Chemical Engineering Journal 129 (2007) 173–180

Chemical Engineering Journal

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# Defluoridation of drinking water using chitin, chitosan and lanthanum-modified chitosan

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Received 16 August 2006; received in revised form 16 October 2006; accepted 20 October 2006

**Abstract**

Chitin, a naturally occurring abundant biopolymer, and its deacetylated product chitosan has been widely used for metal adsorption from water and wastewaters, but the application of these materials as an adsorbent to remove fluoride from drinking water has seldom been explored. In this work the applicability of chitin, chitosan and 20%-lanthanum incorporated chitosan (20% La-chitosan) as adsorbents for the removal of excess fluoride from drinking water was studied. The effects of various physico-chemical parameters such as pH, adsorbent dose, initial fluoride concentration and the presence of interfering ions on adsorption of fluoride were studied. It was observed that the uptake of fluoride was maximum at original pH (pH 6.7). The equilibrium adsorption data were fitted reasonably well for Freundlich isotherm model. The presence of chloride, sulfate, carbonate and bicarbonate ions in drinking water greatly affect the uptake of fluoride indicating that these anions compete with sorption of fluoride on 20% La-chitosan. The rate of adsorption was rapid and maximum fluoride uptake was attained within 20 min. The mechanism of adsorption of fluoride on lanthanum-modified chitosan is also explained. The comparison of uptake of fluoride in distilled water and field water shows relatively higher uptake of fluoride in distilled water. This could be due to the competing effect of other anions present and higher pH of the field water.

*Keywords:* Defluoridation; Chitin and modified chitosan; Effects of pH and anions; Freundlich isotherm model; Kinetic modeling

## 1. Introduction

The presence of fluoride ion in potable water has adverse effects on human health. According to the World Health Organization (WHO) the maximum acceptable concentration of fluoride in drinking water lies below 1.5 $\text{mg l}^{-1}$ [1]. Fluoride is attracted by positively charged calcium in teeth and bones due to its strong electro-negativity, which results in dental, skeletal, and non-skeletal forms of fluorosis, in children as well as adults [1,2]. Nineteen states in India were identified as fluorosis affected states including Madhya Pradesh, which was the study area for present work. 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]. Increasing fluoride concentration in water has already become a very serious issue in many countries [1,4]. Traditional treatment methods such as chemical precipitation as metal hydroxide, electro deposition, ion exchange, and membrane separation have been attempted. The adsorption process is a widely accepted pollution-removal technique, because of its ease of operation and cost-effectiveness. Different types of adsorbents such as natural, synthetic, and biomass, are used for removal of fluoride from water [5].

Chitin is an interesting and abundant polysaccharide, found in a wide range of organisms including bacteria and fungi, but commercially most commonly extracted from shellfish processing waste. It is generally considered to be, the most abundant biopolymer in the ecosphere after cellulose, which it resembles structurally. Chitosan is a copolymer of 2-glucosamine and *N*-acetyl-2-glucosamine, derived from chitin, by deacetylation reaction in hot alkali. The structural unit for chitin and chitosan was shown in Fig. 1. Chitosan is mainly obtained from crustacean shells of prawn, crab, shrimp or lobster and has the ability to coordinate metal ions because of its high concentration

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1385-8947/$ – see front matter © 2006 Published by Elsevier B.V.
doi:10.1016/j.cej.2006.10.032

**Nomenclature**

| | |
|---|---|
| $C_0$ | initial concentrations of fluoride ($mg\,l^{-1}$) |
| $C_e$ | equilibrium concentrations of fluoride ($mg\,l^{-1}$) |
| $K_{ad}$ | rate constant ($min^{-1}$) |
| $K_F$ | Freundlich constants related to adsorption capacity ($mg\,g^{-1}$) |
| $K_p$ | intraparticle diffusion rate constant ($mg\,g^{-1}\,min^{-1/2}$) |
| $n$ | adsorption intensity (heterogeneity factor) |
| $q$ | amount of fluoride adsorbed per unit mass of adsorbent at time $t$ ($mg\,g^{-1}$) |
| $q_e$ | equilibrium adsorbate capacity ($mg\,g^{-1}$) |
| $V$ | volume of the aqueous solution (l) |
| $W$ | mass of adsorbent (g) |

of amine functional groups [6]. It is also a non-toxic, biodegradable and biocompatible material. In spite of its abundant use, the adsorption ability of chitosan has not been realized to a satisfying level because chitosan flake or powder swells and crumbles, and hence often unsuitable for use in an adsorption column [7]. Chitosan also has a tendency to agglomerate or form a gel in aqueous media. Although the amine and hydroxyl groups in chitosan are mainly responsible for adsorption, these active binding sites are not readily available for sorption when it is in a gel or in its natural form. The adsorption capacity can be enhanced by spreading chitosan on physical supports that can increase the accessibility of the adsorbate-binding sites [8].

A number of publications have been reported mainly on alumina, calcium, ferrous-modified clays, however, only few articles have been reported on defluoridation of drinking water using biopolymer adsorbent. Recently, Ma et al. [9] studied adsorption of fluoride on magnetic-chitosan particle from the water solution in the batch system. The different types of adsorption isotherms were used to describe adsorption equilibrium. The effect of temperature and kinetic of adsorption are also studied.

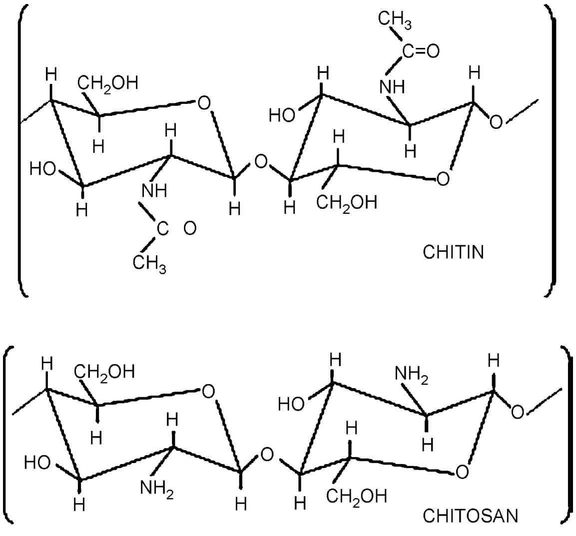


Fig. 1. Structure of chitin and chitosan unit.

Annouar et al. [10] studied defluoridation of underground water by adsorption on the chitosan and by electrodialysis with the help of the CMX-ACS membranes. A comparison of the two processes is also reported.

The present investigation deals with adsorption of fluoride on chitin, chitosan and chemically modified chitosan. The effects of the various physico-chemical parameters such as pH, adsorbent dose, initial fluoride concentration and presence of interfering ions on adsorption of fluoride were investigated. Ground water samples collected from Dhar district of Madhya Pradesh, India, were also used for fluoride removal studies.

## 2. Experimental

### 2.1. Materials

All chemicals used in the present study were of analytical reagent grade. Chitin and chitosan were purchased from Kemphasol, Mumbai and Chemchito Natural Products, Chennai, India, respectively. Sodium fluoride, sodium chloride, sodium sulfate, sodium nitrate, sodium carbonate and sodium bicarbonate was obtained from E. Merck India Ltd., Mumbai, India. Lanthanum acetate was purchased from Himedia, Mumbai, India. A stock solution of fluoride was prepared by dissolving sodium fluoride in distilled water and working fluoride solution of $5\,mg\,l^{-1}$ was prepared from stock fluoride solution by appropriate dilution.

### 2.2. Synthesis of lanthanum incorporated chitosan (La-chitosan)

One gram of chitosan (85% deacetylated) was stirred with different aqueous solutions with targeted lanthanum ($LaNO_3{\cdot}6H_2O$) loading (5, 10, 20, 30 and 50%) on a magnetic stirrer for 6 h. The chitosan was then filtered using Whatman filter-42 paper and washed with deionized water and dried at 75 °C in oven.

### 2.3. Adsorption experiments

Fifty milliliters of the fluoride solution was taken in a PVC conical flask and known weight of adsorbent material was added into it and then kept on a rotary shaker for 24 h in order to attain the equilibrium. The solution was then filtered through Whatman filter paper no. 42 and the filtrate was analyzed for residual fluoride concentration by ion selective electrode. All adsorption experiments were conducted at room temperature of $30 \pm 2\,°C$. Batch adsorption experiments were conducted to investigate the effect of various parameters like adsorbent dose, initial concentration, presence of interfering ions, pH, etc.

The specific amount of fluoride adsorbed was calculated from:

$$q_e = (C_0 - C_e) \times \frac{V}{W} \tag{1}$$

where $q_e$ is the adsorption capacity ($mg\,g^{-1}$) in the solid at equilibrium; $C_0$, $C_e$ the initial and equilibrium concentrations of fluoride (mg $l^{-1}$), respectively; $V$ the volume of the aqueous solution; $W$ is the mass (g) of adsorbent used in the experiments.

The effect of solution pH on fluoride removal was studied by adjusting the pH of the solution by using 0.1N HCl or 0.1N NaOH. In acidic pH, chitosan is not stable and hence adsorption studies were carried out over the pH ranges of 5–9, which is also of practical importance. As per WHO guideline, the normal range for pH in drinking water lies between 6 and 8.5. The pH of the drinking water mainly depends upon geological characteristic of soil as well as weather condition. The pH of the medium is one of the important parameters, which significantly affects the fluoride adsorption. Hence it is necessary to study the effect of pH on removal of fluoride from drinking water. The effects of the presence of co-anions such as chloride, sulfate, nitrate, carbonate, and bicarbonate were studied at optimum experimental conditions. In the study of the effect of pH, and the presence of anions the pH of the aqueous solution was not controlled.

The reusability of used 20% La-chitosan samples obviously depends on the effectiveness of fluoride removal from used adsorbent. For this study, a certain amount of fluoride from aqueous solution (5 mg $l^{-1}$) was initially allowed to adsorb on 20% La-chitosan samples at original pH. After the adsorption experiment the solid was separated by filtration and dried in air. The dried adsorbent repeatedly subjected for the fluoride removal/adsorption experiments to study the extent of reuse. The comparison of fluoride uptake in distilled water and field water was also studied. The detailed characteristics of field water are given in Table 1.

### 2.4. Method of analysis

After the fluoride adsorption equilibrium studies, the experimental samples were filtered through Whatman filter paper no. 42 and the filtrate was analyzed for residual fluoride concentration by ion selective electrode method using Orion Ion electrode instrument supplied by Thermo Electron Corporation, Witchford, UK. Fluoride estimation was also carried out spectrophotometrically using SPANDS dye and a Chemito make UV–vis spectrophotometer (Model UV 2100). The lanthanum if any released from adsorbents after the equilibrium was estimated by ICP-AES (model OPTIMA 4100DV) method. Blank experiments were also carried out to investigate the possibility of any contribution by filter paper, etc. Most of the experiments were repeated twice for better accuracy. The experimental error was observed to be within ±2%. Similar procedure was used for experiments on effect of anions, initial concentrations and pH, etc.

Table 1
Detailed characteristics of field water

| Parameters | Value |
|---|---|
| Turbidity in NTU | <1 |
| Total hardness as $CaCO_3$ (mg $l^{-1}$) | 60 |
| Total iron as Fe (mg $l^{-1}$) | <0.01 |
| Chloride as Cl (mg $l^{-1}$) | 292 |
| Fluoride as F (mg $l^{-1}$) | 10.2 |
| Nitrate as $NO_3$ (mg $l^{-1}$) | <0.01 |
| Sulfate as $SO_4$ (mg $l^{-1}$) | 101 |
| Alkalinity as $CaCO_3$ (mg $l^{-1}$) | 37 |
| Total dissolved solids (mg $l^{-1}$) | 477 |
| pH | 7.0 |
| Cadmium (mg $l^{-1}$) | <0.002 |
| Chromium (mg $l^{-1}$) | <0.002 |
| Copper (mg $l^{-1}$) | <0.01 |
| Lead (mg $l^{-1}$) | <0.002 |
| Manganese (mg $l^{-1}$) | 0.01 |
| Zinc (mg $l^{-1}$) | 0.25 |
| Arsenic (mg $l^{-1}$) | 0.008 |
| Aluminum (mg $l^{-1}$) | 0.023 |

## 3. Results and discussion

### 3.1. Effect of lanthanum loading on chitosan

In order to the study the effect of lanthanum loading on chitosan for the removal of fluoride, the lanthanum loading was varied from 5 to 50 wt.%. The effect of lanthanum loading on the removal of fluoride from water is shown in Fig. 2. It was observed that 20% lanthanum loading is optimum, probably because of two reasons: (i) at higher loading lanthanum release was increased and (ii) permissible fluoride limit in drinking water was achieved at 20% lanthanum loading. Hence 20% lanthanum loading was used for further experiments.

### 3.2. Preliminary adsorption experiments

The preliminary adsorption experiments under identical set of experimental conditions were carried out using chitin, chitosan and 20% La-chitosan. The percentage removal of fluoride by chitin, chitosan and 20% La-chitosan is shown in Fig. 3. It was observed that the 20% La-chitosan shows much better fluoride removal capacity and affinity as compared to the untreated

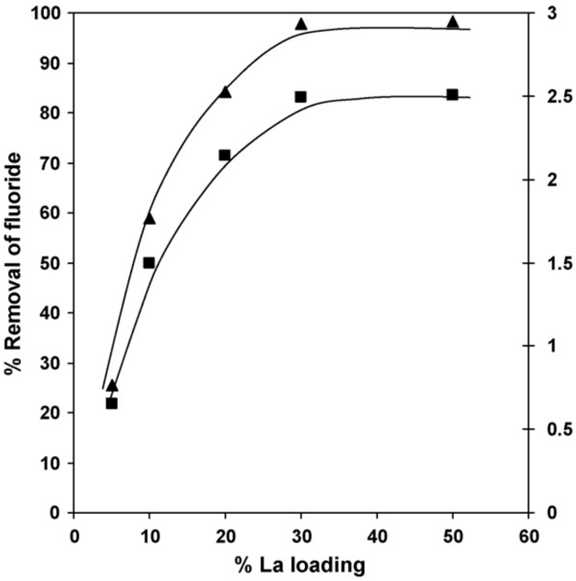


Fig. 2. Effect of lanthanum loading on chitosan for fluoride adsorption (pH 6.7, contact time = 24 h). (▲) % removal of fluoride; (■) equilibrium adsorption capacity ($q_e$) mg $g^{-1}$.

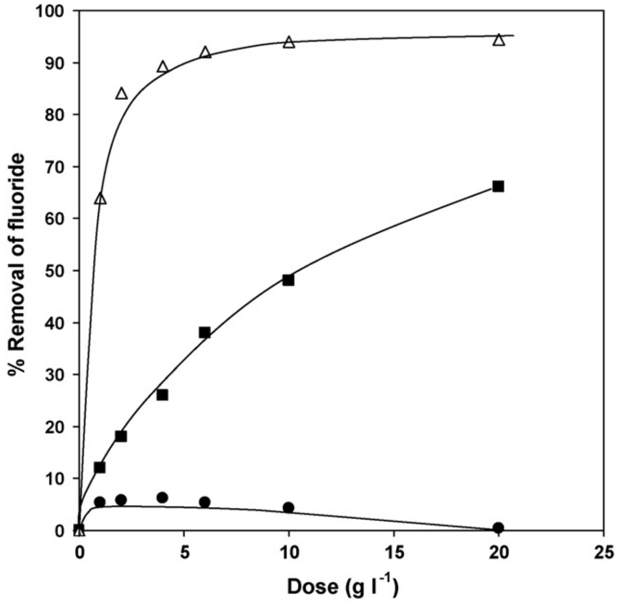


Fig. 3. Comparison of chitin, chitosan and 20% La-chitosan for fluoride removal (pH 6.7, contact time = 24 h). (■) Chitin; (●) chitosan; (△) 20% La-chitosan.

chitin and chitosan. Therefore, further experiments were carried out using 20% La-chitosan for optimization of adsorption parameters.

### 3.3. Effect of adsorbent dose

The effect of adsorbent dose on fluoride removal at fixed initial fluoride concentration is shown in Fig. 4. It was observed that percentage removal of fluoride increased with the increase in adsorbent dose while loading capacity (amount of fluoride loaded per unit weight of adsorbent) gradually decreased for the same. The maximum loading capacity for fluoride was found to be 3.1 mg g$^{-1}$ at an adsorbent dose of 1.5 g l$^{-1}$. This increase in loading capacity is due to the availability of higher number of fluoride ions per unit mass of adsorbent, i.e. higher fluoride/adsorbent ratio. It can also be seen that the fluoride removal markedly increased up to adsorbent dose of 6 g l$^{-1}$ due to increase in adsorbent/fluoride ratio however further increase in adsorbent dose not show any appreciable improvement in fluoride removal. This may be because of the very low equilibrium concentration of fluoride, i.e. driving force responsible for adsorption becomes negligible.

This also indicates the effect of equilibrium concentration on fluoride uptake. It appears that the fluoride removal uptake is relatively very low at lower fluoride concentration.

### 3.4. Effect of initial fluoride concentration

Effect of initial concentration on the percentage removal of fluoride was studied at different initial fluoride concentrations by keeping other parameters constant. The effect of initial concentration on removal of fluoride was shown in Fig. 5. It was observed that with the increase in fluoride initial concentration, the percentage removal of fluoride decreases. This may be because at higher adsorbate concentration, the binding capacity of the adsorbent approaches saturation, resulting in decrease of overall percent removal.

### 3.5. Effect of pH

The pH of the medium is one of the important parameters, which significantly affects the fluoride adsorption. The uptake of fluoride by 20% La-chitosan was investigated in the pH range of 5–9 and is shown in Fig. 6. Maximum adsorption was observed at pH 6.7 while in acidic and alkaline pH the fluoride removal was observed to decrease. The progressive decrease of fluoride

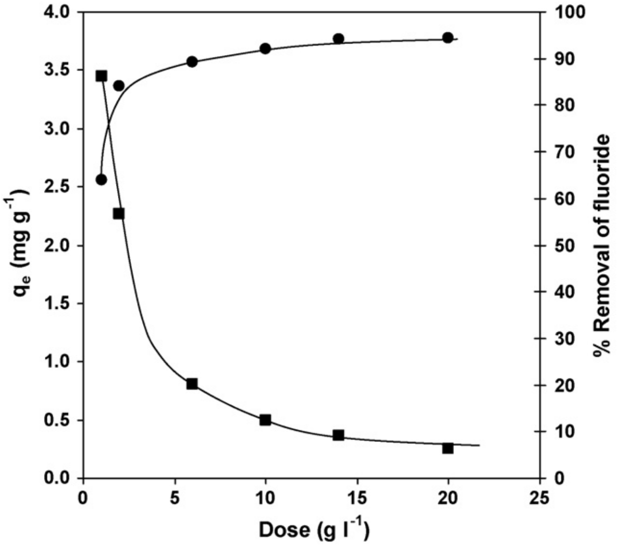


Fig. 4. Effect of adsorbent dose for adsorption of fluoride (pH 6.7, contact time = 24 h). (●) % removal of fluoride; (■) equilibrium adsorption capacity ($q_e$) mg g$^{-1}$.

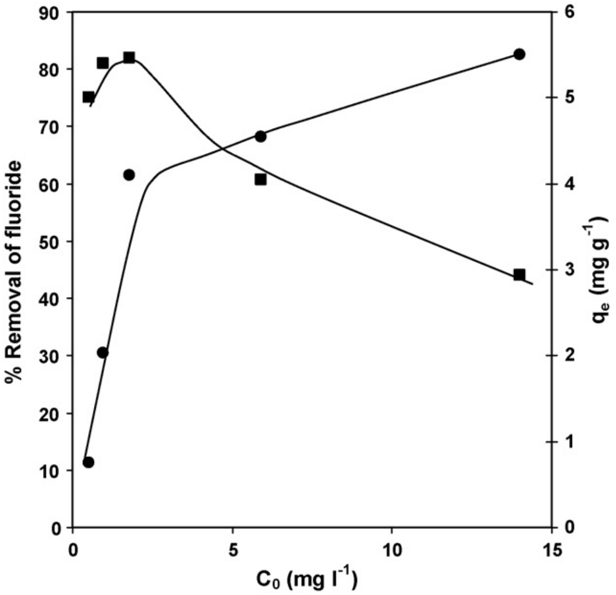


Fig. 5. Effect of concentration on adsorption of fluoride (contact time = 24 h, pH 6.7). (●) % removal of fluoride; (■) equilibrium adsorption capacity ($q_e$) mg g$^{-1}$.

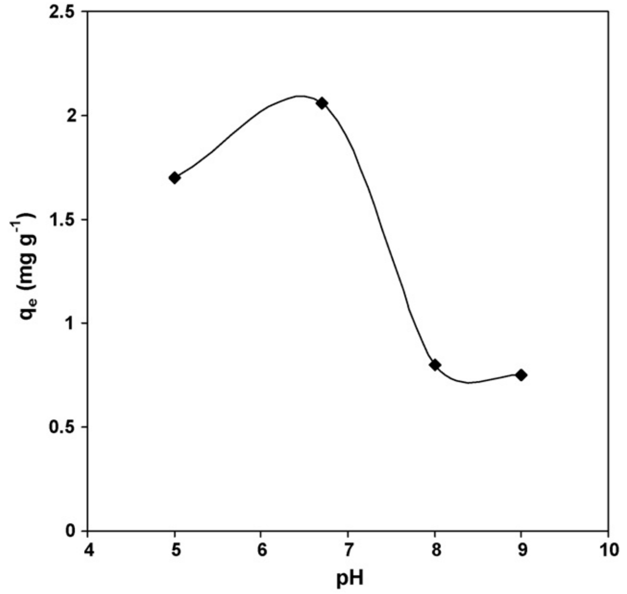


Fig. 6. Effect of pH on adsorption of fluoride (initial concentration = 5 mg $l^{-1}$; optimum dose = 2 g $l^{-1}$; contact time = 24 h).

uptake at alkaline pH could be mainly due to two factors: the electrostatic repulsion of fluoride ion to the negatively charged surface of the 20% La-chitosan and the competition for active sites by excessive amount of hydroxyl ions. The effect of pH on adsorption of fluoride in highly acidic pH (below pH 5) was not investigated because La-chitosan is not stable.

### 3.6. *Effect of the presence of other co-anions*

The fluoride-contaminated drinking water almost always contains several other anions, which can compete in the adsorption process. In order to study the effect of interfering ions, the adsorption studies were carried out in presence of 0.1 M salt solutions of chloride, sulfate, nitrate, carbonate and bicarbonate, separately. The effect of anions on removal of fluoride is shown in Fig. 7. From the adsorption experiment results, it was observed that $Cl^-$, $SO_4{}^{2-}$, $NO_3{}^-$, $HCO_3{}^-$ and $CO_3{}^{2-}$ ions show negative effect on removal of fluoride. It was also found that both the anions $HCO_3{}^-$ and $CO_3{}^{2-}$ showed practically no removal of fluoride. This may be because of the change in pH as well as the competing effect of these co-anions. The pH of the fluoride solution were 7.9, 7.0, 6.97, 8.26, 10.9, respectively, for $Cl^-$, $SO_4{}^{2-}$, $NO_3{}^-$, $HCO_3{}^-$ and $CO_3{}^{2-}$ while the pH of the fluoride solution was 6.7 without addition of salt/anions. This indicates that addition of salt resulted in increased pH of fluoride solution. From our experiments on effect of pH (Section 3.5) it was observed that the adsorption of fluoride decreases in alkaline pH as also explained. Another observation was found that in the absence of anions, lanthanum release was a very negligible amount (below detection limit), while at alkaline pH and in the presence of anions lanthanum release increased marginally from 0.213 to 1.050 mg $l^{-1}$, this indicates that active lanthanum sites available at alkaline pH will be relatively less for adsorption of fluoride.

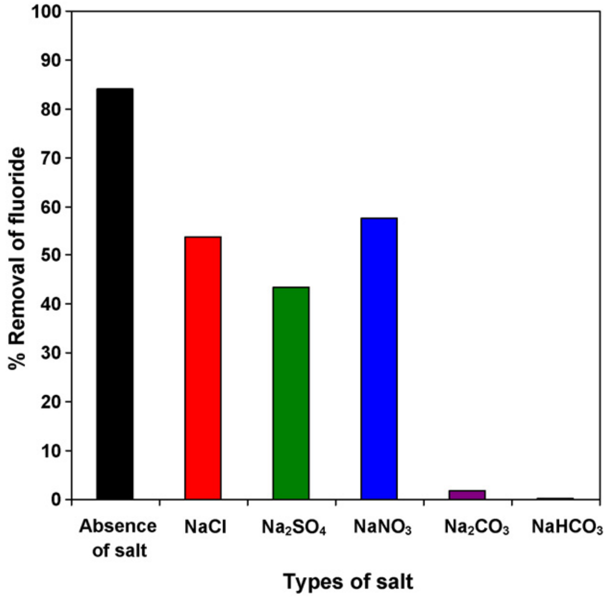


Fig. 7. Effect of the presence of anions on removal of fluoride (initial concentration = 5 mg $l^{-1}$; optimum dose = 2 g $l^{-1}$; contact time = 24 h). (■) Adsorption of fluoride in the absence of salt; (🟥) adsorption of fluoride in the presence of 0.1 M sodium chloride (NaCl); (🟩) adsorption of fluoride in the presence of 0.1 M sodium sulfate ($Na_2SO_4$); (🟦) adsorption of fluoride in the presence of 0.1 M sodium nitrate ($NaNO_3$); (🟪) adsorption of fluoride in the presence of 0.1 M sodium carbonate ($NaCO_3$); (☐) adsorption of fluoride in the presence of 0.1 M sodium bicarbonate ($NaHCO_3$).

The overall effect, therefore, is decrease in the removal of fluoride from water mainly due to the increased pH of the solution and competing effect of anions as well as lesser active lanthanum sites available for adsorption process.

## 4. Equilibrium modeling

The distribution of fluoride between the liquid phase and the solid phase is a measure of the position of equilibrium in the adsorption process and can be expressed by the Freundlich and Langmuir equations. The Freundlich model, which is indicative of surface heterogeneity of the sorbent, is given by the following linearized equation:

$$\log(q_e) = \log K_F + \frac{1}{n}\log(C_e) \qquad (2)$$

where $K_F$ and $n$ are Freundlich constants related to adsorption capacity and adsorption intensity (heterogeneity factor), respectively. To determine the equilibrium isotherms, adsorbent dose were varied, while the initial concentration of fluoride was kept constant. The value of $K_F$ observed for 20% La-chitosan and chitin are 1.27 and 0.344 mg $g^{-1}$, respectively, while $n$ is 0.70 and 0.897 for Freundlich isotherm. The $K_F$ and $n$ value for chitosan was not calculated because very negligible adsorption of fluoride was observed (Fig. 2). Since the value of the constant, $n$ (adsorption intensity) is less than unity, it indicates a favorable adsorption. The value of Freundlich constants ($K_F$) and adsorption intensity ($n$) for 20% La-chitosan are high as compared to chitin, which indicate the higher adsorption capacity as well as adsorption intensity for 20% La-chitosan.

## 5. Kinetic of adsorption of fluoride on 20% La-chitosan

The kinetics of adsorption was studied to explain the fluoride uptake mechanism in the present material. It was observed that the uptake of fluoride increases with time. However, the adsorption of fluoride was rapid in the first 30 min after which the rate slowed down as the equilibrium approached. The rate constant ($K_{ad}$) for adsorption was determined from the following Lagergren first order rate expression [11]:

$$\log(q_e - q) = \log q_e - \frac{K_{ad}}{2.303} \times t \tag{3}$$

where $q_e$ and $q$ (both in $\mathrm{mg\,g^{-1}}$) are the amount of fluoride adsorbed per unit mass of adsorbent at equilibrium and time $t$, respectively, and $K_{ad}$ is the rate constant ($\mathrm{min^{-1}}$).

The value of $K_{ad}$ was calculated from the slope of the linear plot of $\log(q_e - q)$ versus time (Fig. 8). The adsorption rate constants were found to be 0.0208, 0.0166 and 0.0151 $\mathrm{min^{-1}}$ for initial fluoride concentration of 5.26, 9.8 and 14.9 $\mathrm{mg\,l^{-1}}$, respectively. The variation in adsorption rate should be proportional to the first power of concentration for strict surface adsorption. However, the relationship between initial solute concentration and the rate of adsorption will not be linear when pore diffusion limits the adsorption process. The possibility was investigated in terms of a graphical relationship between amount of fluoride adsorbed and square root of time (Fig. 9). In order to show the existence of intraparticle diffusion in the adsorption process, the amount of fluoride sorbed per unit mass of adsorbents, $q$ at any time $t$, was plotted as a function of square root of time, $t^{1/2}$. The rate constant for intraparticle diffusion was obtained using the following equation:

$$q = K_p \times t^{0.5} \tag{4}$$

where $K_p$ ($\mathrm{mg\,g^{-1}\,min^{-1/2}}$) is the intraparticle diffusion rate constant. The plot for intraparticle diffusion shows that initially curved portion reflects film or boundary layer diffusion effect and the subsequent linear portion attribute to the intraparticle diffusion effect. Fig. 9 depicts that intraparticle diffusion is slow and the slope of the linear portion of the curve at each solute concentration gives the value of $K_p$. The $K_p$ values were found to be 0.066, 0.0461 and 0.0923 $\mathrm{mg\,g^{-1}\,min^{-1/2}}$ at initial fluoride concentration of 5.26, 9.8 and 14.9 $\mathrm{mg\,l^{-1}}$, respectively. This suggests that the adsorption is governed by intraparticle diffusion. The linear portions of the curves do not pass through the origin (Fig. 9) indicating that mechanism of fluoride removal on 20% La-chitosan is complex and both the surface adsorption as well as intraparticle diffusion contributes to the rate-determining step.

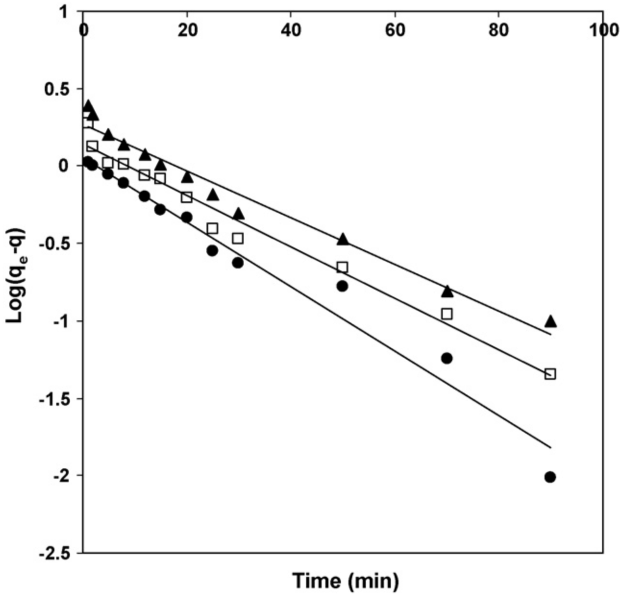


Fig. 8. Lagergren plot for the adsorption of fluoride (pH 6.7). (●) Initial concentration of fluoride = 5.26 $\mathrm{mg\,l^{-1}}$; (□) initial concentration of fluoride = 9.8 $\mathrm{mg\,l^{-1}}$; (▲) initial concentration of fluoride = 14.9 $\mathrm{mg\,l^{-1}}$.

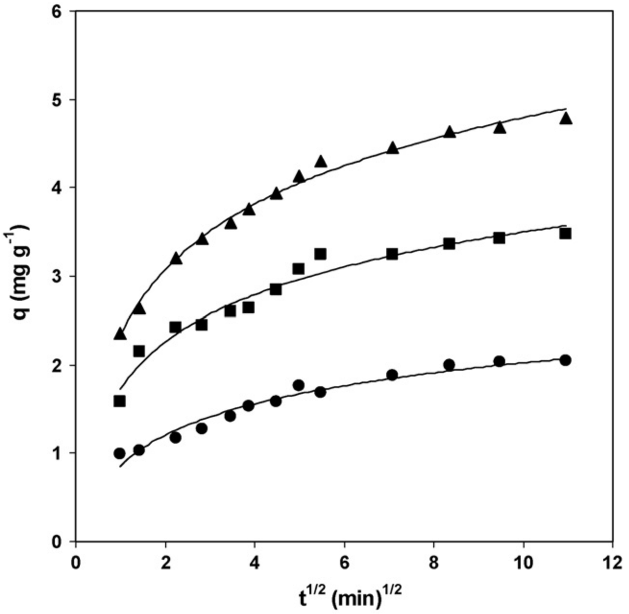
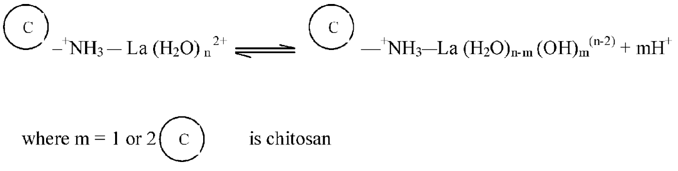


Fig. 9. Intraparticle mass transfer curve for adsorption of fluoride on (pH 6.7). (●) Initial concentration of fluoride = 5.26 $\mathrm{mg\,l^{-1}}$; (■) initial concentration of fluoride = 9.8 $\mathrm{mg\,l^{-1}}$; (▲) initial concentration of fluoride = 14.9 $\mathrm{mg\,l^{-1}}$.

## 6. Mechanism of adsorption of fluoride on La-chitosan

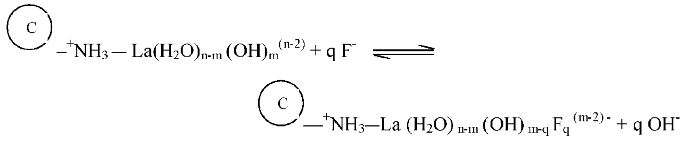
The amount of fluoride adsorbed decreased with the increase of pH. There was sharp drop in fluoride adsorption at pH 7 and above. This result could be interpreted in terms of the ligand exchange mechanism between fluoride ion and hydroxide ion coordinated on lanthanum(III) ion immobilized on the chitosan according to the reactions shown below:



$$\text{C}-{}^{+}\mathrm{NH_3}-\mathrm{La(H_2O)_n}^{2+} \rightleftharpoons \text{C}-{}^{+}\mathrm{NH_3}-\mathrm{La(H_2O)_{n-m}(OH)_m}^{(n-2)} + m\mathrm{H^+}$$

where m = 1 or 2 C is chitosan

(5)



$$\text{C}-{}^{+}NH_3-La(H_2O)_{n-m}(OH)_m^{(n-2)}+q\,F^- \rightleftharpoons \text{C}-{}^{+}NH_3-La(H_2O)_{n-m}(OH)_{m-q}F_q^{(m-2)-}+q\,OH^-$$

where q = 1 or 2

(6)

On dissolution of lanthanum nitrate in water the pH is about 4.0–4.5. When chitosan is suspended in this solution of lanthanum nitrate then the amino groups are protonated. The lanthanum ion also undergoes coordination with water molecules to form the ligand, which then coordinates with protonated amino groups. The water molecules coordinated with lanthanum(III) ion deprotonate to release some hydrogen ions to form hydroxyl ion coordinated on the lanthanum(III) ion as pH increased. The hydroxyl ion was further substituted by fluoride ion according to the ligand exchange mechanism. Eq. (5) showed that the amount of hydroxyl ions coordinated on La(III) and consequently the number of fluoride ion adsorption sites increased with the increase of pH. Nevertheless, according to the ligand exchange reaction expressed by Eq. (6), fluoride adsorption decreased as the pH increased at high pH. The ligand exchange reaction described in Eq. (6) could be confirmed by the fact that pH was increased after the adsorption of fluoride. The pH also increased with the increase of pH at low pH, since the amount of hydroxyl ions coordinated on lanthanum(III) ions and the number of fluoride ion adsorption sites increased with the increase of pH.

## 7. Comparison of fluoride uptake in distilled water and field water

The uptake of fluoride from field samples (Dhar, Tarapur) collected from Madhya Pradesh, India and distilled water by using 20% La-chitosan is shown in Fig. 10. It was observed that the percentage removal of fluoride in distilled water is significantly high as compared to field water sample. This could be due to two reasons: (i) pH of the field water samples is alkaline and (ii) it contains different types of cations and anions. The detailed characteristics of field water are given in Table 1. Table 1 shows that field water contains different types of ions. These ions compete with adsorption of fluoride on 20% La-chitosan and reduce the adsorption of fluoride. In Section 3.5, it has been discussed that in the alkaline pH uptake of fluoride is low as compared to acidic pH. Therefore, overall removal of fluoride in field water is low as compared to distilled water.

## 8. Regeneration and reuse of adsorbents

A fluoride adsorption experiment was performed with oven dried used 20% La-chitosan to determine its reusability. As can be seen from Fig. 11, the used adsorbent has slightly less adsorption capacity as compared to fresh 20% La-chitosan. The fluoride removal decreases by 2.5, 11 and 15.2%, respectively, after 1st, 2nd and 3rd use of adsorbent. However, it may be possible to regenerate the adsorbent by the alkali–acid treatment. The studies on optimization regeneration process are under progress.

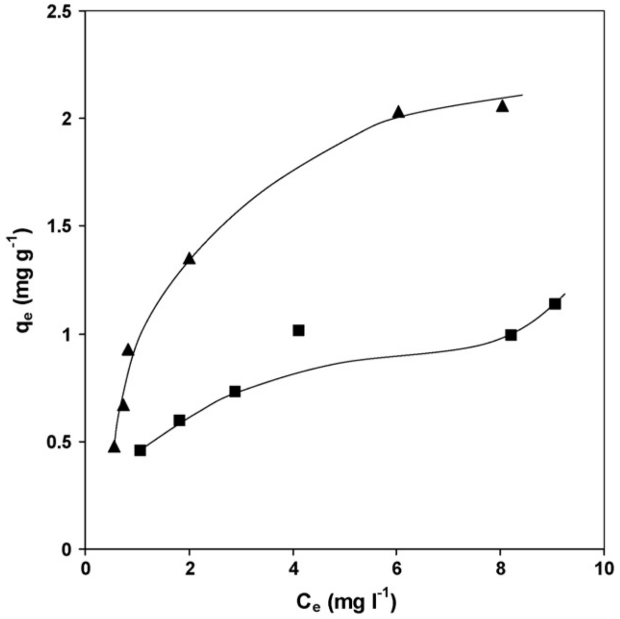


Fig. 10. Comparison of adsorption of fluoride in distilled water and field water (initial concentration = 10.2 mg l$^{-1}$; optimum dose = 2 g l$^{-1}$; contact time = 24 h). (▲) Distilled water; (■) field water.

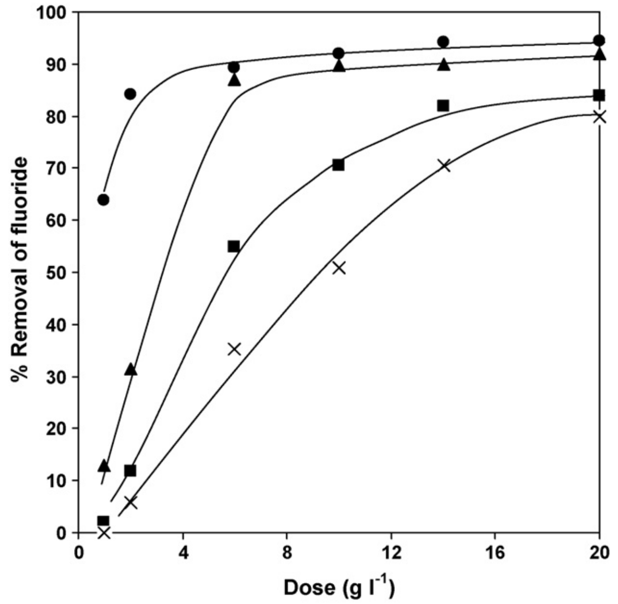


Fig. 11. Reusability of adsorbent for removal of fluoride. (●) Fresh adsorbent; (▲) 1st reuse; (■) 2nd reuse; (×) 3rd reuse.

## 9. Conclusions

The conclusions of this article are as follows:

- Lanthanum chitosan adsorbents show excellent removal of fluoride from water, which is much better than bare chitosan and chitin.

- The adsorption of fluoride on the surface of the adsorbent is found to depend mainly on the pH of the solution as well as the concentration and type of co-anions. It was found that the presence of anions has a deleterious effect on the adsorption of fluoride, particularly carbonate and bicarbonate anions. The adsorption of fluoride at acidic pH (pH 5) was high as compared to alkaline pH.
- From the kinetic studies, it was found that fluoride removal is complex and both the surface adsorption as well as intraparticle diffusion contributes to the rate-determining step.
- The mechanism of adsorption of fluoride on lanthanum-modified chitosan can be explained in terms of the ligand exchange mechanism between fluoride ion and hydroxide ion coordinated to lanthanum(III) ion immobilized on the chitosan.
- The percentage removal of fluoride in distilled water was higher than field water; this may be because latter contains different types of ions.
- No significant leaching of lanthanum was observed from the adsorbent, while it was also possible to regenerate the material.

## Acknowledgement

Financial assistance from, UNIECF Bhopal, India for this work is gratefully acknowledged.

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