/T$.

The calculated values of thermodynamic parameters are shown in Table II. The negative values of ΔG° confirm the feasibility and spontaneous nature of fluoride sorption. The positive value of ΔH° and ΔS° indicates the sorption process is endothermic and stable.

Sorption dynamics

The two main types of sorption kinetic models namely reaction-based and diffusion-based models were adopted to fit the experimental data.

Reaction-based models

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

A simple pseudo-first-order kinetic model[28] is given as follows,

$$\log(q_e - q_t) = \log q_e - \frac{k_{ad}}{2.303} t \qquad (7)$$

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

TABLE II
Thermodynamic Parameters of Ce-CCB

Temp. (K)	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (kJ mol^{-1}K^{-1})
303	−1.39	14.1	41.6
313	−1.20		
323	−0.57		

TABLE III
Kinetic Parameters of Ce-CCB with r and sd Values at Different Temperatures with Different Initial Fluoride Concentrations

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})	0.152	0.124	0.140	0.143	0.127	0.150	0.140	0.154	0.140	0.189	0.136	0.145
	r	0.989	0.961	0.978	0.933	0.983	0.981	0.974	0.955	0.991	0.968	0.976	0.974
	sd	0.127	0.208	0.173	0.318	0.107	0.283	0.173	0.194	0.137	0.171	0.186	0.276
Pseudo-second-order	q_e (mg/g)	5.814	6.667	7.874	9.346	5.682	6.666	7.752	8.696	5.650	6.711	7.576	8.403
	k (g/mg min)	0.033	0.022	0.015	0.009	0.048	0.031	0.021	0.016	0.060	0.040	0.032	0.028
	h (mg/g min)	1.104	0.993	0.946	0.798	1.541	1.364	1.248	1.225	1.901	1.821	1.848	1.969
	r	0.998	0.999	0.997	0.993	0.999	0.999	0.998	0.998	0.999	0.999	0.999	0.998
	sd	0.121	0.096	0.138	0.173	0.067	0.092	0.080	0.096	0.049	0.055	0.073	0.074
Particle diffusion	k_p (min^{-1})	0.161	0.130	0.146	0.143	0.135	0.157	0.146	0.155	0.140	0.165	0.136	0.152
	r	0.989	0.952	0.972	0.933	0.974	0.980	0.967	0.955	0.991	0.982	0.976	0.970
	sd	0.319	0.557	0.467	0.733	0.416	0.426	0.513	0.635	0.245	0.423	0.399	0.506
Intraparticle diffusion	k_i (mg/g min$^{0.5}$)	0.532	0.668	0.836	1.030	0.437	0.580	0.743	0.866	0.396	0.513	0.592	0.683
	r	0.964	0.970	0.970	0.989	0.956	0.968	0.975	0.979	0.944	0.960	0.969	0.961
	sd	0.222	0.252	0.318	0.228	0.204	0.229	0.258	0.273	0.210	0.227	0.229	0.297

(min^{-1}). The slope of the straight-line plot of log ($q_e - q_t$) against t for different experimental conditions give the value of the rate constant (k_{ad}) and are given in Table III. 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,[29] the most popular linear form is given as follows,

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e} \qquad (8)$$

where, $q_t = \frac{q_e^2 kt}{1 + q_e kt}$, 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 ion 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 versus t for fluoride sorption at different temperatures, viz., 303, 313, and 323 K of Ce-CCB are presented in Table III. The plot of t/q_t versus 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.

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 Ce-CCB.

A simple equation for the particle diffusion controlled sorption process[30] is given as follows,

$$\ln\left(1 - \frac{C_t}{C_e}\right) = -k_p t \qquad (9)$$

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 $t^{0.5}$.

The intraparticle diffusion model used here refers to the theory proposed by Weber and Morris[31] and its equation is given as follows,

$$q_t = k_i t^{1/2} \qquad (10)$$

where, k_i is the intraparticle rate constant (mg/g min$^{0.5}$). The slope of the plot of q_t against $t^{0.5}$ will give the value of intraparticle rate constant.
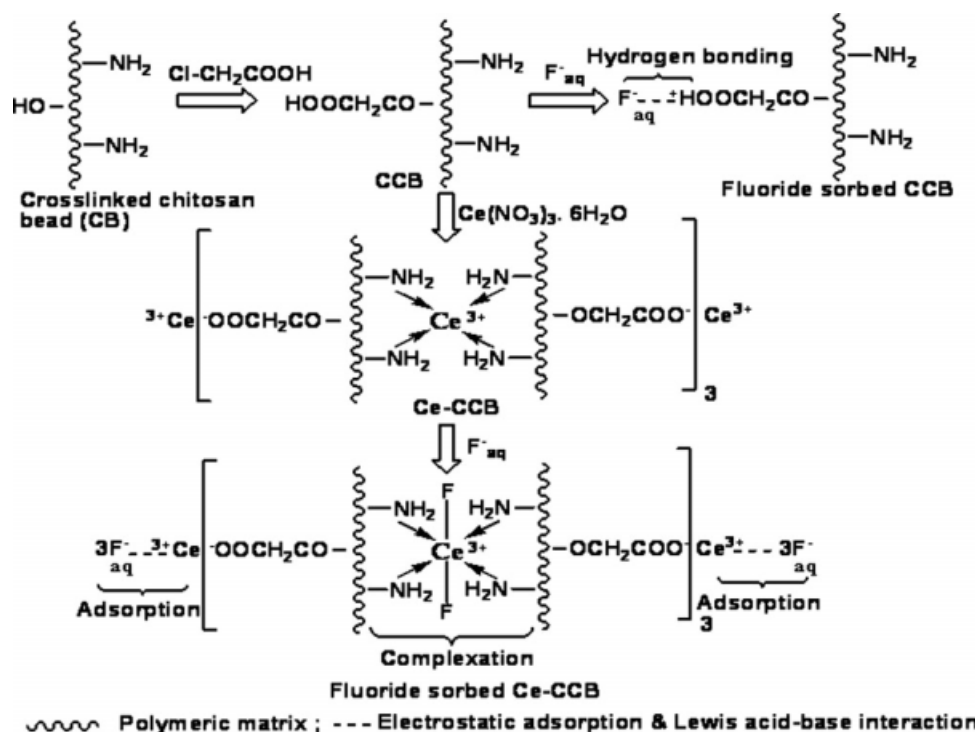
Figure 6 Mechanism of fluoride sorption.

The straight line plots of ln $(1-C_t/C_e)$ versus t and q_t versus $t^{0.5}$ indicates 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 III. The higher r values obtained for both particle and intraparticle diffusion models suggest that the fluoride diffusion on Ce-CCB follows both the models.

Standard deviation (sd) values of all the kinetic models were summarized in Table III. Smaller sd values were observed for pseudo-second-order (reaction-based) and intraparticle diffusion (diffusion-based) models indicate that these two models are significant in defining the fluoride sorption process and suggesting that the sorption of fluoride occurs on internal diffusion of the sorbent.

Mechanism of fluoride removal

During carboxylation of cross-linked chitosan bead, the —COOH group has been introduced in the place of hydroxyl group of the chitosan. Then, the reactive amino groups of chitosan have formed a chelated complex with the added Ce^{3+} ion, simultaneously there is a possibility of exchange of Ce^{3+} ion for H^+ ion in carboxyl group of CCB. The possible mechanism of fluoride removal by Ce-CCB is shown in Figure 6. Both CCB and Ce-CCB removes fluoride by means of electrostatic adsorption and strong Lewis acid-base interaction.[32,33] In case of Ce-CCB, F^- ion is trapped from the solution due to electro-static adsorption, whereas CCB removes fluoride by hydrogen bonding. Simultaneously, Ce(III)-chelated amino groups (Ce-CCB) also form a complex with fluoride. Therefore, Ce-CCB removes fluoride by complexation in addition to adsorption and hence, it shows an enhanced DC than the CCB which in turn is higher than raw chitosan bead. In presence of coions, Ce-CCB shows a higher promising DC confirms, its selectivity toward fluoride as fluoride is the hardest Lewis base among other anions studied.

Field applications

Ce-CCB was also tested with a field sample taken from a nearby fluoride-endemic village. About 0.25 g of the sorbent was added to 50 mL of fluoride water sample and the contents were shaken for 30 min at room temperature and the results are presented in Table IV. In addition to fluoride, there is a

TABLE IV
Field Trial Results of Ce-CCB

Water quality parameters	Before treatment	After treatment
F^- (mg/L)	4.130	0.27
pH	9.60	7.60
Cl^- (mg/L)	85.2	82.0
Total hardness (mg/L)	140.0	90.0
Total dissolved solids (mg/L)	1350.0	1250.0
Na^+ (mg/L)	173.0	130.0
K^+ (mg/L)	23.0	6.0

significant reduction in the levels of other water quality parameters. It is evident from the result that Ce-CCB could be effectively employed as promising defluoridating agent.

CONCLUSIONS

Ce-CCB possesses higher DC than CCB and raw chitosan bead. Fluoride removal by the sorbent is independent of pH of the medium and not affected in the presence of coanions. Ce-CCB removes fluoride by both adsorption and complexation mechanism. The fluoride sorption process follows Freundlich isotherm. The values of thermodynamic parameters indicate that the nature of fluoride sorption is spontaneous and endothermic. The kinetics of Ce-CCB follows pseudo-second-order and particle diffusion models. The results of field trial indicate that Ce-CCB could be effectively employed as promising defluoridating agent.

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