



## Fluoride sorption by nano-hydroxyapatite/chitin composite

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### ABSTRACT

In this study the fluoride adsorption potential of novel nano-hydroxyapatite/chitin (n-HApCh) composite was explored. The sorbent was characterized using FTIR studies. The effects of pH, interfering anions and contact time were studied. The sorption data obtained under optimized conditions were subjected to Langmuir and Freundlich isotherms. Kinetic studies indicate that the rate of sorption of fluoride on n-HApCh composite follows pseudo-second-order and pore diffusion patterns. n-HApCh composite possesses higher defluoridation capacity (DC) of 2840 mgF<sup>-</sup> kg<sup>-1</sup> than nano-hydroxyapatite (n-HAp) which showed a DC of 1296 mgF<sup>-</sup> kg<sup>-1</sup>. Field trials were conducted with the sample collected from a nearby fluoride endemic area.

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### 1. Introduction

Consumption of drinking water containing high levels of fluoride can cause serious health hazard. Research in fluoride removal has resulted in various defluoridation technologies that aim to provide quality drinking water with the prescribed fluoride limit suggested by WHO [1]. Various defluoridation technologies have been developed to reduce the fluoride content to the described level with each method having its own merits and demerits. These include fluoride removal based on the principle of adsorption [2], ion-exchange [3], precipitation [4] and electrochemical methods [5]. Adsorption onto solid surface is considered to be simple, versatile and economical process for treating drinking water, especially for small communities. Literature cites adsorption by activated alumina and magnesia seems to be promising technologies available to treat the fluoride rich water. However, the slow rate of adsorption of commercially available activated alumina limits its use for treating large quantity of water [6]. The ability of magnesia to scavenge fluoride is limited because of the alkaline nature of the treated water and its practical limitation due to its availability in powder form [7]. Nano-hydroxyapatite (n-HAp) was also found to be better sorbent because of its low cost, availability and higher defluoridation capacity (DC) [8]. However, when used in powder form it would cause significant pressure drop during filtration. In order to overcome this limitation

recently an attempt has been made to composite these inorganic exchangers with biopolymers like chitosan [9] which also resulted in enhancement of DC.

Nowadays these composite materials of organic/inorganic origin are extensively studied because of their combined advantages. The mechanical and physical properties of the polymer can compromise the brittleness of the hydroxyapatite which would give better handling properties to hydroxyapatite. In addition, these composite materials could be made into any desirable forms, viz., beads, membranes and candles.

Chitin, a biopolymer consisting of  $\beta$ -(1,4)-2-acetamido-2-deoxy-D-glucose units, is the second most abundant polysaccharide occurring in nature, after cellulose. Recently its ability to chelate metal ions has been studied extensively suggesting the possibility of using this polymer for the removal of metal ions from the waste and natural water [10–12]. Hence in the present investigation, chitin which has low defluoridation capacity was used to prepare the biocompatible composites with n-HAp. The results of the analysis of the DC of the sorbent namely nano-hydroxyapatite/chitin (n-HApCh) composite is presented.

### 2. Materials and methods

#### 2.1. Synthesis of n-HAp/chitin composite

n-HAp was synthesised by the reaction of calcium nitrate and ammonium dihydrogen phosphate. The pH value during mixing was maintained above 10 with ammonia solution. Then they were mixed with a stoichiometric ratio of Ca to P (=1.67). The precipi-

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tate formed was rinsed with water to bring the pH level to 7. The precipitate obtained was dried at 80 °C. The n-HApCh composite was also prepared by precipitation method. The aqueous solution of ammonium dihydrogen phosphate was added to the mixture of aqueous solution of  $\text{Ca}(\text{NO}_3)_2$  and chitin in the ratio 3:2. The precipitate formed was rinsed with water to bring the pH level to 7. The precipitate obtained was dried at 150 °C to get n-HApCh composite [9].

## 2.2. Adsorption studies

Batch technique was selected to obtain the equilibrium and kinetic data. Stock solution ( $100 \text{ mg L}^{-1}$ ) was prepared by dissolving 0.221 g of anhydrous sodium fluoride in distilled water and made upto 1 L and it was further diluted to get the desired concentration. About 0.1 g of sorbent was added to 50 mL of solution containing  $10 \text{ mg L}^{-1}$  as initial fluoride concentration. The mixture was shaken in a thermostated shaker at a speed of 200 rpm at room temperature. The effect of different initial fluoride concentrations in the range of 6, 8, 10 and  $12 \text{ mg L}^{-1}$  at three different temperatures, viz., 303, 313 and 323 K on sorption rate was studied by keeping the mass of sorbent as 0.1 g and volume of solution as 50 mL in neutral pH. The solution was then filtered and the residual fluoride ion concentration was measured using expandable ion analyzer EA 940 and the fluoride ion selective electrode BN 9609 (USA make).

## 2.3. Characterization of the sorbent

FTIR spectra of the samples as solid by diluting in KBr pellets were recorded with JASCO-460 plus model. The results of FTIR spectrophotometer were used to confirm the functional groups present in the sorbent.

## 2.4. Statistical analysis

Computations were made using Microcal Origin (Version 6.0) software. The goodness of fit was discussed using regression correlation coefficient ( $r$ ).

## 3. Results and discussion

### 3.1. Characterization of sorbent

Fig. 1a and b depicts the FTIR spectra of synthesized n-HApCh composite and fluoride treated n-HApCh composite, respectively. The stretching vibrations at 632 and  $3140 \text{ cm}^{-1}$  are due to the hydroxyl groups in HAp. The bands at 1040, 1092 and  $962 \text{ cm}^{-1}$  are the characteristic bands of phosphate stretching vibrations while the bands at 603 and  $565 \text{ cm}^{-1}$  are due to phosphate bending vibrations. The band at  $1636 \text{ cm}^{-1}$  is due to the C=O group of chitin in the composite. The bands at 2850, 1460 and  $1383 \text{ cm}^{-1}$  are attributed to the vibration of -CH group of chitin. The vibration bands of C-O group overlapped with phosphate bands at  $1150\text{--}1040 \text{ cm}^{-1}$ . The shifting of -OH stretching vibrations at  $3140 \text{ cm}^{-1}$  to higher frequencies may be taken as an indicative of adsorption between the sorbent and fluoride [8,9].

### 3.2. Effect of contact time

The effect of DC of the sorbents was determined by varying contact time in the range of 10–60 min and is shown in Fig. 2. It is evident from Fig. 2 that both the sorbents reached saturation after 30 min. Hence, 30 min was fixed as the contact time for the sorbents for further studies. The maximum DC of n-HApCh composite and n-HAp was found to be 2840 and  $1296 \text{ mgF}^- \text{ kg}^{-1}$ , respectively. Further studies were limited to n-HApCh composite only.

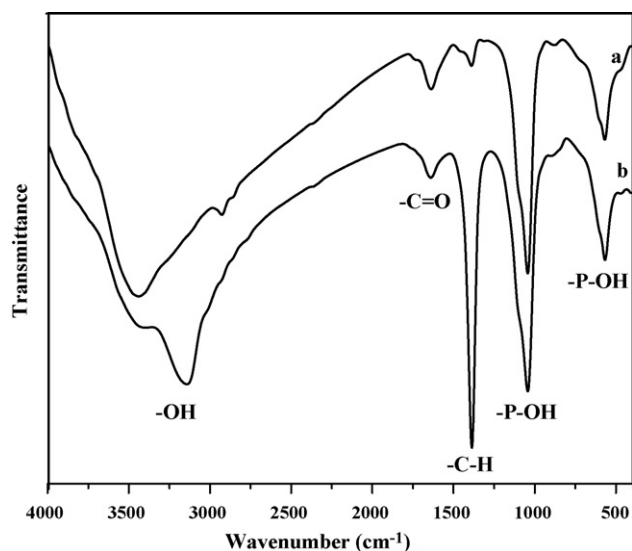


Fig. 1. FTIR spectra of (a) n-HApCh composite and (b) fluoride-sorbed n-HApCh composite.

### 3.3. Effect of pH

The removal of fluoride ions from aqueous solution was highly dependent on the solution pH in many cases as it altered the surface charge on the sorbent. Hence, the DC of the sorbent was determined at five different pH levels, viz., 3, 5, 7, 9 and 11 and the results are given in Fig. 3. The pH of the working solution was controlled by adding HCl/NaOH solution. The maximum DC was recorded at lower pH ranges and showed gradual decreasing trend with the increase in the pH as reported for n-HAp [9], while studying the fluoride removal behaviour of hydroxyapatite/chitosan composite. Below pH 5.9 which is  $\text{pH}_{\text{zpc}}$  of the n-HApCh composite, where the surface acquires positive charge, the DC was found to be maximum. At higher pH ranges the fluoride removal is mainly governed by ion-exchange mechanism. The DC of n-HApCh composite was higher than n-HAp in all the pH ranges studied.

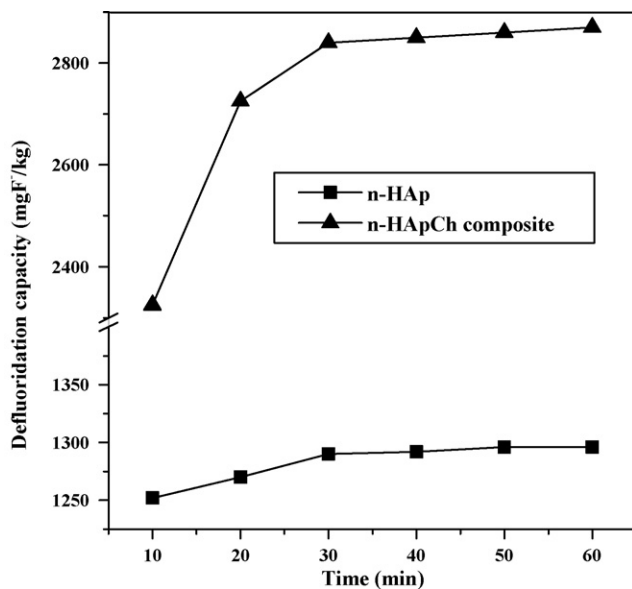


Fig. 2. Effect of contact time on DC of the sorbents in presence of  $10 \text{ mg L}^{-1}$  initial fluoride concentration with pH 7 at 303 K.

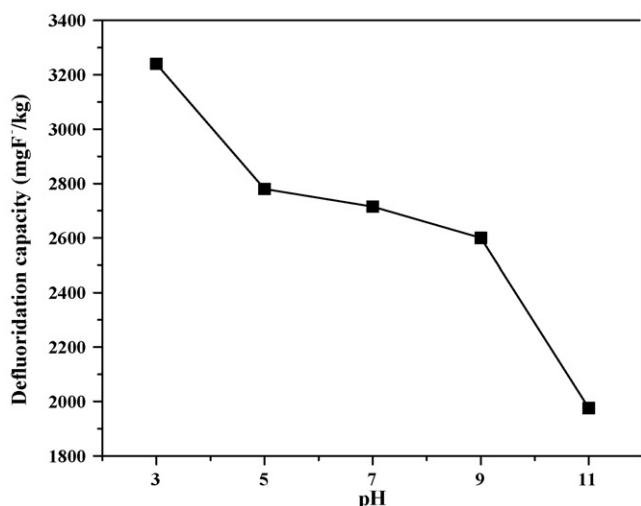


Fig. 3. Influence of pH on DC of n-HApCh composite with  $10 \text{ mg L}^{-1}$  initial fluoride concentration for 30 min at 303 K.

### 3.4. Effect of anions in the medium

The drinking water contains several other anions along with fluoride, which may compete with fluoride for the active sorption sites. The dependence of DC of the sorbent in the presence of other common anions which are commonly present in water namely  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$  and  $\text{NO}_3^-$  was investigated with a fixed  $300 \text{ mg L}^{-1}$  initial concentration of these ions and by keeping  $10 \text{ mg L}^{-1}$  as initial fluoride concentration at room temperature. As shown in Fig. 4 bicarbonate anion interferes with the fluoride sorption, than sulphate, nitrate and chloride anions. However, the overall DC of the sorbent was not significantly reduced in the presence of other anions except bicarbonate.

### 3.5. Isotherm studies

Adsorption isotherms are used for understanding the mechanism and quantifying the distribution of adsorbate between the liquid phase and solid adsorbent phase at equilibrium during the adsorption process. To quantify the sorption capacity of the n-HApCh composite for the removal of fluoride ions, the two

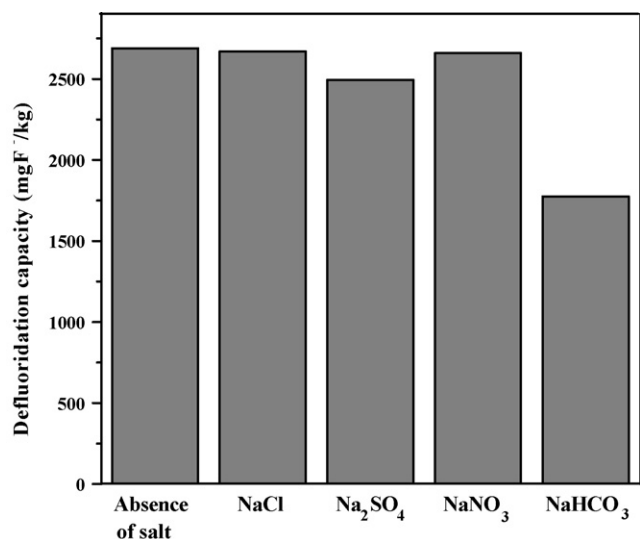


Fig. 4. Effect of co-anions on DC of n-HApCh composite with  $10 \text{ mg L}^{-1}$  initial fluoride concentration at 303 K.

Table 1  
Freundlich and Langmuir isotherms of n-HApCh composite.

Temp (K)	Freundlich isotherm			Langmuir isotherm		
	$1/n$	$k_F (\text{mg g}^{-1})(\text{L mg}^{-1})^{1/n}$	$r$	$Q^0 (\text{mg g}^{-1})$	$b (\text{L mg}^{-1})$	$r$
303	0.738	0.720	0.999	8.410	0.079	0.973
313	0.703	0.792	0.998	7.599	0.097	0.976
323	0.670	0.865	0.998	6.993	0.116	0.979

most commonly used isotherms, namely Freundlich and Langmuir isotherms have been adopted.

#### 3.5.1. Freundlich isotherm

The Freundlich isotherm [13] in its linear form is represented by:

$$\log q_e = \log k_F + \frac{1}{n} \log C_e, \quad (1)$$

where  $q_e$  is the amount of fluoride adsorbed per unit weight of the sorbent ( $\text{mg g}^{-1}$ ),  $C_e$  is the equilibrium concentration of fluoride in solution ( $\text{mg L}^{-1}$ ),  $k_F$  is a measure of adsorption capacity and  $1/n$  is the adsorption intensity. Freundlich isotherm constants of the sorbent were calculated from the slope and intercept of the linear plot  $\log q_e$  vs.  $\log C_e$  and are presented in Table 1. The values of  $1/n$  lying between 0 and 1 confirm the favorable conditions for adsorption. The values of  $k_F$  found to increase with increase in temperature suggesting the endothermic nature of the sorption process. The higher values of  $r$  indicate the applicability of Freundlich isotherm.

#### 3.5.2. Langmuir isotherm

The Langmuir isotherm [14] in its linear form is represented by:

$$\frac{C_e}{q_e} = \frac{1}{Q^0 b} + \frac{C_e}{Q^0}, \quad (2)$$

where  $q_e$  is the amount of fluoride adsorbed per unit weight of the sorbent ( $\text{mg g}^{-1}$ ),  $C_e$  is the equilibrium concentration of fluoride in solution ( $\text{mg L}^{-1}$ ),  $Q^0$  is the amount of adsorbate at complete monolayer coverage ( $\text{mg g}^{-1}$ ) and gives the maximum sorption capacity of sorbent and  $b (\text{L mg}^{-1})$  is Langmuir isotherm constant that relates to the energy of adsorption. Langmuir isotherm constants, viz.,  $Q^0$  and  $b$  were calculated from the slope and intercept of the linear plot of  $C_e/q_e$  vs.  $C_e$ , the values are presented in Table 1. The higher values of  $r$  indicate its applicability of Langmuir isotherm.

### 3.6. Thermodynamic treatment of the sorption process

Thermodynamic parameters associated with the adsorption, viz., standard free energy change ( $\Delta G^\circ$ ) and standard enthalpy change ( $\Delta H^\circ$ ) and standard entropy change ( $\Delta S^\circ$ ) were calculated as follows.

The change in free energy of sorption is given by:

$$\Delta G^\circ = -RT \ln K_0, \quad (3)$$

where  $K_0$  is the sorption distribution coefficient,  $\Delta G^\circ$  is the standard free energy change of sorption ( $\text{kJ mol}^{-1}$ ),  $T$  is the temperature in Kelvin and  $R$  is the universal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ). The sorption distribution coefficient  $K_0$  was determined from the slope of the plot  $\ln(q_e/C_e)$  against  $C_e$  at different temperatures and extrapolating to zero  $C_e$  according to Khan and Singh method [15].

The sorption distribution coefficient can be expressed in terms of  $\Delta H^\circ$  and  $\Delta S^\circ$  as a function of temperature:

$$\ln K_0 = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}, \quad (4)$$

where  $\Delta H^\circ$  is the standard enthalpy change ( $\text{kJ mol}^{-1}$ ) and  $\Delta S^\circ$  is standard entropy change ( $\text{kJ mol}^{-1} \text{ K}^{-1}$ ). The values of  $\Delta H^\circ$  and  $\Delta S^\circ$  can be obtained from the slope and intercept of a plot of  $\ln K_0$

**Table 2**  
Thermodynamic parameters for sorption of fluoride on n-HApCh composite at different temperatures.

$\Delta G^\circ$ (kJ mol <sup>-1</sup> )			$\Delta H^\circ$ (kJ mol <sup>-1</sup> )	$\Delta S^\circ$ (kJ mol <sup>-1</sup> K <sup>-1</sup> )
303 K	313 K	323 K		
-7.13	-6.97	-6.84	11.75	15.28

against  $1/T$ . Calculated thermodynamic parameters are presented in Table 2.

The thermodynamic treatment of the sorption data of the sorbent indicated that  $\Delta G^\circ$  values were negative at all temperatures investigated. The negative values of  $\Delta G^\circ$  confirm the spontaneous nature of sorption of fluoride ion by sorbent. The positive value of  $\Delta S^\circ$  indicates that the freedom of  $F^-$  ions is not too restricted in the sorbent. The positive value of  $\Delta H^\circ$  for fluoride sorption confirms the endothermic nature of sorption process.

### 3.7. Sorption dynamics

#### 3.7.1. Reaction-based models

The most commonly used pseudo-first-order and pseudo-second-order models were employed to explain the solid/liquid adsorption based.

A pseudo-first-order equation of Lagergren [16] is generally expressed as:

$$\log(q_e - q_t) = \log q_e - \frac{k_{ad}}{2.303} t, \quad (5)$$

where  $q_t$  is the amount of fluoride on the surface of the n-HApCh at time  $t$  (mg g<sup>-1</sup>) and  $k_{ad}$  is the equilibrium rate constant of pseudo-first-order sorption (min<sup>-1</sup>). The slope of the straight line plots of  $\log(q_e - q_t)$  against  $t$  for different experimental conditions will give the value of the rate constants.

Pseudo-second-order model was also generally applied to fit the experimental data. The linear form of pseudo-second-order model [17] can be expressed as:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e}, \quad (6)$$

where  $q_t = q_e^2 kt / (1 + q_e kt)$  amount of fluoride on the surface of the n-HApCh at any time,  $t$  (mg g<sup>-1</sup>),  $k$  is the pseudo-second-order rate constant (g mg<sup>-1</sup> min<sup>-1</sup>),  $q_e$  is the amount fluoride ion sorbed at equilibrium (mg g<sup>-1</sup>) and the initial sorption rate,  $h = kq_e^2$  (mg g<sup>-1</sup> min<sup>-1</sup>). The value of  $q_e$  (1/slope),  $k$  (slope<sup>2</sup>/intercept) and  $h$  (1/intercept) of the pseudo-second-order equation can be found out experimentally by plotting  $t/q_t$  against  $t$ .

The slopes of the straight-line plot of  $\log(q_e - q_t)$  against  $t$  for different experimental conditions give the value of the rate constant ( $k_{ad}$ ) and are presented in Table 3. The fitness of the data with the pseudo-second-order model were tested and the values of constants  $q_e$ ,  $k$ , and  $h$  were obtained from the plots of  $t/q_t$  vs.  $t$  for fluoride sorption at different temperatures, viz., 303, 313 and 323 K of n-HApCh composite is presented in Table 4. The plot of  $t/q_t$  vs.  $t$  gives a straight line with higher correlation coefficient ( $r$ ) values than that observed with pseudo-first-order model indicating the applicability of the pseudo-second-order model.

**Table 3**  
Pseudo-first-order model parameters of n-HApCh composite.

$C_0$ (mg L <sup>-1</sup> )	Mass (g)	303 K		313 K		323 K	
		$k_{ad}$ (min <sup>-1</sup> )	$r$	$k_{ad}$ (min <sup>-1</sup> )	$r$	$k_{ad}$ (min <sup>-1</sup> )	$r$
6	0.1	0.140	0.984	0.145	0.942	0.145	0.963
8	0.1	0.161	0.917	0.164	0.944	0.164	0.961
10	0.1	0.159	0.980	0.166	0.964	0.166	0.980
12	0.1	0.173	0.903	0.161	0.930	0.161	0.908

#### 3.7.2. Diffusion-based models

In a solid-liquid sorption process the transfer of solute is characterized by pore diffusion or particle diffusion control.

The pore diffusion model used here was proposed by Weber and Morris [18]. The linear form of the equation is represented by:

$$q_t = k_i t^{0.5}, \quad (7)$$

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

A particle diffusion controlled sorption process [19,20] is represented by the equation:

$$\ln\left(1 - \frac{C_t}{C_e}\right) = -k_p t, \quad (8)$$

where  $C_t$  and  $C_e$  are the fluoride concentration at time  $t$  and equilibrium, respectively, and  $k_p$  is the particle rate constant (min<sup>-1</sup>). The value of particle rate constant is obtained by the slope of the plot of  $\ln(1 - C_t/C_e)$  against  $t$ .

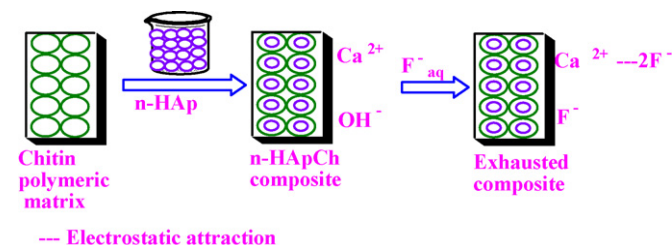
The straight line plots of  $\ln(1 - C_t/C_e)$  vs.  $t$  and  $q_t$  vs.  $t^{0.5}$  indicate the applicability of both particle and intraparticle diffusion models. The  $k_p$ ,  $k_i$  and  $r$  values of particle and intraparticle diffusion models are illustrated in Table 5. The higher  $r$  values obtained for both particle and intraparticle diffusion models suggest that n-HApCh composite follow both the models on fluoride sorption, but better fits to pore diffusion model.

### 3.8. Mechanism of fluoride sorption

The fluoride removal by n-HApCh composite was governed by both adsorption and ion exchange mechanism as in the case of n-HAp [8,9,21,22]. The surface acquired positive charge at lower pH values and hence the fluoride sorption at this pH level was mainly due to electrostatic attraction between the positive surface and negatively charged fluoride ions and chemisorption dominated. As the pH increased slowly, the surface acquired negative charges, physisorption dominated and hence DC decreased. In addition ion exchange mechanism was also involved as the -OH group present in the n-HApCh composite is considered as the charge carrier and gets exchanged with fluoride ions. The enhancement in DC of n-HApCh composite over n-HAp may be due to biosorption by chitin, adsorption by physical forces and fluoride ion entrapped in fibrillar capillaries and spaces of polysaccharide network of the chitin moiety (cf. Scheme 1).

#### 3.9. Field trials

Field trials were conducted with the sample collected from a nearby fluoride endemic area and the results are presented in Table 6. There is almost complete reduction in the fluoride level without much alteration in other water quality parameters also. Hence n-HApCh composite can be effectively used as a defluoridating agent.



**Scheme 1.** Mechanism of fluoride removal by n-HApCh composite.



**Table 4**  
Pseudo-second-order model parameters of n-HApCh composite.

Parameters	303 K				313 K				323 K			
	6 mg L <sup>-1</sup>	8 mg L <sup>-1</sup>	10 mg L <sup>-1</sup>	12 mg L <sup>-1</sup>	6 mg L <sup>-1</sup>	8 mg L <sup>-1</sup>	10 mg L <sup>-1</sup>	12 mg L <sup>-1</sup>	6 mg L <sup>-1</sup>	8 mg L <sup>-1</sup>	10 mg L <sup>-1</sup>	12 mg L <sup>-1</sup>
$q_e$ (mg g <sup>-1</sup> )	1.618	2.320	2.747	3.257	1.938	2.5	2.747	3.322	1.996	2.681	2.874	3.356
$k$ (g mg <sup>-1</sup> min <sup>-1</sup> )	0.083	0.075	0.080	0.058	0.076	0.055	0.094	0.058	0.083	0.044	0.077	0.057
$h$ (mg g <sup>-1</sup> min <sup>-1</sup> )	0.622	0.405	0.606	0.618	0.284	0.346	0.709	0.645	0.332	0.315	0.639	0.645
$r$	0.999	0.991	0.997	0.989	0.992	0.995	0.998	0.993	0.995	0.987	0.999	0.998

**Table 5**  
Particle and intraparticle diffusion model parameters for fluoride sorption on n-HApCh composite at different initial fluoride concentrations with different temperatures.

$C_0$ (mg L <sup>-1</sup> )	303 K				313 K				323 K			
	Particle DM <sup>a</sup>		Intraparticle DM <sup>a</sup>		Particle DM <sup>a</sup>		Intraparticle DM <sup>a</sup>		Particle DM <sup>a</sup>		Intraparticle DM <sup>a</sup>	
	$k_p$ (min <sup>-1</sup> )	$r$	$k_i$ (mg g <sup>-1</sup> min <sup>-0.5</sup> )	$r$	$k_p$ (min <sup>-1</sup> )	$r$	$k_i$ (mg g <sup>-1</sup> min <sup>-0.5</sup> )	$r$	$k_p$ (min <sup>-1</sup> )	$r$	$k_i$ (mg g <sup>-1</sup> min <sup>-0.5</sup> )	$r$
6	0.016	0.971	0.205	0.900	0.021	0.992	0.215	0.993	0.022	0.972	0.219	0.983
8	0.019	0.992	0.230	0.985	0.022	0.993	0.287	0.995	0.026	0.988	0.328	0.994
10	0.018	0.968	0.270	0.978	0.018	0.967	0.250	0.978	0.020	0.967	0.291	0.981
12	0.019	0.982	0.302	0.974	0.020	0.992	0.319	0.989	0.020	0.978	0.312	0.979

<sup>a</sup> DM: Diffusion model.**Table 6**  
Field trial results of n-HApCh composite.

Water quality parameters	Before treatment	After treatment
F <sup>-</sup> (mg L <sup>-1</sup> )	1.98	0.16
pH	8.55	7.59
Cl <sup>-</sup> (mg L <sup>-1</sup> )	362.00	334.00
Total hardness (mg L <sup>-1</sup> )	602.00	423.00
Total dissolved solids (mg L <sup>-1</sup> )	720.00	503.00

#### 4. Conclusions

n-HApCh composite possesses higher DC of 2840 mgF<sup>-</sup> kg<sup>-1</sup> than n-HAp which showed a DC of 1296 mgF<sup>-</sup> kg<sup>-1</sup>. The fluoride removal of the chitin composite is influenced by the pH of the medium. The sorbent selectively removes the fluoride in presence of the coexisting anions except bicarbonate. The adsorption follows both Langmuir and Freundlich isotherms but better fits to Freundlich isotherm. The nature of the sorption process is spontaneous and endothermic. The rate of the reaction follows pseudo-second-order and pore diffusion patterns. The main advantages of n-HApCh composite are biocompatible, low cost material, indigenously synthesized and can be effectively utilized as promising defluorinating agent.

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