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Synthesis of La-incorporated chitosan beads for fluoride removal from water

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ABSTRACT

In this study, lanthanum incorporated chitosan beads (LCB) were synthesized using precipitation method and tested for fluoride removal from drinking water. The effect of various parameters like complexation and precipitation time, lanthanum loading and ammonia strength on fluoride removal have been studied. It is observed that the parameters for the synthesis of LCB have significant influence on development of LCB and in turn on fluoride removal capacity. The optimal condition for synthesis of LCB includes lanthanum loading: 10 wt%, complexation time: 60 min, precipitation time: 60 min, drying temperature: 75 °C for 72 h. The maximum fluoride adsorption capacity of LCB was found to be 4.7 mg/g and negligible release of lanthanum ion was observed. XRD analysis shows the presence of lanthanum hydroxide and amorphous nature of LCB. SEM of LCB shows the presence of oval lanthanum hydroxide particles spread over the chitosan matrix. Fluoride adsorption capacity has been calculated by applying Langmuir and Freundlich isotherms. The comparative study suggests that LCB shows four times greater fluoride adsorption capacity than the commercially used activated alumina.

1. Introduction

Fluoride is a dissolved constituent of drinking water and is essential for human as well animal health. Fluoride is perhaps the only substance producing health effect on the consumer depending upon their relative proportions. Fluoride concentration higher than 1.5 mg/L is harmful to the teeth and bone structure of human and animals. The excess intake of fluoride leads to severe dental and skeletal fluorosis [1,2]. Fluoride contamination is a worldwide problem especially in Africa, Asia and United states [3]. Drinking water is the main source for fluoride ingestion to human body therefore it is necessary to remove excess of fluoride. WHO permissible limit for fluoride in drinking water is 1.5 mg/L [4].

The different defluoridation methods developed can be broadly classified into four categories: (a) adsorption method [5], (b) ion exchange [6], (c) precipitation [7] and (d) miscellaneous method (e.g. reverse osmosis) [8]. Activated alumina (AA) is widely used adsorbent for defluoridation of drinking water [9]. Several other adsorbents reported for fluoride removal include oxides [5], zeolite [10], and low cost clays [11].

In our previous publication we have used chitin, chitosan, modified chitosan flakes and LCB for fluoride removal. We have also studied detailed batch studies which includes various parameters such as adsorbent dose, initial fluoride concentration, pH, effect of co-ions, kinetics, thermodynamics of fluoride adsorption and regeneration study of LCB [12,13].

However, there are only a few articles reported for defluoridation of drinking water using lanthanum modified adsorbent. In the present work, synthesis of lanthanum incorporated chitosan beads (LCB) and the effect of different synthesis conditions on fluoride removal has been studied. Lanthanum ion supported on chitosan biopolymer matrix has been investigated for fluoride removal. As lanthanum is highly electropositive, it shows high affinity for highly electronegative fluoride ions [14]. Chitosan is well reported biopolymer for removal of heavy metals from water and wastewater. Chitosan is a cationic biopolymer of 2-glucosamine and N-acetyl-2-glucosamine. The amine groups in chitosan have tendency to form complex with metal ions. Nitrogen acts as an electron donor and hence chitosan co-ordinates with metal ions to form stable complex [15].

The main objective of this study, to utilize the metal binding characteristic of chitosan to incorporate the La(III) metal to develop a new material and to study various parameters for the synthesis of LCB which alters the properties and fluoride adsorption capacity of LCB. However, chitosan naturally occurs in the form of flakes or powder which has a limited utility particularly for column applications due to swelling, low mechanical strength, crumbling, etc. Attempts have also been made to overcome these drawbacks through formation of chitosan beads. The complex formation of lanthanum with chitosan also prevents the leaching of lanthanum ion in treated water.

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2. Materials and methods

2.1. Materials

Chitosan (85% deacetylated) was purchased from local sources. Lanthanum acetate was purchased from Himedia, Mumbai and all other reagents were of analytical grade procured from E. Merck India. Fluoride stock solution of 1000 mg/L was prepared by dissolving 2.21 g anhydrous sodium fluoride in distilled water and making up to 1000 mL in volumetric flask. Working fluoride solutions of 5 mg/L was prepared by appropriate dilution of stock solution.

2.2. Synthesis of LCB

5–9 g of chitosan (85% deacetylated) was dissolved in 200–400 mL of acetic acid (CH_3COOH) solution (5%, v/v). Lanthanum acetate was dissolved in 100–150 mL of distilled water. The lanthanum loading was varied from 1 to 20 wt%. The lanthanum acetate solution was then added to the chitosan solution with stirring for 15–360 min (complexation reaction). The resulting La–chitosan solution was precipitated drop wise into NH_4OH solution (10–50%, v/v) under vigorous stirring, using a syringe pump. The gel macro spheres formed were allowed to stabilize in NH_4OH solution for 15–360 min. The beads were separated from the NH_4OH solution and washed with deionized water and dried at 50–80 °C in oven.

2.3. Adsorption experiment

Batch adsorption studies were carried out with 50 mL of fluoride solution of initial fluoride concentration 5.34 mg/L. The different quantity of the adsorbent was mixed with 50 mL fluoride solution in PVC conical flasks. The flasks were shaken at 150 rpm on a horizontal rotary shaker (Model No. CIS-24, Remi Instruments, Mumbai, India) for 24 h in order to attain equilibrium. The solution was then filtered using Whatman 42 filter paper and the fluoride concentrations were determined in filtrates and the amount of fluoride adsorbed was calculated from following equation [10]:

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

where q_e is the adsorption capacity (mg/g) at equilibrium, C_0 and C_e are the initial and equilibrium fluoride concentrations (mg/L), respectively, V is the volume (mL) of solution and W is the mass (g) of adsorbent used.

2.4. Method of analysis

Fluoride concentrations in the experimental samples were analyzed using a fluoride ion-selective electrode (Orion 9490 on a Sargent Welch Model PAX 900 pH/activity meter). XRD patterns of LCB as such and after fluoride treatment were recorded on Rigaku X-ray diffractometer. The sample was scanned for 2θ range from 10° to 60°. The surface morphology of chitosan and LCB was determined by using scanning electron microscope (JEOL, JXA-840 A) coupled with electron probe microanalyzer at different magnification.

2.5. Synthesis optimization of LCB

Design and development of any new adsorbent involves optimization of synthesis by varying various parameters like reaction stoichiometry, reaction/contact time, temperature, etc. The optimum synthesis of LCB was achieved by synthesizing the LCB under varying conditions of amount of functional moiety, which is lanthanum in this case, reaction time of chitosan and lanthanum, precipitation time, drying temperature, time, etc. The LCB synthesized under different conditions were then evaluated for fluoride removal. Besides fluoride uptake capacities, the stability, mechanical strength, size and shape of beads, etc. were also taken into consideration for final selection of the adsorbent.

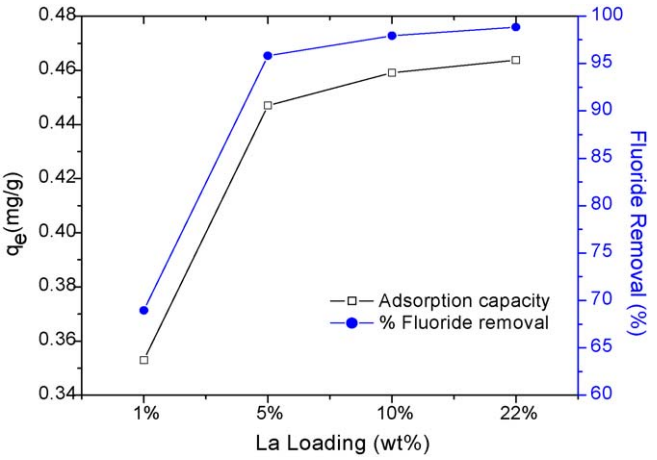

Fig. 1. Effect of La loading on fluoride removal by LCB-10 (initial F concentration 5.34 mg/L, contact time: 24 h, and adsorbent dose: 0.4 g/50 mL).

3. Results and discussion

3.1. Effect of lanthanum loading

The most important parameter from the point of view of fluoride uptake is the lanthanum loading. The lanthanum loading was varied from 1 to 20 wt% (Fig. 1). It is evident from the results that fluoride uptake increases with increase in La loading and maximum uptake was observed for LCB loaded with 20 wt% La. LCB loaded with more than 20 wt% La resulted in only marginal improvement in removal efficiency [13]. However, traces of La release was observed for LCB loaded with more than 10 wt%. Therefore, LCB containing 10 wt% La (LCB-10) was selected for further studies.

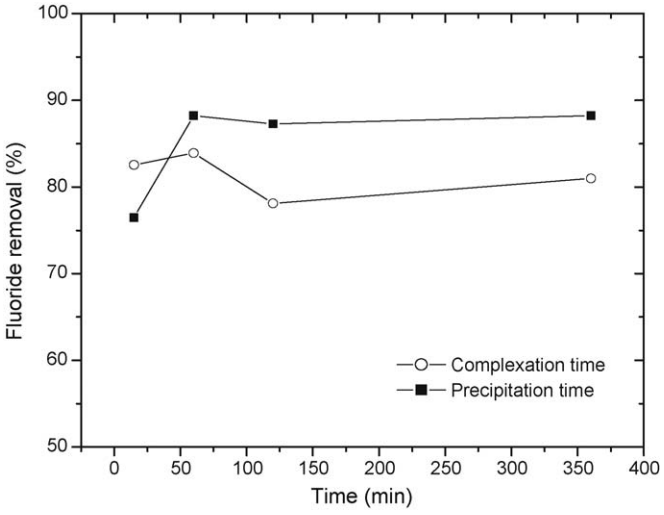

Fig. 2. Effect of complexation time of chitosan and lanthanum and precipitation time in ammonia solution on fluoride removal by LCB-10 (initial F concentration 5.34 mg/L, contact time: 24 h, and adsorbent dose: 0.4 g/50 mL).

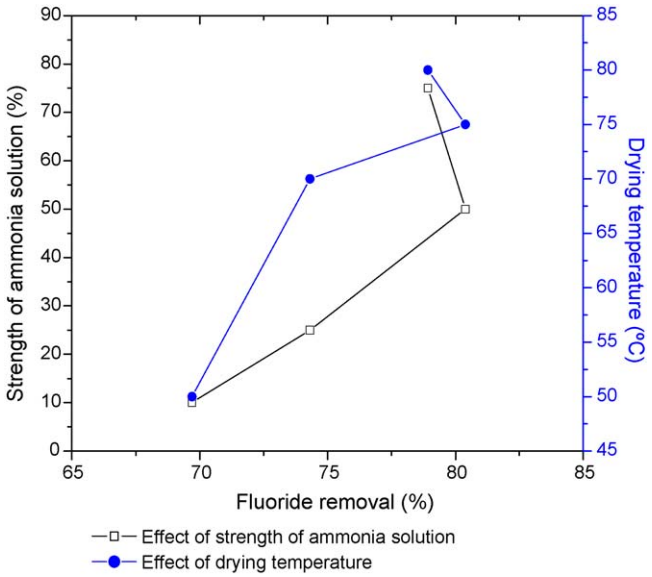

Fig. 3. Effect of concentration of ammonia and drying temperature on fluoride uptake capacities of LCB-10 (initial F concentration 5.34 mg/L, contact time: 24 h, and adsorbent dose: 0.4 g/50 mL).

3.2. Effect of complexation and precipitation time

The effect of complexation time of chitosan and lanthanum and precipitation time in ammonia solution on fluoride removal by LCB-10 is presented in Fig. 2. It was observed that fluoride removal improves slightly when complexation time was increased from 15 to 60 min after which fluoride removal efficiency decreases. Also, LCB-10 beads synthesized with precipitation time of 60 min shows maximum fluoride uptake. No further increase in fluoride uptake capacity was observed with the increase in precipitation time from 60 to 360 min.

3.3. Effect of ammonia concentration

Fig. 3 shows the fluoride uptake capacities of LCB-10 synthesized with precipitation using different concentrations of ammonia solution ranging from 10 to 75%. As evident from the results, the maximum fluoride uptake was shown by LCB-10 synthesized with precipitation in 50% ammonia solution. Also, it was observed that the non-uniform flaky beads were obtained when lower strength of ammonia solution was taken.

3.4. Effect of drying temperature

Fig. 3 also shows the effect of drying temperature on fluoride uptake. The drying temperature was varied from 50 to 80 °C. Drying steps also shows significant impact on the shape, stability and strength of beads. The beads dried at temperatures other than 75 °C shows not only lower fluoride uptake, but also results in unstable beads, which swells in water suspension.

The results obtained from the optimization studies reveal that optimal parameters for the synthesis of LCB for LCB-10 are lanthanum loading: 10 wt%, complexation time: 60 min, precipitation time: 60 min, drying temperature: 75 °C for 72 h.

3.5. Characterization of LCB

Fig. 4a and b shows the XRD of LCB and LCB after treatment with fluoride respectively and Fig. 4c shows SEM of LCB. XRD pattern of LCB (Fig. 4a) shows amorphous nature of adsorbent, which allows a better accessibility to fluoride and thus a better activity. The peak at

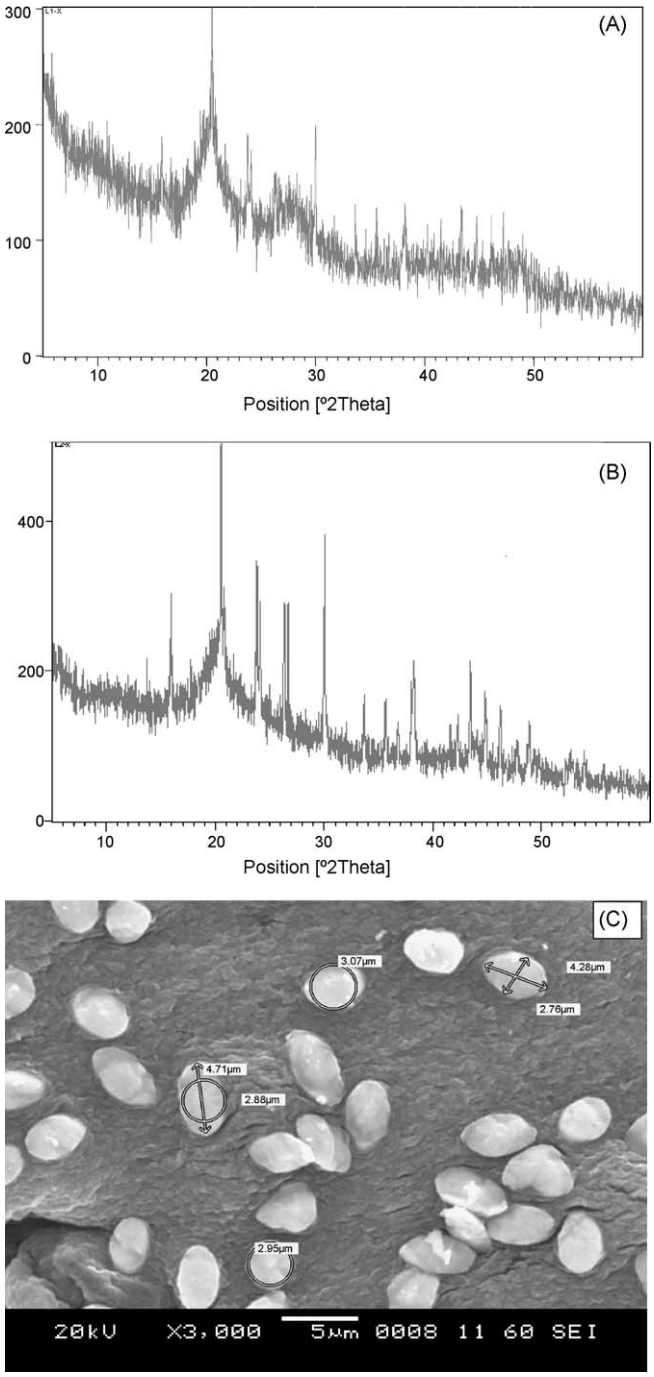

Fig. 4. XRD of (A) LCB, (B) LCB after fluoride treatment and (C) SEM of LCB.

$2\theta = 30°$, 43.35°and 49.78° shows the presence of lanthanum hydroxide [13]. XRD pattern of LCB after fluoride treatment (Fig. 4b) shows peaks at $2\theta = 24.11°$, 27° and 44.82° which can be assign to lanthanum fluoride formation (JCPDS 84-0943). SEM micrograph of LCB-10 (Fig. 4c) reveals dense and firm structure with minimum porosity and small oval shaped particles of lanthanum hydroxide of diameter 2.5–3.0 μm and length of 4.0–5.0 μm uniformly spread over the surface of chitosan [13]. The optimum size of LCB-10 was found in the range of 1114.76–1154.81 μm.

3.6. Fluoride removal by LCB

A preliminary adsorption experiment was carried out using LCB-10, chitosan and AA at initial F^- concentration 5 mg/L, contact

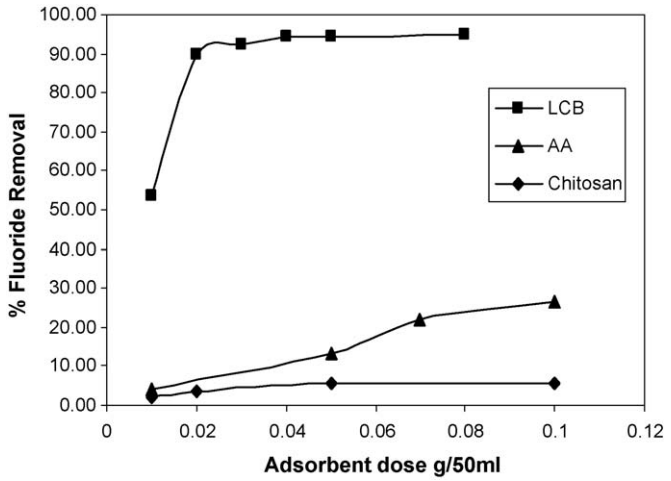

Fig. 5. Fluoride removal by LCB-10, AA and chitosan (volume: 50 mL, temperature: 30 ± 1 °C, initial F concentration: 5.35 mg/L, and contact 24 h).

time 24 h, to compare the fluoride removal efficiency of LCB with chitosan and AA. Fig. 5 shows the plot of C_e versus q_e for LCB-10. It is observed that chitosan has no significant fluoride removal capacity. LCB-10 shows much higher fluoride removal efficiency compared to chitosan and AA.

3.7. Adsorption capacity

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.

These two models are widely used, the former being purely empirical and the latter assumes that maximum adsorption occurs when the surface is covered by the adsorbate. The Freundlich model, which is an indicative of surface heterogeneity of the sorbent, is given by the following linearized equation [16]:

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

where K_F and $1/n$ are Freundlich constants related to adsorption capacity and adsorption intensity, respectively (Fig. 6). The value of K_F is 0.106 mg/g and n is 0.864 for Freundlich isotherm. The

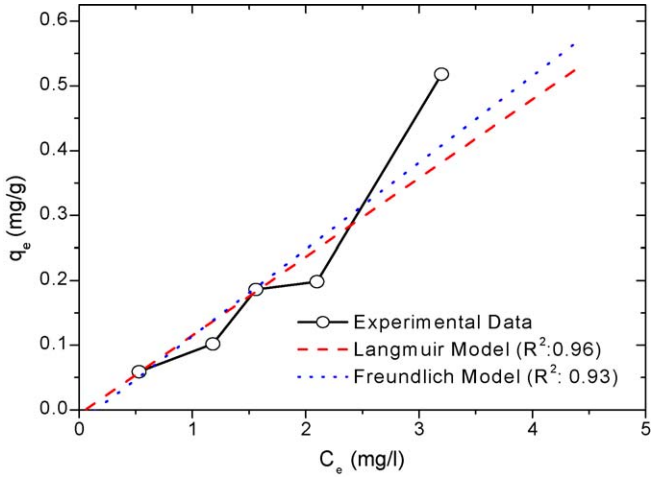

Fig. 6. Adsorption isotherms for removal of fluoride by LCB-10 (volume: 50 mL, temperature: 30 ± 1 °C, initial F concentration: 5.34 mg/L, and contact time 24 h).

Table 1
Langmuir and Freundlich constants of LCB-10 and AA.

	Langmuir constants			Freundlich constants		
	q_{max} (mg/g)	K (L/g)	R^2	K_F (mg/g)	n	R^2
LCB	4.7	0.023	0.96	0.106	0.864	0.93
AA	1.73	1.19	0.95	–	–	–

Langmuir equation, which is valid for monolayer sorption onto a surface with a finite number of identical sites, is given by [17]:

$$\frac{1}{q_e} = \frac{1}{q_{max}K} \times \frac{1}{C_e} + \frac{1}{q_{max}} \quad (3)$$

where q_{max} is the maximum amount of the fluoride ion per unit weight of chitin to form a complete monolayer on the surface bound at high C_e and K is a constant related to the affinity of the binding sites. q_e represents a particle limiting adsorption capacity when the surface is fully covered with solute and assists in the comparison of adsorption performance, particularly in case where the sorbent did not reach its full saturation in experiments. The linear plot of $1/C_e$ versus $1/q_e$ (Fig. 6) indicates better applicability of Langmuir adsorption isotherm with R^2 value 0.96 than Frendluich isotherm with R^2 value 0.93. The values of Langmuir parameters, q_{max} and K are 4.7 mg/g and 0.023 L/g, respectively. Similarly, Langmuir and Freundlich constants have been calculated for AA and compared with LCB in Table 1. LCB has high fluoride adsorption capacity than AA.

3.8. Conclusion

Synthesis of LCB-10 was optimized by varying different parameters for the synthesis of LCB for fluoride removal. It is observed that parameters for the synthesis of LCB like complexation time, precipitation time, ammonia strength and lanthanum loading shows significant effect on fluoride removal. The experimental data are well fitted in Langmuir and Freundlich isotherm. The fluoride adsorption capacity of LCB, i.e. 4.7 mg/g was found to be much greater than the commercially used activated alumina (1.7 mg/g). The LCB-10 not only have much higher fluoride adsorption capacity but also has numerous advantages namely relatively fast kinetics, high chemical and mechanical stability, high resistance to attrition, negligible Lanthanum release, suitability for column applications, etc. LCB can reduce the fluoride concentration below the permissible level of 1.5 mg/L and therefore, can be used as an effective adsorbent for defluoridation of drinking water. The performance of LCB-10 for fluoride removal in continuous flow fix bed column experiment is in progress.

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