Development and characterization of chitosan coated biopolymer sorbent for the removal of fluoride ion from aqueous solutions

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ABSTRACT

A novel biosorbent, chitosan coated calcium alginate (CCCA), was developed by coating chitosan, a naturally and abundantly available cationic biopolymer, onto an anionic biopolymer calcium alginate for the removal of fluoride ion from aqueous solutions. The results were compared with calcium alginate (CA) beads obtained from natural biopolymer sodium alginate. Further the biosorbents were characterized by FTIR, SEM and TGA techniques and surface area analysis. Defluoridation of water was studied by using the biosorbent under batch equilibrium and column flow experimental conditions. The effect of various process parameters such as pH, contact time, concentration of fluoride and amount of biosorbent was investigated in order to optimize the process. The equilibrium data were used to study the kinetics of defluoridation process such as pseudo first order, pseudo-second order and Weber–Morris intraparticle diffusion models. The data were fitted to Langmuir and Freundlich adsorption isotherms. The column flow adsorption data were utilized to obtain break through curves. The maximum monolayer adsorption of fluoride on CA and CCCA were found to be 29.3 and 42.0 mg/g. The experimental results demonstrated that chitosan coated calcium alginate beads could be used for the defluoridation of drinking water.

Keywords: Defluoridation; Adsorption; Chitosan; Characterization; isotherms

1. Introduction

Fluoride is an essential microelement for human health. Smaller quantities in the order of 1 mg/L in the ingested water are usually considered good to have a beneficial effect in reducing the occurrence of dental carries, particularly among children [1]. On the other hand due to its strong electro negativity, fluoride is attracted by positively charged calcium ions in teeth and bones. Excessive intake results in pathological changes in teeth and bones, such as mottling of teeth or dental fluorosis

followed by skeletal fluorosis [2]. Fluoride may cause an increase in the concentration of thyroid stimulating hormone (TSH) and a decrease in the concentration of T3 and T4 hormones in the thyroid gland resulting in hypothyroidism [3,4]. According to WHO [1] permissible limit for fluoride in drinking water is 1 mg/L, whereas, USPHS [5] has set a range of allowable concentrations for fluoride in drinking water for a region depending on its climatic conditions because the amount of water consumed and consequently the amount of fluoride ingested being influenced primarily by the air temperature. Lesan [6] suggests a limit of fluoride in drinking water as low as 0.6 mg/L under tropical conditions. Several

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methods, namely adsorption [7–9], precipitation [10,11], electrodialysis [12], ion exchange [13] and electrochemical methods [14,15] have been tried to remove fluoride from water. Of these, adsorption is still one of the most extensively used methods for defluoridation of water. In recent years, the use of low cost adsorbents has been investigated to remove fluoride from water. Such materials include: hydroxyl apatite, calcite, fluorspar, quartz [16], flyash [17], silica gel [18], bone char [19], spent catalyst [20], zeolites [21], red mud [22] and bentonite [23].

Biopolymers are non-toxic, selective, efficient and inexpensive and thus highly competitive with ion-exchange resins and activated carbon. Immobilizing biomass in a biopolymeric matrix may also improve biomass performance, biosorption capacity and facilitate the separation of biomass from adsorbate-bearing solutions. Chitosan is a partially deacetylated product of chitin, which has many useful features such as biocompatibility, biodegradability, and antibacterial property [24–26]. Several investigators have attempted to modify chitosan to facilitate mass transfer and to expose the active binding sites to enhance the adsorption capacity [27,28]. Grafting specific functional groups onto native chitosan backbone allows its sorption properties to be enhanced. To overcome some of the problems associated with its softness and tendency to agglomerate or to form a gel in aqueous solutions, in this study a new biosorbent is prepared by coating chitosan, a glucosamine biopolymer over calcium alginate, and formed into beads. It is expected that the more active sites of chitosan will be available due to coating, thus enhancing the adsorption capacity.

The aim of this work is to prepare calcium alginate (CA) and chitosan coated calcium alginate (CCCA) and to determine the ability of these biosorbents in removing fluoride ion from aqueous medium under batch equilibrium and column flow experimental conditions. Further the biosorbents are characterized by FTIR, SEM, TGA and surface area analysis to understand the surface morphology.

2. Materials and methods

2.1. Materials

Chitosan, having an average molecular weight of 300,000 was purchased from Aldrich Chemical Corporation, USA. Sodium alginate was used for preparation of calcium alginate beads were obtained from Loba Chemie, Mumbai, India. Acetic acid and calcium chloride, used for the treatment of beads, were obtained from Ranboxy Fine chemicals. Analytical reagent grade sodium fluoride, hydrochloric acid and sodium hydroxide from S.D. Fine Chemicals were used as source of fluoride and for the pH adjustment. Total ionic strength adjustment buffer (TISAB) was used to eliminate the interference effect of complexing ions from fluoride solution was obtained

from Thermo Electron Corporation, USA. Doubly distilled water was used in all experimental work.

2.2. Equipment

A pH/IES meter (Orion Model, EA 940 Expandable Ion Analyzer) equipped with combination fluoride-selective electrode (Orion model 96-09) was employed for the measurement of fluoride ion concentration. The method of direct potentiometry was used, where the concentration of fluoride can be read directly. The fluoride ion selective electrode was calibrated prior to each experiment in order to determine the slope and intercept of the electrode. The pH was measured with pH/ion meter using pH glass electrode.

2.3. Preparation of biosorbents

2.3.1. Calcium alginate beads

4% sodium alginate solution was prepared by gentle heating of 4 g of alginate in 100 ml water. The solution was then dropped into 20% calcium chloride solution through the tip of the transfer pipette. The drops of sodium alginate solution gelled into 3.5 ± 0.1 mm diameter beads upon contact with calcium chloride solution. The beads were stored in calcium chloride solution for 4 h. In this way insoluble and stable beads were obtained. Water soluble sodium alginate was converted to water insoluble calcium alginate beads using $CaCl_2$ solution. The beads were rinsed with double distilled water and dried until the water was completely evaporated. The size of the beads decreases after drying. Size of fine samples of the completely dried beads was measured by using the micrometer screw gauge with an accuracy of ±0.01 mm and the size of the beads were observed to be 2.05 mm.

2.3.2. Chitosan coated calcium alginate

The prepared calcium alginate beads were dropped in a 4% chitosan solution. Chitosan solution was prepared by dissolving 4 g of chitosan in 2% CH_3COOH solution. Then chitosan coated beads were transferred into a 0.1 N NaOH solution. Chitosan forms a layer on calcium alginate bead after falling into the alkaline solution. Then the beads were removed from the base and thoroughly washed with double distilled water until neutral pH.

2.4. Batch adsorption studies

An adsorbate stock solution 100 mg/L of fluoride solution was prepared by dissolving 0.221 g of sodium fluoride (NaF) in double distilled water. The stock solution was diluted to get desired concentration. Equilibrium batch adsorption experimental studies were carried out with known weight (0.5 g) of adsorbent and 100 ml of fluoride solution of desired concentration at optimum pH in 125 ml stoppered bottles. The bottles were agitated at

200 rpm for 120 min time intervals at room temperature in a mechanical shaker. After attaining equilibrium, the biosorbent was separated by filtration and the aqueous-phase concentration of fluoride was analyzed with ion-selective electrode (I.S.E. 96-09) using total ionic strength adjustment buffer (TISAB) solution [29]. TISAB consists of 1 mole of sodium chloride (NaCl), 1 mole of acetic acid (CH$_3$COOH), 4.0 g of 1, 2-cyclo-hyxylene dinitro tetra acetic acid (CDTA) and sufficient sodium hydroxide (NaOH) to give a final pH in the range of 5–5.5 in 1.0 L of solution and to eliminate the interference effect of complexing ions. In all cases, the amount of complexed fluoride, other than NaF and HF species, was found to be insignificant.

The equilibrium uptake capacity was calculated according to mass balance on fluoride ions,

$$Q_e = \left(\frac{C_i - C_e}{m} \right) v \tag{1}$$

where C_i and C_e are, respectively, initial and equilibrium concentrations of fluoride ion, m is the mass of adsorbent and v is volume of the solution in liters. Experiments were conducted with fluoride ion solution in the absence of adsorbent and it was found that there was no fluoride adsorption by the walls of the container. All other water quality parameters were analyzed by using standard methods [30].

2.5. Column adsorption studies

Column flow adsorption experiments were conducted in a glass column of about 1.5 cm internal diameter and 10 cm length. The column was filled with a known weight of the adsorbent while tapping the column such that the column was filled without voids. The adsorbate solution was allowed to flow through the column at a constant flow rate (2 ml/min) throughout the experiment. The pH of the inlet solution was adjusted to 6 for CA 5 for CCCA at the start of the experiment. The effluent solution was collected at different time intervals and the concentration of fluoride in the effluent solution was monitored by Ion-selective electrode. The solutions were diluted with TISAB appropriately prior to analysis. Samples at 10 min time intervals from the start of the experiment were collected for analysis. Breakthrough curves for each adsorbent individually were obtained by plotting the volume of solution against the ratio of the concentration of effluent at any time (C_e) to that of the inlet solution (C_i), C_e/C_i.

2.6. Desorption studies

After the column exhausted, it was drained off the remaining aqueous solution by pumping air. Desorption of fluoride from loaded adsorbents, CA and CCCA, was carried out by using 0.1 N NaOH as eluent. The NaOH solution was pumped into the column maintained at constant temperature and fixed flow rate (1 ml/min). From the start of the experiment effluent samples at different time intervals, were collected at the bottom of the column for analysis. After the regeneration, the adsorbent column was washed with distilled water to remove sodium hydroxide from the column before the influent fluoride solution was reintroduced for the subsequent adsorption–desorption cycles. Adsorption-desorption cycles are performed thrice for fluoride using the same bed to check the sustainability of the bed for repeated use.

3. Results and discussion

At a pH close to 5, the free carboxylic groups of the alginic acid chains are mostly present as carboxylate and the amino groups of chitosan are protonated, resulting in the formation of new salt bonds [31]. Fig. 1 exhibits the ionic complexation reaction between cationic group (–NH$_3^+$C) of chitosan polymer and anionic group (–COO$^-$) of alginate. The carboxylate groups of alginate were dissociated to COO$^-$ groups which complexed with protonated amino groups from chitosan through electrostatic interaction. Moreover, as the polyion complex formation proceeded, the O–H bonding would also be expected because of an increase in intermolecular interaction such as hydrogen bonding between calcium alginate and chitosan.

The positive surface of the chitosan may attract fluoride by weak electrostatic interaction [32]. Simultaneously the fluoride removal by CCCA composite too was mainly governed by electrostatic adsorption mechanism. The positive charge Ca^{2+} at the surface of the alginate attract negatively charged fluoride ions by means of electrostatic attraction.

3.1. Characterization of biosorbents

The influence of the surface properties on the extent of adsorption is evaluated by measuring the surface area (144.6 m^2 g^{-1} for CA and 178.3 m^2 g^{-1} for CCCA) and pore volume (0.202 cm^3 for CA and 0.231 cm^3 for CCCA). Porosity is one of the factors that influence the activity and physical interaction of solids with liquids and gases. Among the two adsorbents, the CCCA possesses high surface area and pore volume when compared to CA. Obviously the fluoride uptake capacity of the sorbent will be high due to its free amine groups.

The FTIR spectra of pristine CA (Fig. 2a) show peaks at 3430 cm^{-1}, 1618 cm^{-1}, 1125 cm^{-1} and 1065 cm^{-1} due to the presence of hydroxyl, ether and alcohol groups, respectively. In the FTIR spectrum of CA loaded with fluoride (Fig. 2b), an interesting phenomenon is the sharp shift in the position and intensity of the bands after fluoride binding. The peak appears at 1000–1100 cm^{-1} indicates the presence of C–F stretching. The FTIR spectrum of CCCA biosorbent (Fig. 2c) indicates the presence of predominant
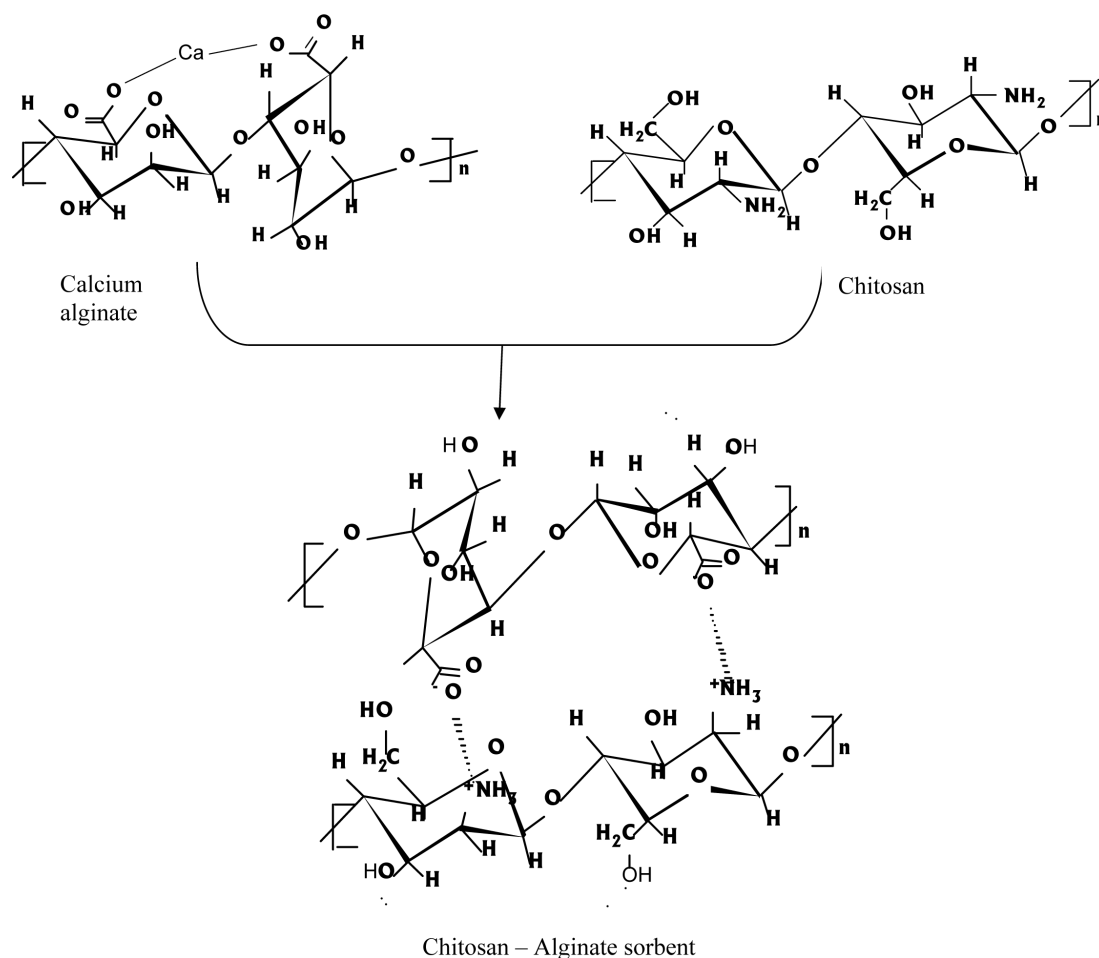
Fig. 1. Interactions of chitosan and alginate.

peaks at 3352 cm⁻¹ (–OH and –NH stretching vibrations), 2987 cm⁻¹ (–CH stretching vibration) 1393 cm⁻¹ (–NH deformation vibration), and 1065 cm⁻¹ (–CO stretching vibration). This reveals that all functional groups originally present on chitosan and alginate are still present even after coating process and are available for interaction with fluoride. A slight widening of –NH₂ stretching band at 3352 cm⁻¹ in the fluoride-sorbed CCCA (Fig. 2d) was observed which confirmed the presence of hydrogen bonding between protonated amine (NH3+) and fluoride, suggesting that the CCCA removed fluoride by means of hydrogen bonding which was due to electrostatic interactions between positively charged surface and negatively charged fluoride ions.

SEM images of the biosorbents before and after fluoride sorption of CA are shown in Figs. 3a and 3b, respectively. The respective SEM images of CCCA before and after treatment are shown in Figs. 3c and 3d, respectively. An examination of the SEM micrographs indicates the presence of many pores and also some cracks on the surface of the biosorbents. Comparison of these micrographs before and after fluoride sorption indicates that there is no significant change in the morphology of the surface of the

biosorbents. Similar results were observed by Diaz-Nava et al. [33]. The thermo gravimetric analysis (TGA) of CA and CCCA (Fig. 4) showed that the biosorbent undergo two steps decomposition stages with one starting at 238°C and another starting at around 320oC. Thermal behavior of CA and CCCA is not much different. Maximum weight loss due to degradation takes place at 320°C in the second stage. This indicates that the biosorbents could be used even at higher temperatures.

3.2. Effect of pH

The effect pH of the aqueous solution is a controlling factor in the adsorption process. Thus the role of hydrogen ion concentration is examined with 100 ml solution of 10 mg/L of fluoride in contact with 0.5 g of adsorbent in the pH range 1–8 at room temperature. The influence of pH on the sorption rate is shown in Fig. 5. Maximum adsorption is observed at pH 6 and 5 for CA and CCCA, respectively. The fluoride removal was observed to decrease, after pH 6. The progressive decrease of fluoride uptake at alkaline pH could be mainly due to two factors: the electrostatic repulsion of fluoride to the negatively
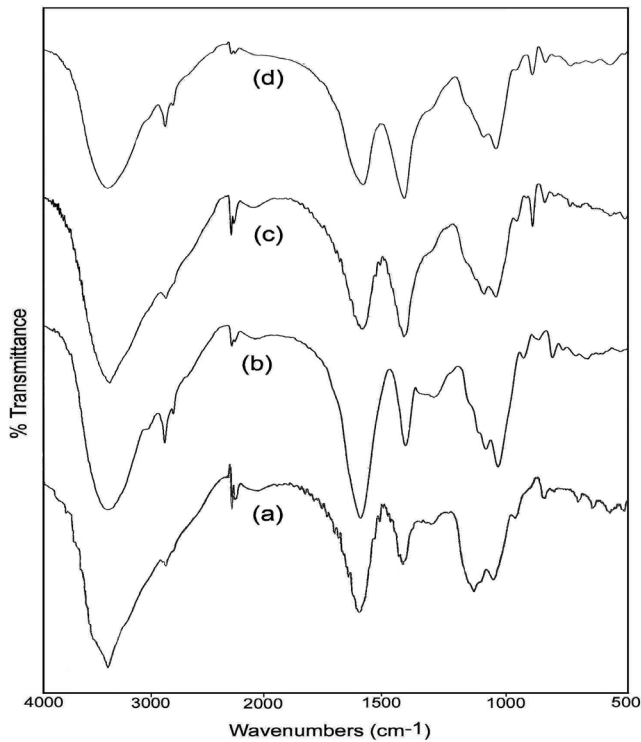
Fig. 2. FTIR spectra of (a) calcium alginate (CA) (b) calcium alginate (CA) loaded with fluoride (c) chitosan coated calcium alginate (CCCA) (d) chitosan coated calcium alginate (CCCA) loaded with fluoride.

charged surface of the CA and CCCA, and the competition for active sites by excessive amount of hydroxyl ions.

3.3. Isothermal studies

To obtain these isotherms, initial concentration of fluoride ion solution is varied from 5 to 30 mg/L while keeping the weight of adsorbent, pH and contact time constant.

Langmuir isotherm [34], used to describe the sorption phenomenon on homogenous surfaces and for a simple solute, is given by

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

where C_e is the equilibrium concentration (mg/L), Q_e is the amount of fluoride adsorbed for unit weight of CA or CCCA, b is a constant related to the affinity of the binding sites and Q^o represents a practical limiting biosorption capacity when the surface is fully covered with fluoride.

The linear form of the Freundlich isotherm [35] is represented by the equation,

$$Q_e = K_f C_e^{1/n} \tag{3}$$

K_f is a measure of adsorption capacity, and $1/n$ is the adsorption intensity. The parameters of Langmuir and Freundlich adsorption isotherms, evaluated from the linear plots, are presented in Table 1 along with the correlation coefficients. Though both the isotherms are capable of representing the data satisfactorily, the Langmuir model gives a better representation.

The essential features of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor, R_L, which is used to predict if an adsorption is favorable or unfavorable. The separation factor, R_L is defined by Hall et al. [36] as;

$$R_L = \frac{1}{1 + b C_o} \tag{4}$$

where b is the Langmuir constant (L/mg) and C_o is the initial fluoride concentration (mg/L). If the R_L values are equal to zero or one, the adsorption is either linear or irreversible, and if the values are in between zero and one, adsorption is favorable. The values of R_L for sorption of fluoride on CA and CCCA are less than 1 and greater than 0, indicating the favorable uptake of fluoride by the biosorbents.

3.4. Effect of agitation time and kinetic studies

The effect of contact time on adsorption capacity of fluoride is depicted in Figs. 6 and 7. The extent of adsorption increases with time and attained equilibrium for all the concentrations of fluoride ion studied at 120 min. After this equilibrium period, the amount of fluoride adsorbed did not change significantly with time. The sorption kinetics of fluoride on the biosorbents is studied on the basis of pseudo first order [37], pseudo second order kinetic models [38]. Pseudo first order kinetic equation takes the form,

$$\log(q_e - q_t) = \log qe - k_1 t \tag{5}$$

Pseudo second order equation may be expressed as:

Table 1
Langmuir and Freundlich isotherm constants for fluoride biosorption

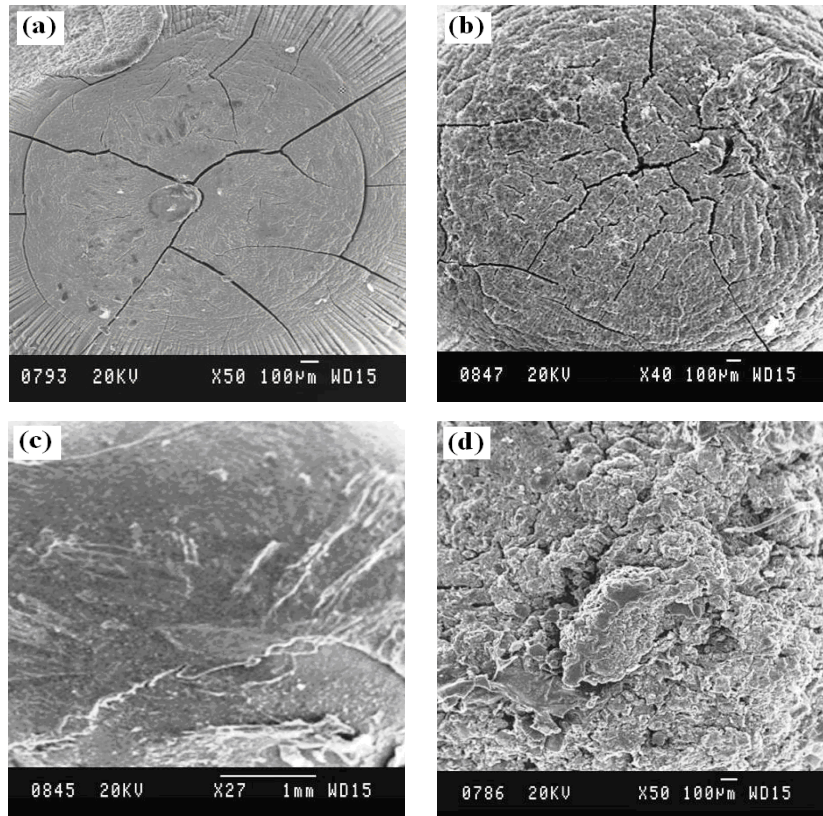| Biosorbent	Langmuir			Freundlich			
	Q^o (mg/g)	b (L/mg)	r^2	K_f	$1/n$	n	r^2
Calcium alginate	29.3	0.013	0.998	0.385	0.922	1.084	0.996
Chitosan coated calcium alginate	42.0	0.009	0.999	0.384	0.953	1.049	0.996

Fig. 3. SEM images of (a) calcium alginate (CA) (b) calcium alginate (CCCA) loaded with fluoride (c) chitosan coated calcium alginate (CCCA) (d) chitosan coated calcium alginate (CCCA) loaded with fluoride
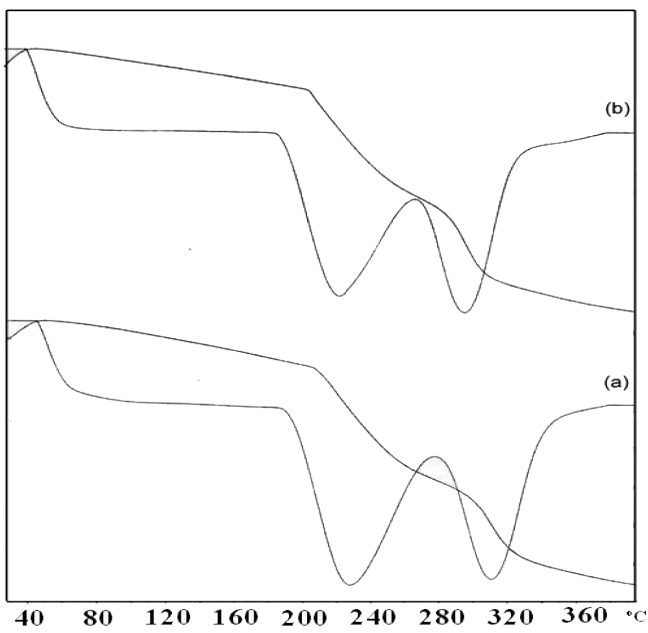

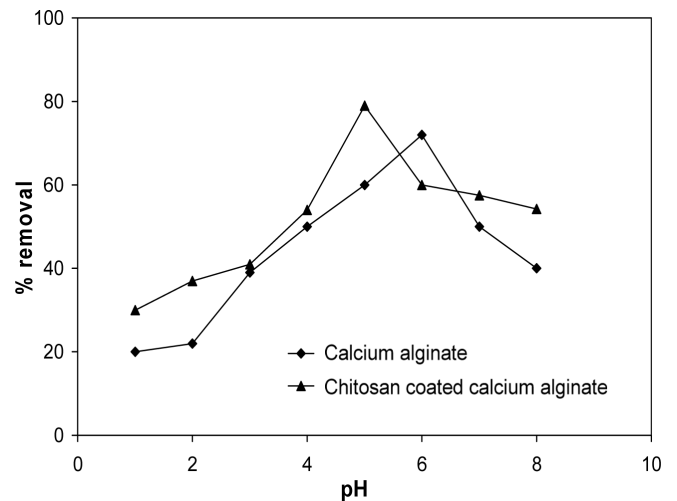Fig. 4. Thermogravemetric curve of (a) calcium alginate (CA) (b) chitosan coated calcium alginate (CCCA)

Fig. 5. Effect of PH on biosorption of fluoride on (a) calcium alginate (CA) (b) chitosan coated calcium alginate (CCCA) (Initial fluoride concentration = 10 mg/L; adsorbent dose = 0.5 g/100 ml; temperature = 28°C, contact time = 120 min).
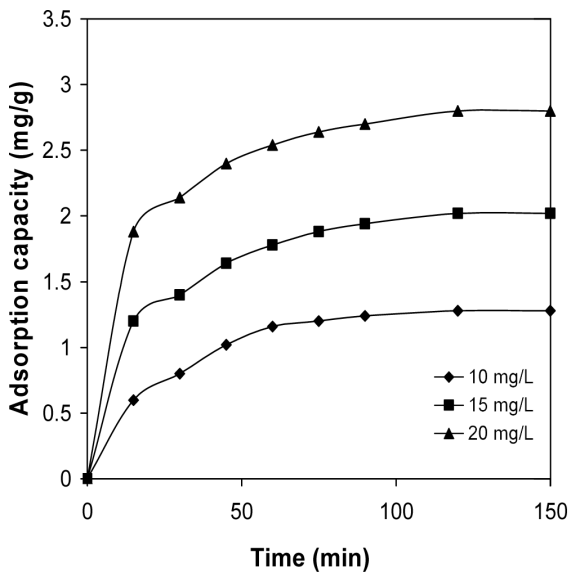
Fig. 6. Effect of time on biosorption of fluoride on calcium alginate (CA) (initial fluoride concentrations = 10, 15 and 20 mg/L; adsorbent dose = 0.5 g/100 ml; pH = 6; temperature = 28°C; contact time = 15–150 min).
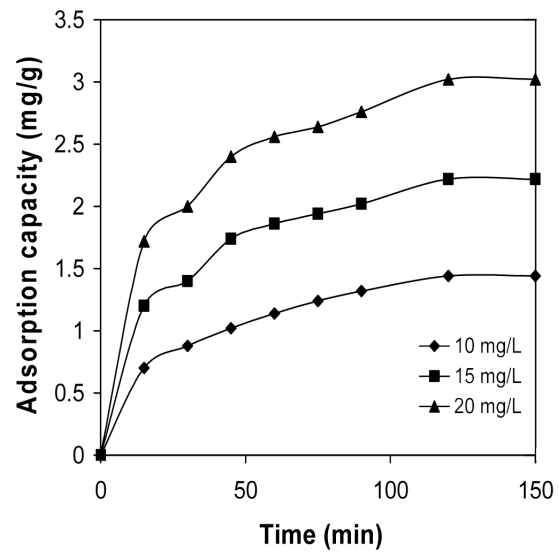

Fig. 7. Effect of time on biosorption of fluoride on chitosan coated calcium alginate (CCCA) (initial fluoride concentrations = 10, 15 and 20 mg/L; adsorbent dose 0.5 g/100 ml; pH = 5; temperature = 28°C; contact time = 15–150 min).

$$\frac{t}{q_t} = \frac{1}{k_2 q^2 e} + \frac{t}{q_e} \qquad (6)$$

where q_e and q_t are the amount of fluoride adsorbed per unit mass of adsorbent (mg/g) at equilibrium and any time t (min), k_1 (1/min) and k_2 (g/mg. min) are the rate constant of first and second order sorption respectively. k_1 is calculated according to the linear plot of log $(q_e - q_t)$ vs. t and k_2 is determined by plotting t/q_t against t. The rate constants of pseudo-first order and pseudo-second order kinetic models are shown in Tables 2 and 3. The adsorption data from CA and CCCA followed pseudo second order reactions. It was found that the value of correlation coefficient r^2 for the pseudo-second-order adsorption model is relatively high (>0.993). The larger k_2 value, the slower the adsorption rate. Therefore, the values of the pseudo second order rate follow the order CCCA<CA.

The results are also analyzed in terms intraparticle diffusion model to investigate whether the intraparticle diffusion is the rate controlling step in adsorption of

fluoride on CA and CCCA. The mathematical expression for Weber–Morris intraparticle diffusion model [39] is

$$q_e = k_{id} t^{0.5} \qquad (7)$$

where k_{id} is the intraparticle diffusion rate constant (mg/g min$^{-0.5}$) and C is the intercept. The amount adsorbed for the unit mass of the adsorbent, q_e at any time t, was plotted as a function of square of time, $t^{0.5}$. The plots are

Table 2
Legergren first-order rate constants for fluoride biosorption

Initial concentration (mg/L)	Calcium alginate		Chitosan coated calcium alginate	
	k_1	r^2	k_1	r^2
10	0.038	0.991	0.024	0.985
15	0.031	0.992	0.022	0.987
20	0.030	0.997	0.021	0.987

Table 3
Pseudo second-order rate constants for fluoride biosorption

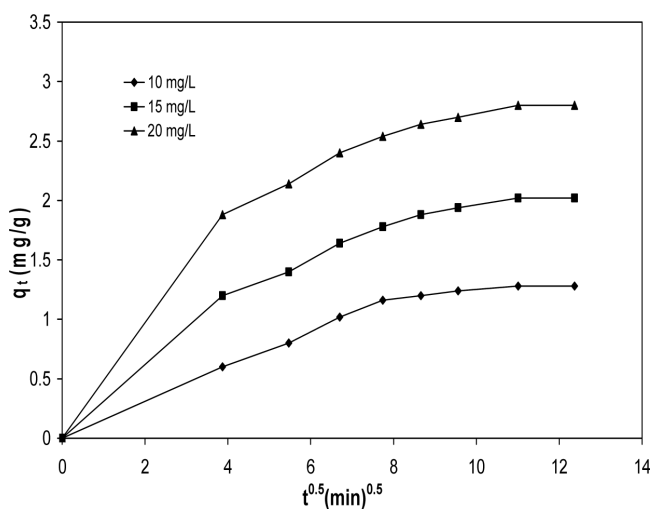| Initial concentration (mg/L)	Calcium alginate				Chitosan coated calcium alginate			
	$Q_{e\,exp.}$ (mg/g)	$Q_{e\,cal.}$ (mg/g)	k_2	r^2	$Q_{e\,exp.}$ (mg/g)	$Q_{e\,cal.}$ (mg/g)	k_2	r^2
10	1.3	1.5	0.032	0.995	1.5	1.7	0.023	0.995
15	2.0	2.3	0.030	0.998	2.2	2.5	0.020	0.996
20	2.8	3.0	0.031	0.999	3.0	3.4	0.020	0.997

Fig. 8. Weber–Morris model for biosorption of fluoride on calcium alginate (CA) (pH = 6).
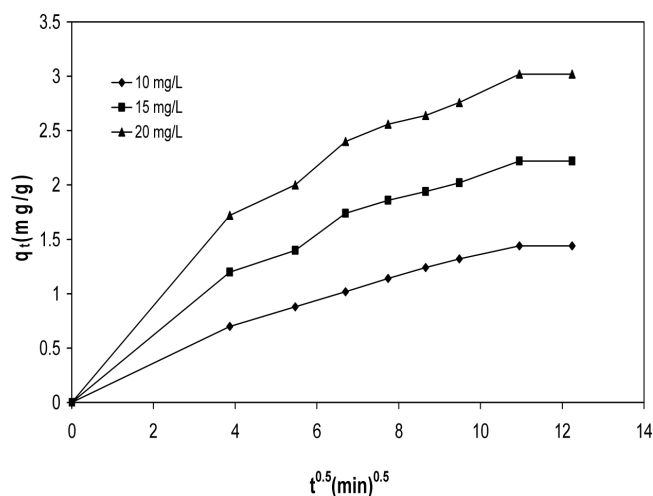

Fig. 9. Weber–Morris model for biosorption of fluoride on chitosan coated calcium alginate (CCCA) (pH = 5).

shown in Figs. 8 and 9 for the system investigated. The plots in the figures are multi linear with three distinct regions indicating three different kinetic mechanisms. It can be seen that all the plots have an initial curved portion, followed by a linear portion. The initial curve of the plot is due to the diffusion of fluoride through the solution to the external surface of both CA and CCCA. The second linear portion of curves describes the gradual adsorption stage, where intraparticle diffusion of fluoride on CA and CCCA takes place and final plateau region indicates equilibrium uptake. The rate constants of Weber-Morris intraparticle diffusion model are shown in Table 4. Based on the results it may be concluded that intra particle diffusion is not only the rate determining factor.

3.5. Effect of adsorbent dose

The dependence of fluoride sorption on biosorbent dose is studied by varying the amount of adsorbent from 0.1 to 0.8 g while keeping all other variables (pH, agitation time and concentration (10 mg/L)) constant. The results are presented in Fig. 10. It is observed that percentage removal of fluoride increased with the increase in adsorbent
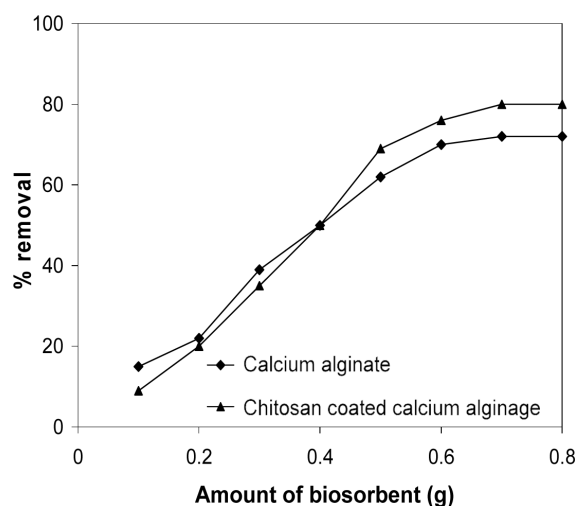

Fig. 10. Effect of adsorbent dose on percent removal of fluoride on (a) calcium alginate (CA) (b) chitosan coated calcium alginate (CCCA) (initial fluoride concentration = 10 mg/L; adsorbent dose 0.1-0.8 g/100 ml, pH = 6 and 5 for CA and CCCA, temperature = 28°C; contact time = 120 min).

Table 4
Weber–Morris rate constants for fluoride biosorption

Initial concentration (mg/L)	Calcium alginate			Chitosan coated calcium alginate		
	k_{id}	C	r^2	k_{id}	C	r^2
10	0.107	0.175	0.905	0.118	0.163	0.953
15	0.158	0.390	0.875	0.178	0.334	0.919
20	0.210	0.681	0.817	0.238	0.511	0.904

dose. This is expected due to the fact that the higher dose of adsorbent in the solution results in greater availability of exchangeable sites for the ions. The maximum fluoride ion removal efficiencies are 70% with CA and 78% with CCCA. This suggests that the fluoride ion can be removed effectively by using <1 g of the biosorbent.

3.6. Column studies

The way in which an experiment is carried out is another parameter that can affect the capacity of particular type of adsorbent to sequester fluorides. The column adsorption of fluoride from aqueous solution on CA and CCCA is investigated and graphically represented in Figs. 11 and 12. The results of the column experiment are used to obtain breakthrough curves by plotting volume of aqueous solution (ml) vs. C_e/C_i. Breakthrough is attained when the concentration of solute in the effluent is almost equal to influent concentration and remains unchanged. The fluoride concentration in each column is given as a function of the total volume of the solution treated at an initial concentration of 10 mg/L. As can be seen from the Figs. 11 and 12 the out flow concentration profile shows that fluoride removal is fast and highly effective during the initial phase and is decreases subsequently. After passing 500 and 560 ml of fluoride solution for CA and CCCA through the column, the column gets saturated. The adsorption capacity of the biosorbent in the column is obtained by dividing the concentration of fluoride adsorbed by the total amount of biosorbent used. From the graphs, it can be concluded that CCCA is a good biosorbent of fluoride removal from aqueous medium compared to that of CA, due to the presence of NH_2 groups.
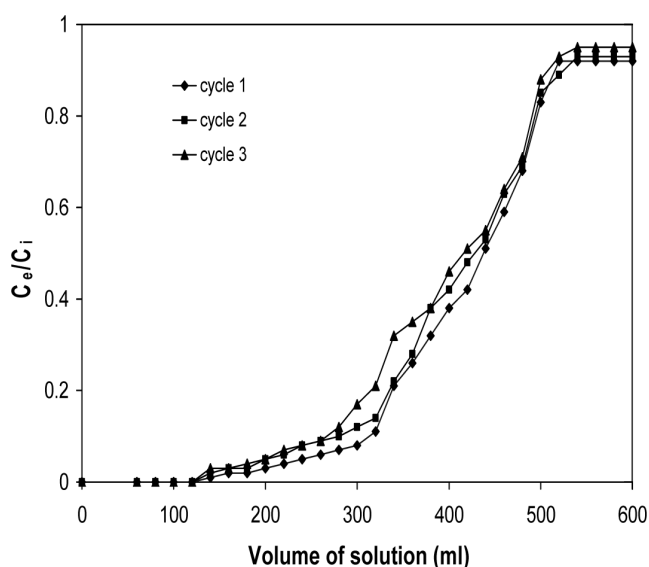

Fig. 11. Column break-through curves for adsorption of fluoride on calcium alginate (CA) (initial fluoride concentration = 10 mg/L; adsorbent dose 3 g, pH = 6, temperature = 28°C; contact time = 300 min; flow rate = 2 ml/min).
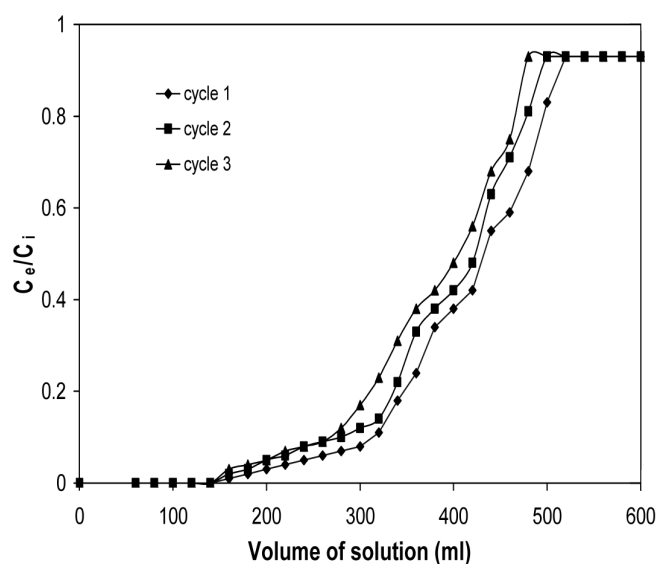

Fig. 12. Column break-through curves for adsorption of fluoride on chitosan coated calcium alginate (CCCA) (initial fluoride concentration = 10 mg/L; adsorbent dose 3 g, pH = 5, temperature = 28°C; contact time = 300 min; flow rate = 2 ml/min).

Table 5
Maximum adsorption capacity (mg/g) of different chitosan based adsorbents for fluoride

Adsorbent	Maximum adsorption capacity (mg/g)	pH	Reference
Magnetic chitosan particle	22.49	7	40
Chitin	8.85	7	41
Chitosan	I5.08	7	41
Lanthanum modified chitosan	84.2	6.7	41
Chitosan	1.39	6	42
Chitosan coated silica	44.4	4	43
Calcium alginate (CA)	29.3	6	Present work
Chitosan coated calcium alginate (CCCA)	42.0	5	Present work

Table 5 gives the comparison of adsorption capacities of CCCA with other chitosan based sorbents reported in the literature. The values of fluoride ion uptake found in this work are significantly higher than reported elsewhere.

3.7. Desorption studies

Among different eluents 0.1 N NaOH was chosen as it was found to be effective, non-damaging and non-polluting desorbent. The fixed bed column of CA and CCCA beads saturated with fluoride was regenerated by passing 0.1 N NaOH as an eluent at an fixed flow rate of 1 ml/min. Figs. 13 and 14 show that the elution curves are sharp at the initial stages of cycle 1, 2, and 3 and decrease with higher eluent volumes. More specifically, maximum desorption 90 and 93% occurs at 30 ml of 0.1 N NaOH solution and complete regeneration 27 and 25% occurs at about 90 and 100 ml volume of 0.1 N NaOH for both CA and CCCA respectively. These adsorption-desorption cycles were repeated thrice. It was observed that there is an early saturation of the bed with fluoride ion in 2nd and 3rd cycles. The regenerated column was further used for the removal of fluoride. The results indicate that the column gets saturated early and the adsorption capacity decreases slightly. As a result the percent desorption also decreases from first cycle to second cycle. Similar behaviour is observed in case of third cycle of adsorption-desorption experiments.
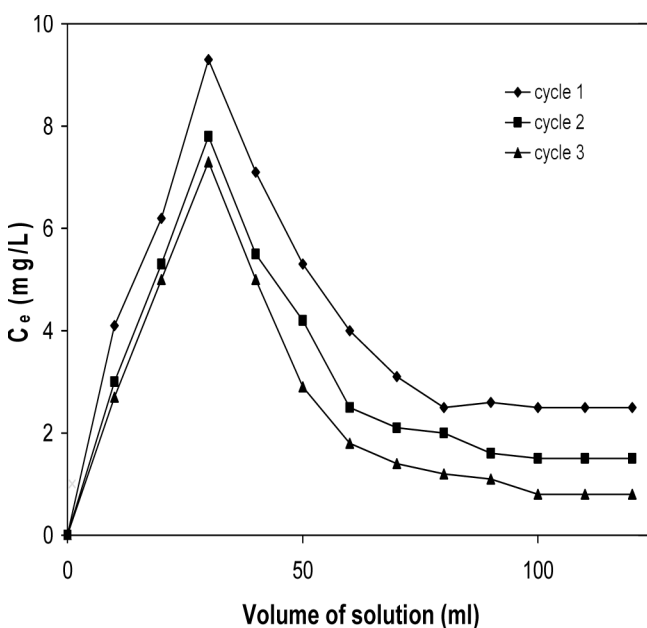
4. Conclusions

The results of this study indicate that the chitosan coated calcium alginate is an effective adsorbent for removal of fluoride from aqueous solution, which is much better than calcium alginate. The adsorption of fluoride on the surface of the adsorbent is found to depend on the pH of the solution as well as on the concentration of fluoride ion. The adsorption of fluoride at acidic pH (pH 6 for CA and 5 for CCCA) is high as compared to alkaline pH. From the kinetic studies, it is found that fluoride removal is complex and both the surface adsorption as well as intraparticle diffusion contribute to the rate-determining step. The data were fitted to Langmuir and Freundlich adsorption isotherms. The maximum monolayer adsorption of fluoride on CA and CCCA found to be 29.3 and 42.0 mg/g. Column adsorption and desorption experiments show that it is possible to fully remove the fluoride ions bound with the adsorbent and regenerate the adsorbent.

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Fig. 13. Desorption curves of fluoride adsorbed on calcium alginate (CA) (desorbing agent NaOH; contact time 120 min; flow rate = 1 ml/min).
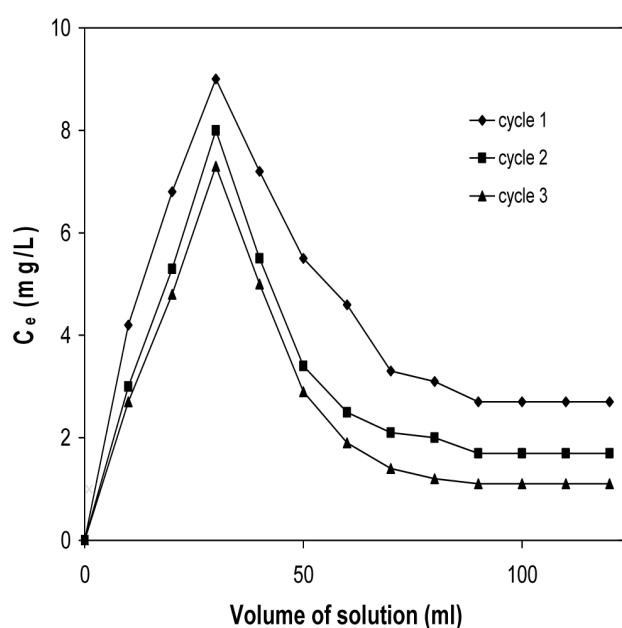

Fig. 14. Desorption curves of fluoride adsorbed on chitosan coated calcium alginate (CCCA) (desorbing agent NaOH; contact time = 120 min; flow rate = 1 ml/min).

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