Development of multifunctional chitosan beads for fluoride removal

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ABSTRACT

Chitosan beads (CB) which have negligible defluoridation capacity (DC) have been chemically modified by introducing multifunctional groups, viz., NH_3^+ and COOH groups by means of protonation and carboxylation in order to utilize both amine and hydroxyl groups for fluoride removal. The protonated cum carboxylated chitosan beads (PCCB) showed a maximum DC of 1800 mg F^-/kg whereas raw chitosan beads displayed only 52 mg F^-/kg. Sorption process was found to be independent of pH and slightly influenced in the presence of other common anions. The fluoride sorption on modified forms was reasonably explained by Freundlich and Langmuir isotherms. The sorbents were characterised by FTIR and SEM with EDAX analysis. The sorption process follows pseudo-second-order and intraparticle diffusion kinetic models. The suitability of PCCB has been tested with field sample collected from a nearby fluoride endemic area.

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1. Introduction

Fluoride in drinking water resembles a two-edged sword. The presence of a large amount of fluoride induces dental and skeletal fluorosis (>1.5 mg/L) and an inadequate amount results in dental caries (<1.0 mg/L). The World Health Organisation has specified the tolerance limit of fluoride content of drinking water as 1.5 mg/L [1,2]. Fluoride normally enters the environment and human body through water, food, industrial exposure, drugs, cosmetics, etc. However, drinking water is the single major source of daily intake [3]. A number of methods, viz., adsorption [4,5], chemical precipitation [6], ion-exchange [7], reverse osmosis [8], nano-filtration [9], electrodialysis [10] and Donnan dialysis [11] have been attempted for water defluoridation. Among the methods reported adsorption seems to be the effective and promising technique for selective fluoride removal. But the efficiency of adsorption technique depends upon the nature of adsorbents. Some of the adsorbents, viz., activated alumina [4], polymeric resins [5], modified cellulose [12], activated carbon [13], clay [14,15], hydroxyapatite [16], composites [17,18], metal loaded sorbents [19,20], hydrotalcite [21], etc., have been successfully employed for fluoride removal.

Nowadays biosorption is a promising technique to remove toxic ions present in water [12,22,23]. Chitosan produced from N-deacetylation of chitin is normally recognized as a sorbent for removing cations and extensively studied for heavy metal removal [24]. Only a few reports are available about its capacity to remove fluoride [25–28]. In sorption process, chitosan is often used in the form of flakes or powder which is less stable and causes a significant pressure drop which would affect filtration during field applications. The DC of the unmodified chitosan was found to be minimum. These disadvantages outweigh its advantages of biodegradability and indigenous. If chitosan has been suitably modified into a form which could overcome the above mentioned challenges, then definitely it would throw more light on the field of defluoridation. Hence, in the present study, chitosan has been employed for the removal of fluoride from drinking water.

The present investigation aims at the development of cross-linked chitosan beads for fluoride sorption which are stable and can be regenerated and reused in subsequent operations and also avoid pressure drop during field applications. However, the enhanced DC could be achieved only after suitable chemical modifications as the chitosan possesses a minimum DC. Hence, in order to effectively utilize the amine and hydroxyl groups of chitosan they have been modified into H^+ form so that the DC of the chitosan could be significantly increased. A comparative evaluation of the DC of chitosan beads and the modified forms were made. Suitability of PCCB was tested under field conditions.

2. Materials and methods

2.1. 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 make). The
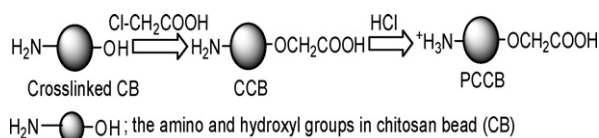
Scheme 1. Synthesis of PCCB.

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 and all other chemicals and reagents used were of analytical grade. For the field study, water containing fluoride was collected from a nearby fluoride endemic village.

2.2. Preparation of protonated cum carboxylated cross-linked chitosan beads (PCCB)

Chitosan beads were prepared and cross-linked with glutaraldehyde as previously reported by authors [26]. For sorption studies three kinds of chemically modified beads, viz., protonated chitosan beads (PCB), carboxylated chitosan beads (CCB) and PCCB were prepared separately. The PCB was prepared in order to effectively utilize the amino groups of cross-linked chitosan beads for fluoride sorption [26]. The CCB was prepared as suggested by Jeon and Höll [29] to make use of the hydroxyl groups of chitosan beads. Finally, the multifunctional chitosan beads, viz., PCCB was prepared by both carboxylation followed by protonation in order to convert the respective –OH and –NH$_2$ groups into H$^+$ form as follows. The wet cross-linked chitosan beads were treated with aqueous 0.5 M chloroacetic acid maintained at pH 8.0 using 0.1 M NaOH for 10 h at room temperature to convert hydroxyl groups of chitosan to carboxyl groups. The CCB was washed with distilled water to remove unreacted acid groups. Then CCB was treated with con. HCl with continuous stirring for 30 min for protonation (PCCB) and the possible reaction is shown in Scheme 1. The PCCB beads were washed with distilled water to neutral pH, dried at room temperature and used for sorption studies.

2.3. Sorption experiments

All experiments were performed by the batch equilibration method in duplicate. The sorbents used in this study were sieved to obtain uniform particle size of 0.6–1.2 mm. About 0.25 g of dry sorbent was added into 50 mL of 10 mg/L sodium fluoride solution with a desired pH value. The pH of the medium was adjusted with 0.1 M HCl or 0.1 M NaOH. The mixture was shaken in a shaker with a speed of 200 rpm at room temperature. Samples were taken at predetermined time intervals for the analysis of fluoride concentrations in the solutions until sorption equilibrium was reached. The DC of the sorbents was studied at different conditions, viz., contact time, pH of the medium and the effect of competitor anions on defluoridation. The fluoride sorption on the sorbent was studied at different initial fluoride concentrations, viz., 11, 13, 15 and 17 mg/L of 50 mL solution and in the temperature range of 303, 313 and 323 K at neutral pH. The fluoride ion concentration was measured using an expandable ion analyzer EA 940 and the fluoride ion selective electrode BN 9609 (Orion, MI). The pH measurements were done with the same instrument with pH electrode. All other water quality parameters were analyzed using standard methods [30]. pH at zero point of charge (pH$_{zpc}$) was determined by a pH drift method [31].

2.4. Characterisation of beads

FTIR spectra of the chitosan samples were obtained using JASCO-460 plus model to confirm the presence of functional groups of sorbents. Examination of beads with scanning electron microscope (SEM) with HITACHI-S-3000H model fitted with an energy dispersive X-ray analyzer (EDAX) allows a qualitative detection and localization of elements in the beads. The bead samples are coated with a thin layer of carbon in a vacuum coating unit. The SEM enables a direct observation of the surface microstructures of the fresh and fluoride-sorbed beads.

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

3. Results and discussion

3.1. Effect of contact time

Fig. 1 shows the variation of DC of the sorbents with respect to time and also the comparative difference between the unmodified and modified chitosan beads. Evidently, all the modified chitosan beads have higher sorption ability for the uptake of fluoride than the raw beads. The PCCB possesses higher DC of 1800 mg F$^-$/kg than the other modified chitosan beads. The PCB and CCB possesses the DCs of 1664 and 1385 mg F$^-$/kg, respectively. In contrast, the chitosan beads have lower DC of 52 mg F$^-$/kg. This clearly indicates that the H$^+$ groups of the modified chitosan beads are responsible for higher DC than the original –NH$_2$ and –OH groups of chitosan beads. Therefore, further discussions focus only on modified chitosan beads in order to explore the possibility of utilizing modified chitosan beads as effective defluoridating agents. With respect to contact time, all the materials reached saturation after 30 min and for further experiments, 30 min was fixed as the period of contact for sorption studies.

3.2. Influence of pH of the medium

The pH effect of the sorbents was studied at five different pH levels, viz., 3, 5, 7, 9 and 11 by keeping all other parameters constant as shown in Fig. 2. All the sorbents recorded maximum DC at pH 7 hence throughout the study pH of the medium was maintained at neutral pH. Even though there appears to be a decline in DC of the sorbents in acidic as well as in alkaline medium, the error bar plot indicates that the differences are not so significant. Among the modified chitosan beads, PCCB shows higher DC when compared to PCB and CCB for a wide pH range studied and hence further studies were limited only to PCCB.
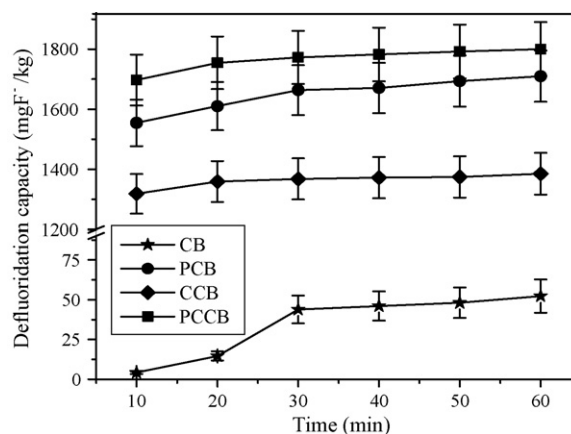

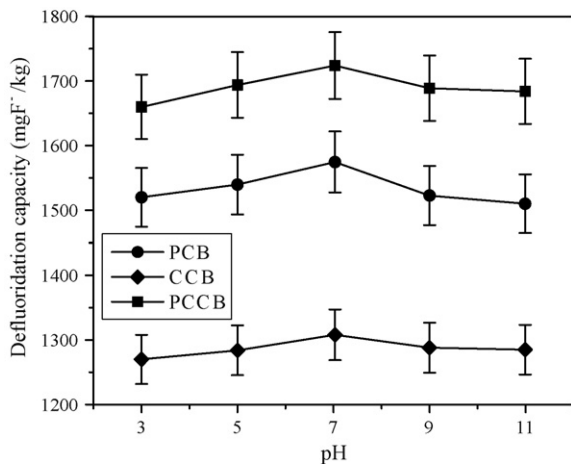**Fig. 1.** Effect of contact time on the DC of the sorbents.

Fig. 2. Effect of pH on the DC of sorbents.

3.3. 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 sorption capacity of PCCB and hence the dependence of DC on PCCB 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. 3 shows the dependence of DC on PCCB in the presence of other co-anions. In the presence of other anions, a slight reduction in DC was observed which may be due to the competition among them for the sites on the sorbent surfaces, which is decided by the concentration, charge and size of the anions. Even though there is a slight decrease in DC of sorbent in presence of other anions, PCCB has significant DC suggesting its selectivity towards fluoride and hence it could be used as a promising defluoridating agent. This is further supported by the field trial studies of PCCB.

3.4. Characterisation of PCCB

The characteristics of PCCB are shown in Table 1. Fig. 4a and b represents the FTIR spectra of before and after fluoride treated PCCB. In Fig. 4a, a sharp peak at 1643 cm^{-1} confirms the presence of carbonyl group in PCCB. The presence of –OH group in PCCB is confirmed by the broad peak at 3421 cm^{-1} [32]. The widening of the broad –OH band at 3421 cm^{-1} in the fluoride-sorbed PCCB (Fig. 4b)
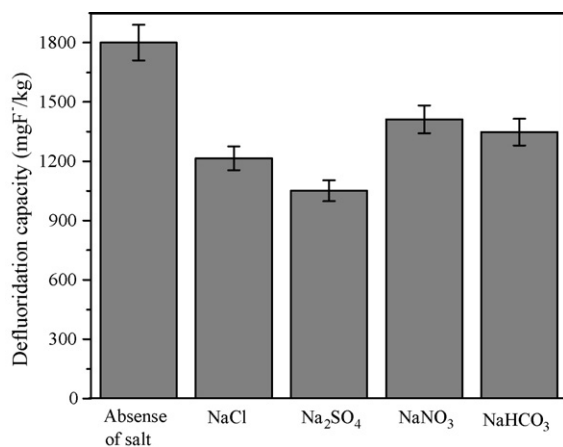
Table 1
Characteristics of PCCB.

Constituents	PCCB
Polymeric matrix	Chitosan cross-linked with glutaraldehyde
Appearance	Brown coloured spherical beads
Particle size (mm)	0.6–1.2
Density (g/cm^3)	0.73
Surface area (m^2/g)	2.12
pH$_{zpc}$	3.90

indicates the presence of hydrogen bonding (H-bonding) between –COOH$^+$···F$^-$. The –NH$_2$ and –OH stretching bands are often fall in the same region. However, the H-bonding in amines is weaker than that of –OH groups, so –NH$_2$ stretching bands are not as broad or intense as –OH stretching bands. A slight broadening of the –NH$_2$ band at 3260 cm^{-1} in the fluoride-sorbed PCCB (Fig. 4b) may be taken as an indicative of H-bonding between the protonated amine (–NH$_3^+$) and the fluoride [32–34].

SEM images were used to examine the structure of the sorbents. Fig. 5a and b shows the SEM pictures before and after fluoride sorption with PCCB. There are apparent differences between the beads with many cavities before sorption and no such cavities are observed after sorption, it indicates fluoride sorption onto PCCB. The EDAX spectrum of PCCB is shown in Fig. 5c. The presence of a fluoride peak in the EDAX spectra of fluoride-sorbed PCCB confirms the fluoride sorption onto PCCB which is shown in Fig. 5d.

The surface morphological change of PCCB was also confirmed by the shifting of pH$_{zpc}$ values [26–28]. The pH$_{zpc}$ of CB is 7.88 whereas for the PCCB this value shifted to 3.90. This clearly indicates the occurrence of structural changes in PCCB.

3.5. Sorption isotherm

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

3.5.1. Freundlich isotherm

The linear form of Freundlich [35] 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
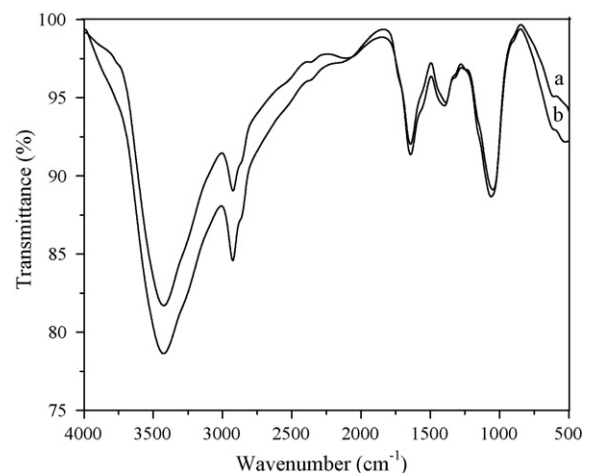

Fig. 3. Effect of co-existing anions on the DC of PCCB.

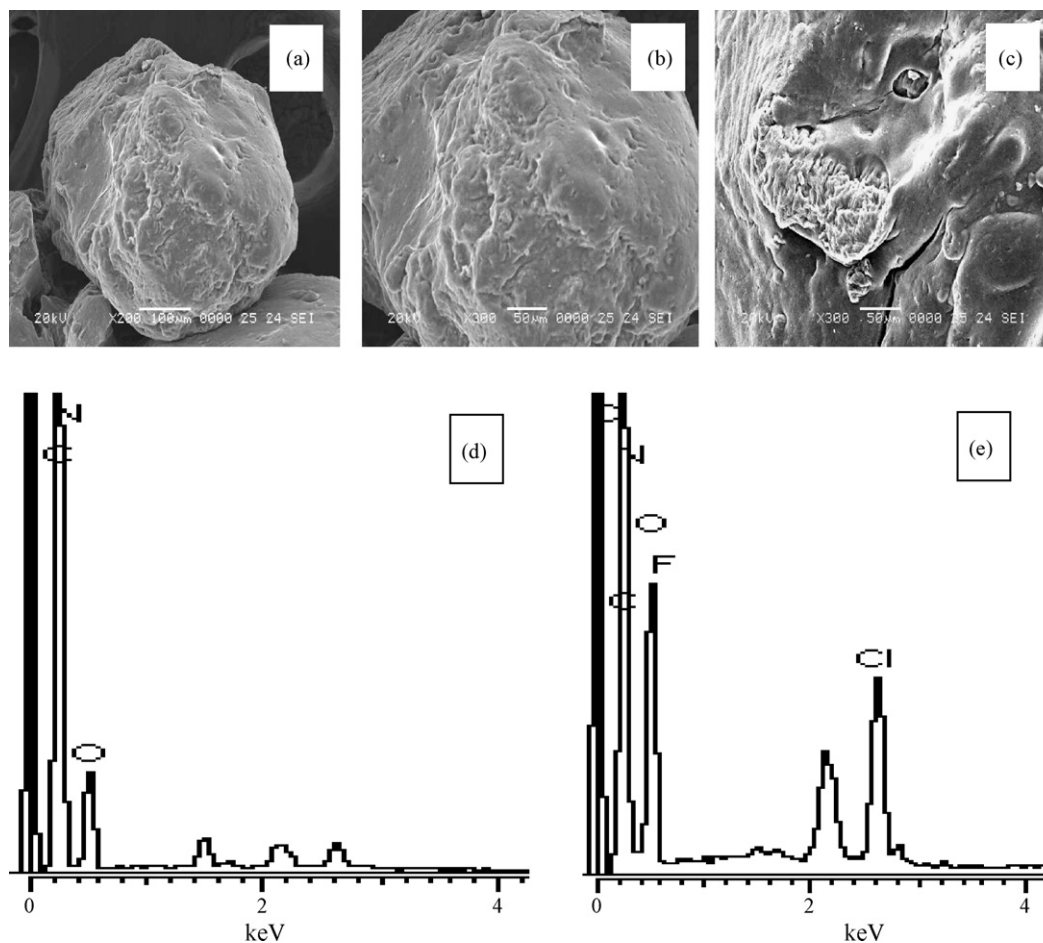**Fig. 4.** FTIR spectra of (a) PCCB and (b) fluoride treated PCCB.

Fig. 5. SEM micrographs of (a), (b) PCCB and (c) fluoride-sorbed PCCB, EDAX spectra of (d) PCCB and (e) fluoride-sorbed PCCB.

the adsorption intensity. The values of $1/n$ and k_F of the sorbent was calculated from the slope and the intercept of the linear plot of $\log q_e$ vs. $\log C_e$ and are listed in Table 2. The values of k_F almost remained constant in all the temperatures studied. The magnitude of the exponent $1/n$ lying between 0 and 1, and the values of n greater than 1 indicate favourable conditions for adsorption. The higher correlation coefficient (r) values show that the Freundlich isotherm fits well with the experimental data of PCCB.

3.5.2. Langmuir isotherm

Langmuir [36] isotherm model can be represented in the form of equation

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

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 results are listed in Table 2. The slight decrease in the values of Q^o with increasing temperature confirms the preference for low temperature for adsorption. The correlation coefficient (r) >0.9 indicates the applicability of Langmuir isotherm for the sorption data. In order to find out the feasibility of the isotherm, the essential characteristics of the Langmuir isotherm can be expressed in terms of the dimensionless constant separation factor or equilibrium parameter [37]

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

where b is the Langmuir isotherm constant and C_0 is the initial concentration of fluoride (mg/L). The R_L values at different temperatures studied were calculated and are given in Table 2. The R_L values lying between 0 and 1 indicate the favourable conditions for fluoride sorption at all the temperatures studied.

3.5.3. Chi-square analysis

To identify the suitable isotherm for sorption of fluoride, the chi-square analysis was carried out. The mathematical statement

Table 2
Freundlich and Langmuir isotherms of PCCB.

Temperature (K)	Freundlich isotherm					Langmuir isotherm				
	$1/n$	n	k_F (mg/g) (L/mg)$^{1/n}$	r	χ^2	Q^o (mg/g)	b (L/g)	R_L	r	χ^2
303	0.620	1.612	1.455	0.999	6.49E−5	6.25	0.282	0.244	0.994	2.46E−4
313	0.534	1.873	1.387	0.998	1.22E−4	4.93	0.345	0.209	0.994	3.88E−4
323	0.496	2.016	1.374	0.980	1.84E−3	4.43	0.390	0.189	0.984	1.51E−3

for chi-square analysis 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 on 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 necessary to analyze the dataset using the non-linear chi-square test to confirm the best-fit isotherm for the sorption system. The χ^2 values of PCCB were tabulated in Table 2. The χ^2 values of both the models do not differ much which implies that the system follows both Freundlich and Langmuir isotherms.

3.6. Thermodynamic treatment of fluoride sorption process

The feasibility of the sorption process was assessed by the thermodynamic parameters, viz., standard free energy change (ΔG°), standard enthalpy change (ΔH°) and standard entropy change (ΔS°) were calculated according to Khan and Singh method [38]. The negative values of ΔG° confirm the spontaneous nature of the sorption of the fluoride ion by PCCB. The positive values of ΔS° which suggest F$^-$ ions are not too restricted in the beads. The positive values of ΔH° confirm the endothermic nature of the sorption process.

3.7. Sorption dynamics

The two main types of sorption kinetic models, namely reaction-based and diffusion-based models, were adopted to fit the experimental data. In this study, the initial sorbate concentration and the reaction temperature are considered for examining the influence of sorption capacity on the rate of the reaction.

3.7.1. Reaction-based models

To investigate the sorption mechanism of PCCB, pseudo-first-order and pseudo-second-order kinetic models have been used at different experimental conditions.

A simple pseudo-first-order kinetic model [39] 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}). Linear plots of $\log(q_e - q_t)$ against t gives a straight line that indicates the applicability of Lagergren equation. The values of k_{ad} and the correlation coefficient (r) computed from these plots for the sorbent are given in Table 3. The pseudo-first-order model seems to be viable 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 [40] 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 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 vs. t for fluoride sorption at different temperatures, viz., 303, 313 and 323 K of PCCB

are presented in Table 3. 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. This indicates the applicability of pseudo-second-order than pseudo-first-order model. The q_e values of the sorbent decreased with increase in temperature, which indicates the preference of lower temperature for sorption.

3.7.2. Diffusion-based models

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

A simple equation for the particle diffusion controlled sorption process [5,41] 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 [42] and its equation is

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

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

The values of k_p, k_i and r of PCCB are shown in Table 3, and the higher r values in both the cases indicate the possibility of sorption process being controlled by both particle and intraparticle diffusion models.

3.7.3. Fitness of the sorption kinetic models

The best-fit among the kinetic models was assessed by the squared sum of errors (SSE) values. It is assumed that the model which gives the lowest SSE values is the best model for the particular system [43]. The SSE values were calculated by the equation,

$$SSE = \sum \frac{(q_{t,e} - q_{t,m})^2}{q_{t,e}^2} \tag{9}$$

where $q_{t,e}$ and $q_{t,m}$ are the experimental sorption capacity of fluoride (mg/g) at time t and the corresponding value that is obtained from the kinetic models. SSE values for all the kinetic models were calculated and are summarized in Table 3. It was once again confirmed that pseudo-second-order model which has lower SSE values seems to be best reaction-based model than the pseudo-first-order model. Among the diffusion-based models, the intraparticle diffusion model was found to have less SSE values, and hence the sorbent prefer to remove fluoride by intraparticle diffusion rather than particle diffusion.

3.8. Mechanism of fluoride sorption by PCCB

The protonated amine groups of chitosan may cause electrostatic interaction with fluoride via H-bonding [44]. Simultaneously the carboxyl groups also involve electrostatic interaction with fluoride by H-bonding. This is confirmed by FTIR studies [26,32]. The above discussion clearly indicates that the PCCB remove fluoride by means of H-bonding. The mechanism of fluoride removal by PCCB is shown in Scheme 2. Moreover PCCB may be considered as Lewis acid as they possess H$^+$ ion and it prefers to bind with fluoride as it is the hardest Lewis base among all other anions. Hence, the PCCB shows an enhanced DC than raw chitosan beads indicates its selectivity towards fluoride.

Table 3
The parameters of various kinetic models of PCCB with r and SSE 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})	0.246	0.227	0.216	0.189	0.158	0.186	0.199	0.232	0.158	0.167	0.144	0.161
	r	0.997	0.981	0.982	0.963	0.978	0.991	0.976	0.950	0.978	0.967	0.969	0.972
	SSE	2.1E−3	1.1E−3	2.1E−3	3.5E−4	1.8E−3	6.9E−3	2.9E−3	2.3E−4	2.3E−3	4.7E−3	1.2E−2	5.9E−3
Pseudo-second-order	q_e (mg/g)	2.203	2.545	2.950	3.356	2.037	2.283	2.551	2.841	1.988	2.208	2.525	2.786
	k (g/mg min)	0.109	0.097	0.072	0.061	0.170	0.238	0.280	0.227	0.198	0.298	0.281	0.225
	h (mg/g min)	0.531	0.631	0.630	0.683	0.707	1.241	1.821	1.835	0.783	1.451	1.792	1.745
	r	0.998	0.997	0.998	0.995	0.999	0.999	0.999	1.00	0.999	1.00	1.00	0.999
	SSE	4.1E−4	3.7E−4	4.8E−4	3.2E−4	1.3E−3	5.8E−3	2.6E−3	2.1E−3	8.9E−3	3.9E−3	1.9E−3	4.2E−3
Particle diffusion	k_p (min^{-1})	0.069	0.087	0.130	0.276	0.051	0.052	0.058	0.070	0.045	0.041	0.053	0.052
	r	0.933	0.938	0.993	0.987	0.927	0.899	0.891	0.987	0.947	0.926	0.976	0.833
	SSE	0.290	0.250	0.198	0.135	0.316	0.252	0.220	0.181	0.335	0.295	0.227	0.243
Intraparticle diffusion	k_i (mg/g min$^{0.5}$)	0.236	0.272	0.325	0.387	0.180	0.159	0.149	0.147	0.157	0.126	0.127	0.186
	r	0.913	0.894	0.931	0.907	0.910	0.889	0.858	0.973	0.926	0.912	0.958	0.821
	SSE	0.089	0.094	0.063	0.032	0.032	0.046	0.054	0.059	0.038	0.055	0.060	0.048
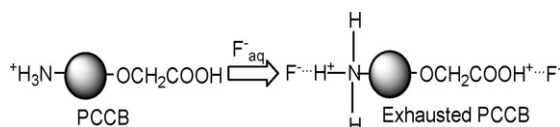
Scheme 2. Mechanism of fluoride sorption by PCCB.

Table 4
Field trial results of PCCB.

Water quality parameters	Before treatment	After treatment
F$^-$ (mg/L)	2.33	0.85
pH	9.10	6.85
Electrical conductivity (ms/cm)	0.87	0.55
Cl$^-$ (mg/L)	56.80	35.00
Total hardness (mg/L)	70.00	50.00
Total dissolved solids (mg/L)	473.00	450.00
Na$^+$ (mg/L)	55.10	48.00
K$^+$ (mg/L)	8.80	5.70

3.9. Field trial

The applicability of PCCB in the field condition was tested with water samples taken from a nearby fluoride endemic area and the results are listed in Table 4. The sorbent reduced the level of fluoride from 2.33 mg/L to the desired level using 0.5 g of PCCB for 50 mL of sample, and the time of contact was fixed at 30 min at room temperature. To some extent the material also removed other ions present in water in addition to fluoride. Even though the sorbent used is slightly influenced by the presence of foreign anions, this factor does not affect lowering the fluoride level to the tolerance limit in field conditions.

4. Conclusions

All the modified chitosan beads possess higher DC than the unmodified chitosan beads. Among the modified forms, PCCB have higher DC than the other modified forms. The PCCB removes fluoride by H-bonding. The adsorption pattern follows both Langmuir and Freundlich isotherms. Fluoride sorption onto PCCB is spontaneous and endothermic in nature. The rate of reaction follows pseudo-second-order kinetics. The sorption of fluoride ion occurs through intraparticle diffusion pattern. Field trial results indicate that PCCB reduces the fluoride level below the tolerance limit and it can be effectively used to remove other ions in addition to fluoride. So, PCCB can be used as an effective, inexpensive and promising defluoridating agent.

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