



Defluoridation of water using neodymium-modified chitosan

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ABSTRACT

The water containing high fluoride ions could do harm to human and environment. In this work, the applicability of neodymium-modified chitosan as adsorbents for the removal of excess fluoride ions from water was studied. The effect of various physico-chemical parameters such as temperature (283–323 K), pH (5–9), adsorbent dose (0.2–2.0 g L⁻¹), particle size (0.10–0.50 mm) and the presence of co-anions (NO₃⁻, Cl⁻ and SO₄²⁻) on removal of fluoride ions were studied. The equilibrium sorption data were fitted reasonably well for Langmuir isotherm model, the maximum equilibrium sorption had found to be 11.411–22.380 mg g⁻¹. Sorption dynamics study revealed that the pseudo-second-order was suitable to describe the kinetics process of fluoride ions sorption onto the adsorbent with the initial sorption rate 1.70, 2.10 and 2.67 mg g⁻¹ min⁻¹ at 283, 303 and 323 K, and the sorption process was complex, both the boundary of liquid film and intra-particle diffusion contributed to the rate-determining step. The used adsorbents could be regenerated in 24 h by 4 g L⁻¹ of sodium hydroxide.

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1. Introduction

Fluorosis, an endemic public health problem, prevails in 22 nations around the globe. It is a crippling disorder known to occur due to the entry of fluoride ions into the body [1]. But as a necessary dilute element in human body, fluoride ions in drinking water may be beneficial or detrimental depending on its concentration. The excessive ingestion of fluoride ions through drinking water causes dental, skeleton, and nonskeletal forms of fluorosis [2,3]. According to the World Health Organization (WHO) the maximum acceptable concentration of fluoride ions in drinking water lies below 1.5 mg L⁻¹ [4]. Also the Ministry of Water Resources in China on the bases of economical, practical and technical considerations proposed guideline for drinking water quality of fluoride ions at 1.0 mg L⁻¹ (GB5949-2006, China).

Traditional treatment technologies, based on the principle of precipitation, ion exchange, electrolysis, membrane and sorption process have been proposed and tested for removal efficiency of excess of fluoride ions from drinking water and industrial effluent [5–12]. Among various processes, sorption is reported to be effective [13]. Sorption process involves the passage of the water through a contact bed where fluoride ions are removed by ion exchange or surface chemical reaction [14]. The efficiency of this technique mainly depends on adsorbents. Among them, ion exchange, and

membrane processes are effective and can remove the fluoride ions to a suitable level, but they are too expensive and the residual fluoride ions are always over 1.5 mg L⁻¹ [15].

Many adsorbents have been used for fluoride ions removal, such as clay, bleaching earth, red mud, limestone reactor and activated alumina [5,16–18]. Among the different adsorbents, adsorbents of rare earth element are attracting more and more attention for their selective affinity to fluoride ions, high sorption capacity, little pollution, easy operation and other merits [12]. In recent years, considerable amount of work has been done on developing adsorbents based on rare earth elements for sorption of fluoride ions. Nd³⁺ and Y³⁺-impregnated alumina [19], La³⁺-loaded fiber [20], and La³⁺ loaded chelating resins [21] have been used for sorption of fluoride ions successfully. Rare earth element impregnation of porous adsorbents or carrier materials has shown very promising results for preparing new adsorbents to remove fluoride ions from aqueous solutions.

The cost of adsorbent is a vital factor, which will restrict the broad application of adsorbent in industrial sectors. So, recently, numerous approaches have been studied for the cheaper and more effective adsorbents containing natural polymers, especially using chitosan obtained from seafood processing wastes. Chitosan represents attractive adsorbents because of its unique properties like biodegradability, biocompatibility and low cost biomaterial of properties, in addition to its particular physical and mechanical properties, resulting from the presence of chemical reactive groups (hydroxyl, acetamido or amino functions) in polymer chains [22]. Moreover, it is well known that polysaccharides which are abundant, renewable resources have a capacity to associate by physical

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and chemical interactions with fluoride ions. Ma et al. [23] studied sorption of fluoride ions on magnetic-chitosan particle from the water solution in the batch system. The different types of sorption isotherms were used to describe sorption equilibrium. The effect of temperature and kinetic of sorption were also studied. Kamble et al. [24] studied the removal of fluoride ions by chitin, chitosan modified by lanthanum nitrate as adsorbent, the effect of various physico-chemical parameters such as pH, adsorbent dose, initial fluoride concentration and the presence of co-anions on sorption of fluoride ions were studied. The biosorbent derived from shellfish processing waste is considered to be one of the key aspects of ecological engineering to suit domestic, biological and environmental conditions.

In the present work, chitosan was modified by neodymium(III) and employed to remove fluoride ions from synthesized water solution with analytical grade reagents NaF and double distilled water. The effect of various physico-chemical parameters such as temperature, pH, adsorbent dose, particle size and the presence of co-anions on removal of fluoride ions were studied. The Langmuir isotherms and Freundlich isotherms were employed to evaluate the sorption process. The pseudo-first-order, pseudo-second-order and intra-particle diffusion kinetic model were also used to study the dynamic process of sorption.

2. Experimental

2.1. Materials

All chemicals used in the present study were of analytical reagent grade. Chitosan was purchased from Qingdao Haihui Biological Co. Ltd. (China). Neodymium nitrate was supplied by Sinopharm Chemical Reagent Co. Ltd. (China).

2.2. Synthesis of neodymium incorporated chitosan

One gram of chitosan (85% deacetylated) was stirred with aqueous solutions with 50 mL 0.5 g L^{-1} of neodymium ions loading on a magnetic stirrer for 8 h at a agitation speed was 500 rpm. The neodymium-modified chitosan was then filtered using filter paper and washed with double distilled water and dried at 333 K in oven. Finally, the neodymium-modified chitosan was milled and sieved using standard griddles, it could be kept in desiccator, which was ready for sorption experimental test.

2.3. Sorption experiments

Fifty milliliters 20 mg L^{-1} of the fluoride ions solution was taken in a PVC conical flask and known weight of adsorbent material was added into it and then kept on a magnetic stirrer for 24 h in order to attain the complete equilibrium. The solution was analyzed for equilibrium fluoride ions concentration by ion selective electrode. The removal efficiency of fluoride ions and equilibrium sorption could be obtained by the following equations:

$$\eta = \frac{C_0 - C_e}{C_0} \times 100\% \quad (1)$$

$$q_e = \frac{V(C_0 - C_e)}{W} \quad (2)$$

where η (%) is the removal efficiency of fluoride ions, q_e the equilibrium sorption (mg g^{-1}) in the solid at equilibrium, C_0 , C_e the initial and equilibrium concentrations of fluoride ions (mg L^{-1}), respectively, V (L) the volume of the aqueous solution and W is the mass (g) of adsorbent used in the experiments.

2.4. Sorption isotherms studies

The equilibrium sorption studies at initial pH 7.0 were conducted at 283, 303 and 323 K, with varying fluoride ions concentration ($10\text{--}100 \text{ mg L}^{-1}$), and treatment time was 24 h.

2.5. Desorption studies

The adsorbent that was used for the removal of 20 mg L^{-1} of fluoride ions solution was separated from solution by filtration. The filtered samples were dried and weighted for further desorption study. It was agitated with 4 g L^{-1} of sodium hydroxide at the ratio of 1:10, the concentration of fluoride ions was measured after continuing stirring 24 h at agitation speed of 500 rpm. The efficiency of desorption was obtained by m_2/m_1 . Where m_1 was the mass of fluoride ions linked firstly, and m_2 was the mass of fluoride ions in desorption solution.

2.6. Method of analysis

The concentration of fluoride ions was analyzed by ion selective electrode using F-1 fluoride ion electrode supplied by Jiangfen Electroanalysis Corporation (China). The pH value was analyzed by PHS-3C precision pH/mv meter supplied by Shanghai Lida Instrument Company (China). The griddle was provided by Shangyu Huijiang Voile Company (China). FT-IR experiments were recorded in a Nicolet FT-IR Avatar-360 Spectrophotometer. The concentration of neodymium was estimated by inductively coupled plasma atomic emission spectrometer (ICP-AES, PerkinElmer, Optima 5300DC).

3. Results and discussion

3.1. Synthesis of neodymium incorporated chitosan

The FT-IR results show in Fig. 1, where it as can be seen that peaks at -1080 cm^{-1} attribute to the oxygen atom of hydroxyls coordinate with Nd(III), the electron density of oxygen atom is lowered and the C=O bond is weakened too. The presence of -OH group is confirmed by having a band at -3414 cm^{-1} . Although there is a possibility of overlapping between the $-\text{NH}_2$ and the -OH stretching vibrations, the band at -3414 cm^{-1} corresponding to $-\text{NH}_2$ stretching vibration of amino group [25]. The N-H group

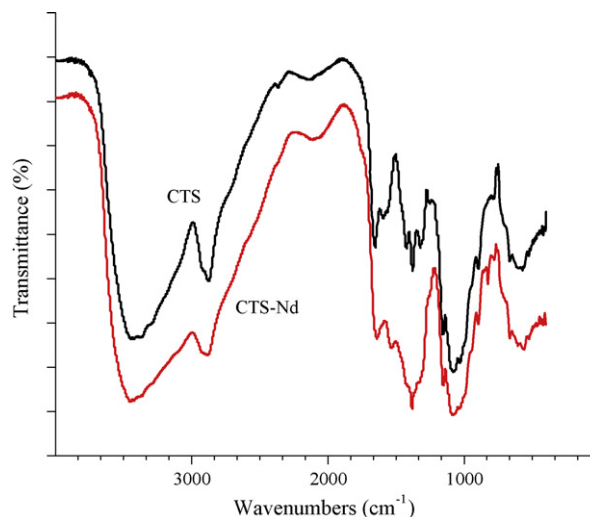


Fig. 1. FT-IR spectra of the Nd(III) incorporated chitosan and chitosan.

is the main complex site with Nd(III), the peaks at -1580 cm^{-1} have changed to at -1530 cm^{-1} which contribute to the N–H bond bending under spacial steric influence. A broad band can be seen at -1637 cm^{-1} , which attribute to the acetamido I.

3.2. Effect of pH and temperature

According to WHO guideline, the normal range for pH value in drinking water lies between 6 and 8.5; the normal temperature is below 323 K, therefore, the two factors were considered and the treatment was optimum condition by orthogonal process.

Initial pH of solution was one of the most important parameters in the sorption process. In acidic pH, chitosan was not stable and hence sorption studies were carried out in the pH ranges of 5–9, which was also of practical importance. Effect of pH on equilibrium sorption of fluoride ions was presented in Fig. 2. This could be explained by the fact that at low pH, more protons would be available to protonate amine groups to form groups $-\text{NH}_3^+$, reducing the number of binding sites for the sorption of Nd(III). While, at higher pH sorption of Nd(III) increased due to the inhibitory effect of H^+ decreased with the increase in pH [19,26]; but at pH higher than 7, Nd(III) precipitation occurred, OH^- could compete the sorption sites with fluoride ions simultaneously [27]. Thus pH 7 was chosen for the sorption of Nd(III) ions reasonably.

Temperature was an important parameter for the sorption process. Fig. 2 revealed that the fluoride ions removal efficiency increased with increasing temperature. The removal of fluoride ions was found to be greater than that at lower temperature. It indicated the strong tendency for the process for monolayer formation process to occur [28]. The increase in temperature would increase the mobility of the fluoride ions as well as produce a swelling effect with in the internal structure of the chitosan, thus enabling fluoride ions to penetrate further [29]. Therefore, the sorption capacity should largely depend on the chemical interaction between the functional groups on the adsorbent surface and the adsorbate, and should increase as the temperature rised. This could be explained by an increase in the diffusion rate of the adsorbate into the pores. At higher temperatures the adsorbent might contribute to the sorption of fluoride ions, as diffusion was an endothermic process, so, 323 K was the best temperature in the investigation area. Sorption removal of fluoride ions from aqueous phase using waste fungus had obtained the same result [30].

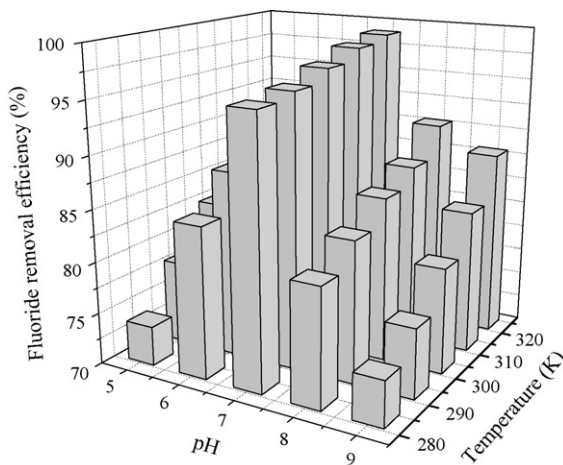


Fig. 2. Effect of pH and temperature on removal efficiency of F^- (dosage of sorbent was 2.0 g L^{-1} ; initial concentration was 20 mg L^{-1} ; contact time was 50 min; stirring speed was 500 rpm).

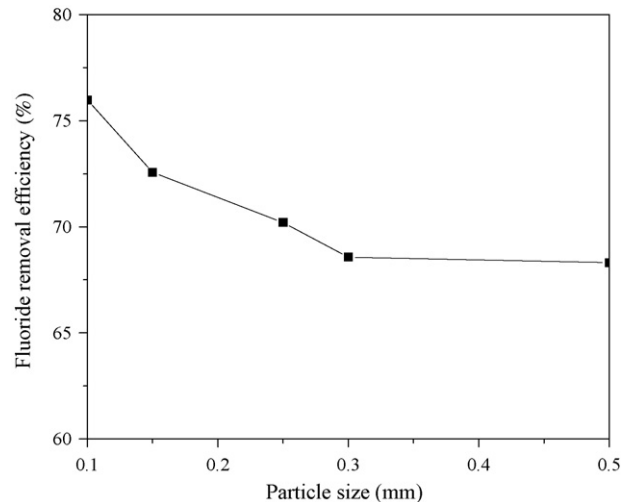


Fig. 3. Effect of adsorbent particle size on the adsorption of F^- (dosage of sorbent was 2.0 g L^{-1} ; initial concentration was 20 mg L^{-1} ; temperature was 323 K; pH value was 7; contact time was 50 min; stirring speed was 500 rpm).

3.3. Effect of adsorbent particle size

Sorption was a surface phenomenon, the extent of removal was proportional to specific surface area, to that portion of the total surface area that was available for sorption [31]. The effect of particle size was determined by conducting the sorption process with chitosan of different particle sizes, namely, <0.10 , $0.1-0.15$, $0.15-0.25$, $0.25-0.3$ and $0.3-0.5\text{ mm}$. Fig. 3 illustrated the effect of adsorbent particle size on fluoride ions removal efficiency for five different particle sizes. The equilibrium sorption of fluoride ions increased as the particle size decreased. It was obvious that for smaller particles, which had a higher solid–liquid interracial area, the removal efficiency and equilibrium sorption would be better. A similar phenomenon in relation to the sorption of certain dyes on various adsorbents had been reported previously [32]. This was due to the larger surface area made available for sorption. The increase in equilibrium sorption with decreasing the particle size during sorption process is reported [33].

3.4. Effect of adsorbent dose

The effect of adsorbent dose on fluoride ions removal efficiency at fixed initial fluoride concentration was shown in Fig. 4. It was observed that removal efficiency of fluoride ions increased with the increase in adsorbent dose while loading capacity gradually decreased for the same [16]. When the initial concentration of fluoride ions was 20 mg L^{-1} , the removal efficiency of fluoride ions was 26.97% at an adsorbent dose of 0.2 g L^{-1} ; while the removal efficiency of fluoride could increase up to 98.15% at an adsorbent dose of 2.0 g L^{-1} ; q_e decreased from 16.07 to 9.73 mg g^{-1} . It could also be seen that the fluoride ions removal markedly increased up to adsorbent dose of 1.2 g L^{-1} due to increase in adsorbent/ F^- ratio however further increased in adsorbent dose not show any appreciable improvement in fluoride ions removal. This might be because of the very low equilibrium concentration of fluoride ions, driving force responsible for sorption becomes negligible. When the concentration of fluoride ions was 20 mg L^{-1} in underground water, the residual of fluoride ions was 0.37 mg L^{-1} at the dosage of adsorbent was 2.0 g L^{-1} , which was lower than the WHO's acceptable concentration (1.5 mg L^{-1}).

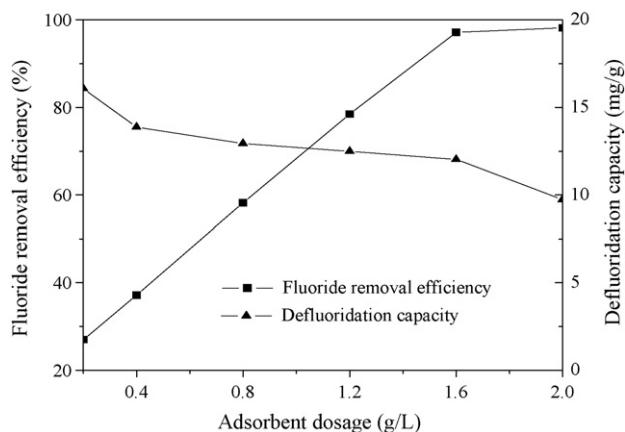


Fig. 4. Effect of sorption dosage on removal efficiency of F^- (initial concentration was 20 mg L^{-1} ; temperature was 323 K ; pH value was 7; contact time was 50 min; stirring speed was 500 rpm).

3.5. Effect of the presence of other co-anions

Groundwater contains other anions such as sulfate, nitrate and chloride in addition to fluoride ions. The initial concentration of fluoride ions was fixed at 20 mg L^{-1} while the concentrations of other anions varied from 2 to 500 mg L^{-1} . The impact of other anions over the efficiency of fluoride ions sorption by present adsorbent is shown in Fig. 5. The efficiencies of fluoride ions sorption were (of course little) found decreasing with increasing the initial concentrations of Cl^- and SO_4^{2-} co-anions. The pH of fluoride solution was 7.54, 7.32 and 7.16, respectively, for Cl^- , SO_4^{2-} and NO_3^- while the pH of the fluoride solution was 6.95 without addition of salt/anions. This indicated that addition of salt resulted in increased pH of fluoride solutions. From our experiments of effect of pH it was observed that the sorption of fluoride decreased in alkaline pH as also explained.

The presence of anions (chloride, sulfate and nitrate) has no significant effect within the concentration range tested. The results are in good agreement with the similar work done by Shihabuddeen for magnesia-amended activated alumina. It was found that fluoride ions removal efficiency of magnesia-amended activated alumina is not significant affected by chloride, sulfate, nitrate and other co-

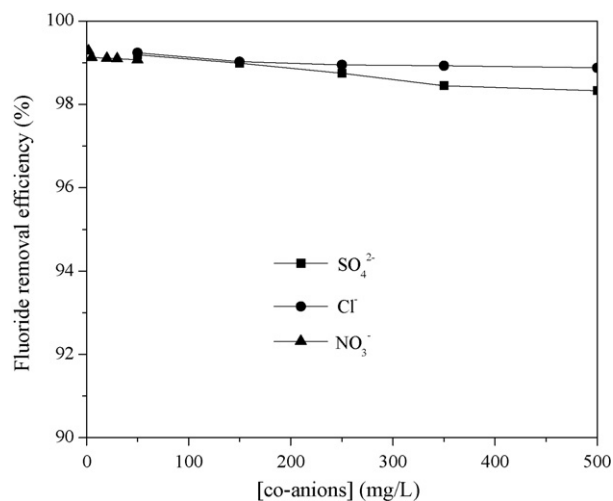


Fig. 5. Effect of the co-anions on removal efficiency of F^- (dosage of sorbent was 2.0 g L^{-1} ; initial concentration was 20 mg L^{-1} ; temperature was 323 K ; pH value was 7; contact time was 50 min; stirring speed was 500 rpm).

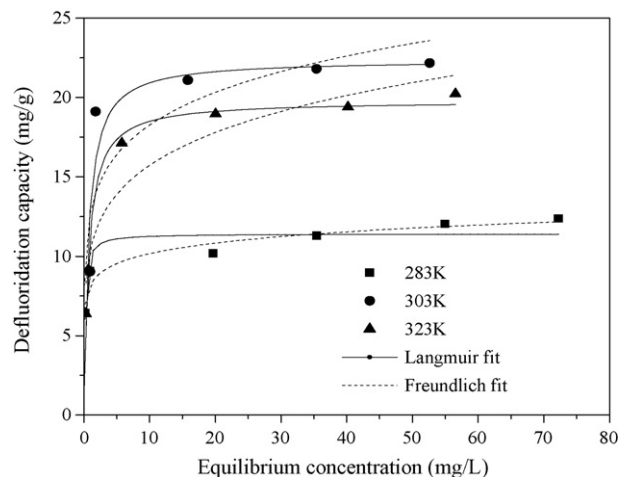


Fig. 6. Correlations of Langmuir and Freundlich isotherm models with the experimental data.

existing ions [18]. The sorption of fluoride ions is not adversely affected by the presence of other ions in solution thus making the rare earth oxide adsorbent selective to fluoride ions [12].

3.6. Sorption isotherm

Analysis of equilibrium data is important for developing an equation that can be used to compare different biomaterials under different operational conditions and to design and optimize an operating procedure. The sorption isotherms of fluoride ions were simulated by the mathematical equations of Langmuir and Freundlich. Using these two isotherms fit the experimental data at pH of 7.0, the results were shown in Fig. 6 and Table 1.

The Langmuir isotherm has higher correlation coefficients R values than the Freundlich isotherm, which indicates that the Langmuir isotherm fits well for the sorption of fluoride ions on the Nd-chitosan. The general shape of the isotherm curve including sharp curvature near to the saturation point and short equilibrium time are also very characteristics of a Langmuir equilibrium with high sorption capacity. In the Langmuir model, slope of the curve q_{max} represents the theoretical monolayer saturation capacity of the adsorbent on the adsorbent and K_L is related to the sorption energy. High value of K_L at 303 K obtains in the present case indicates strong binding and with rise in temperature; the value of K_L reduces significantly indicating the binding force weakened at higher temperature. The experimental findings also corroborate the saturation capacities predicted by Langmuir equation at different temperatures. The q_{max} of adsorbent for fluoride ions is found to be 11.411, 22.380 and 19.795 mg g^{-1} at 283, 303 and 323 K.

3.7. Sorption dynamics

The kinetics of sorption of fluoride from synthetic solutions was carried out at pH 7.0 and 20 mg L^{-1} of fluoride ions, and the results are shown in Fig. 7. It can be seen that the sorption kinetics is very

Table 1
Isotherm parameters for the removal of F^- by the Nd(III) incorporated chitosan.

T/K	Langmuir constants			Freundlich constants		
	$q_{\text{max}}/\text{mg g}^{-1}$	k_L/mg^{-1}	R	K_F/g^{-1}	n	R
283	11.411	2.945	0.991	8.244	10.979	0.751
303	22.380	1.437	0.987	12.812	6.492	0.723
323	19.795	1.425	0.981	10.454	5.631	0.875

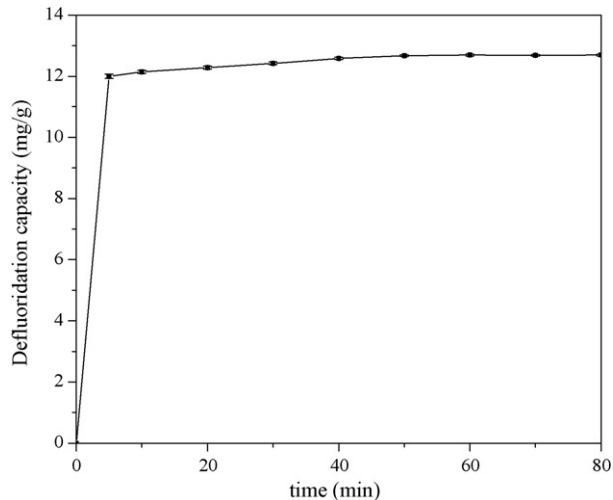


Fig. 7. Equilibrium contact time for the Nd(III) incorporated chitosan (dosage of sorbent was 2.0 g L⁻¹; initial concentration was 20 mg L⁻¹; temperature was 323 K; pH value was 7; stirring speed was 500 rpm).

fast, i.e. in the first 5 min most of fluoride ions is adsorbed. With further increase in time, a marginal increase in sorption is observed up to 50 min after which it is essentially constant. The kinetics of sorption was much faster compared to those of other commonly used adsorbents such as activated alumina.

Several kinetic models had been applied to express the mechanism of solute sorption onto a sorbent [19,21,32,33]. The pseudo-first-order equation (Lagergren and Svenska), pseudo-second-order equation (Ho et al.) and the intra-particle diffusion models with equations from (3) to (5) were employed to the kinetic analysis of fluoride ions onto adsorbent particle at 283, 303 and 323 K, respectively.

Pseudo-first-order model:

$$\frac{dq_t}{dt} = k_1(q_1 - q_t) \Rightarrow \lg(q_1 - q_t) = \lg q_1 - \frac{k_1 t}{2.303} \quad (3)$$

Pseudo-second-order model:

$$\frac{dq_t}{dt} = k_2(q_2 - q_t)^2 \Rightarrow \frac{t}{q_t} = \frac{1}{k_2 q_2^2} + \frac{t}{q_2} \quad (4)$$

Intra-particle diffusion model:

$$q_t = k_t t^{0.5} + C \quad (5)$$

where q_t (mg g⁻¹) is the uptake of fluoride ions at time t , q_1 (mg g⁻¹) the maximum sorption capacity for pseudo-first-order, and k_1 (min⁻¹) is the pseudo-first-order rate constant for fluoride ions in sorption process, respectively. And k_2 (min⁻¹) is the rate constant of fluoride ions in the pseudo-second-order sorption process, q_2 (mg g⁻¹) is the maximum sorption capacity for pseudo-second-order, and the initial sorption rate is $k_2 q_2^2$ (mg g⁻¹ min⁻¹).

Table 2

The kinetics parameters of first-order, second-order and intra-particle models.

T/K	$q_{e,exp}/\text{mg g}^{-1}$	Pseudo-first-order			Pseudo-second-order			Intra-particle diffusion	
		k_1/min^{-1}	$q_{e,cal}/\text{mg g}^{-1}$	R	$k_2/\text{mg g}^{-1} \text{min}^{-1}$	$q_{e,cal}/\text{mg g}^{-1}$	R	$k_t/\text{g mg}^{-1} \text{min}^{-0.5}$	R
283	11.411	0.16	20.597	0.992	1.70	11.136	1	0.031	0.970
303	22.380	0.17	21.341	0.899	2.10	21.827	1	0.114	0.982
323	19.795	0.28	18.834	0.959	2.67	19.335	1	0.083	0.957

$q_{e,exp}$ was determined in equilibrium experiments.

$q_{e,cal}$ was determined by fitting model parameters to the kinetics data.

The k_t (mg g⁻¹ min^{-0.5}) is the intra-particle diffusion rate constant and C of sorption constant is the intercept.

Linear form of pseudo-first-order and second-order kinetic rate models, were studied with the dynamic experimental data to examine the controlling mechanism of sorption [18,32]. Table 2 showed that correlation coefficient for both forms of rate models were almost same but calculated and experimental equilibrium uptake as well as linearity of the experimental data fit well to pseudo-second-order model. This had further been confirmed by experimental and generated kinetic rate profiles. Chitosan bead was an open porous system; as such there was every possibility that the fluoride ions might be transported within the bead through its porous network. However, cross-section of F⁻-sorbed beads showed no sign of intra-particle diffusion. Molecular shape and size were the prime parameters in the intra-particle diffusion process. Reported studies showed that the pseudo-second-order rate equation was a reasonably good fit of the data over the entire fractional approach to equilibrium and therefore was employed extensively in the study of sorption kinetics [12–14]. The applicability of intra-particle diffusion model suggested that sorption process of fluoride ions onto adsorbent was rather a complex process involving both boundary layer and intra-particle diffusion [15]. It indicated intra-particle diffusion was not the only rate-controlling step and other process might affect the rate of sorption [33].

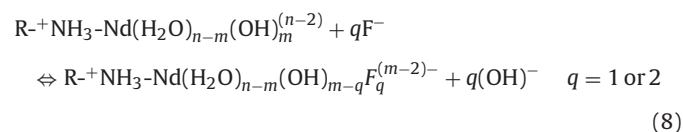
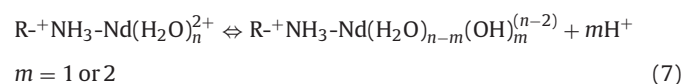
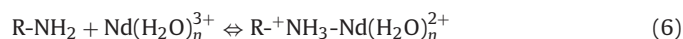
Compared the Q_{max} values obtained from Langmuir equation and that from pseudo-second-order at different temperature, they are comparable (Table 2). The difference may be due to the initial fluoride ions concentration, the initial concentration of kinetics equation was only 20 mg L⁻¹, and the equilibrium sorption studies were conducted with varying fluoride concentration (10–100 mg L⁻¹). The adsorption capacity increases with increasing initial fluoride ions concentration, which can be attributed to the utilization of less accessible or energetically less active sites, because of increased diffusivity and activity of fluoride ions upon the increased concentrations [15].

3.8. Mechanism of sorption of fluoride on Nd-modified chitosan

During the synthesis of neodymium incorporated chitosan, the neodymium ions and chitosan are the main component, the former act as a bridge to connect fluoride ions onto sorbent surface and enhance the sorption of fluoride. Also, the main characteristic of latter is the ability to coordinate metal ions because of its high concentration of amine functional groups and low-cost, non-toxic, biodegradable and biocompatible material.

As concerning sorption characteristics of fluoride ions on the surface of the neodymium incorporated chitosan particle, IR spectroscopy of experimental sample (Fig. 1) show that the main groups are amino groups (RNH₂, RNH₃), etc., that is useful in determining sorption of fluoride ions mechanism. Although group of amine play a major role in the synthesis of neodymium incorporated chitosan, it should be noted that the others groups also effect the fluoride ions sorption due to it is a surface complexation reaction.

The maximum removal efficiency of fluoride ions was at pH 7. The amount of fluoride ions adsorbed decreased with the increase of pH. This result could be interpreted in terms of the ligand exchange mechanism between fluoride ions and hydroxide ions coordinated on Nd(III) immobilized on the adsorbent according to the reaction shown below with equations from:



R = chitosan (9)

On dissolution of neodymium nitrate in water the pH is about 5.0. When chitosan was suspended in this solution of Nd^{3+} then the $-\text{NH}_2$ were protonated. The Nd^{3+} also undergone coordination with H_2O to form $\text{Nd}(\text{H}_2\text{O})_n^{3+}$, which then coordinated with protonated amino groups Eq. (6). The water molecules coordinated with Nd^{3+} deprotonate to release some H^+ to form OH^- coordinated on the Nd^{3+} Eq. (7). The pH value of synthesis solution is about 4.2.

When the fluoride ions were absorbed onto Nd-modified chitosan at pH 7.0, OH^- was further substituted by fluoride ions according to the ligand exchange mechanism and OH^- was released into solution Eq. (8). At the sorption equilibrium was reached, the pH value increased to 7.5. According to the ligand exchange reaction expressed by Eq. (8), the removal efficiency of fluoride ions decreased as the pH increased when pH was over 7.0, the result cohered to the effect of pH on the removal of fluoride ions.

3.9. Desorption studies

Desorption studies helped to elucidate the mechanism and recovery of the adsorbate and adsorbent. Under the situation of pH value was 7, temperature was 323 K, agitation speed was 500 rpm, contact time was 50 min, a salt rejection against the 50 mL water containing fluoride ions of 20 mg L^{-1} was 98.15% at the dosage of adsorbent was only 2.0 g L^{-1} , m_1 was 0.9815 mg; after desorption experiment by $5 \text{ mL } 4 \text{ g L}^{-1}$ of sodium hydroxide in 24 h, the concentration of fluoride ions was 176.68 mg L^{-1} , m_2 was 0.8834 mg, the ratio of desorption was over 90%. The adsorbent could be recovered and reused in the removal of fluoride ions [19,24]. Also, the desorption solution could be re-used for the production of sodium fluoride chemical reagent.

4. Conclusion

In the present study, a new adsorbent was studied for removal of fluoride ions from synthetic solution. The method is simple and has shown great potential for removal of fluoride ions. The main conclusions that can be drawn from the above study are given below:

- (1) The treatment conditions were optimized: pH value was 7, water temperature was at 323 K, particle size was 0.10 mm.
- (2) A salt rejection against the water containing 20 mg L^{-1} of fluoride ions was 98.15% at the dosage of adsorbent was only 2.0 g L^{-1} . 500 mg L^{-1} of chloride, 500 mg L^{-1} of sulfate,

50 mg L^{-1} of nitrogen of nitrate in water respectively, it had no significant effect on the removal rate of fluoride.

- (3) The equilibrium sorption data were fitted reasonably well for Langmuir isotherm model. The maximum equilibrium sorption was 22.380 mg g^{-1} at 303 K.
- (4) Sorption dynamic study revealed that the sorption process followed pseudo-second-order equation; the sorption process was complex, both the boundary of liquid film and intra-particle diffusion contributed to the rate-determining step.
- (5) The used adsorbents could be regenerated by 4 g L^{-1} of sodium hydroxide in 24 h.

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