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Synthesis of alginate bioencapsulated nano-hydroxyapatite composite for selective fluoride sorption

Kalimuthu Pandi, Natrayasamy Viswanathan*

Department of Chemistry, Anna University, University College of Engineering, Dindigul, Reddiyarchatram, Dindigul 624 622, Tamilnadu, India

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ABSTRACT

This article focuses on the development of eco-friendly adsorbent by alginate (Alg) bioencapsulating nano-hydroxyapatite (n-HAp) namely n-HApAlg composite for defluoridation studies in batch mode. n-HAp powder utilized as a promising defluoridating material, but it causes a significant pressure drop during field applications. To overcome such technological bottlenecks, n-HApAlg composite was synthesized. The defluoridation capacity (DC) of synthesized n-HApAlg composite possesses an enhanced DC of 3870 mg F^-/kg when compared to n-HAp and calcium alginate (CaAlg) composite which possess DC of 1296 and 680 mg F^-/kg, respectively. The biocomposite features were characterized using FTIR and SEM with EDAX analysis. The various adsorption influencing parameters like contact time, pH, co-anions, initial fluoride concentration and temperature were optimized. The adsorption process was enlightened by various isotherms and kinetic models. The suitability of the biocomposite at field conditions was also tested.

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1. Introduction

Fluorosis is a global health problem, occurs when the fluoride concentration in water exceeds its tolerance limit (>1.5 mg/L). Drinking water is the major source of fluoride intake. The fluoride will enter public water systems either from natural and/or anthropogenic sources. Different methods have been adopted to abate excess fluoride from aqueous solution, such as precipitation (Lu & Liu, 2010), electrolysis (Amor et al., 2001), nanofiltration (Simons, 1993), ion exchange (Meenakshi & Viswanathan, 2007) and adsorption (Viswanathan & Meenakshi, 2010). Among the methods reported, adsorption is one of the most effective methods used for fluoride removal because of its ease of operation and cost effectiveness.

Researchers tried numerous adsorbent materials such as activated carbon (Srimurali et al., 1998), activated alumina (Meenakshi, 1992), bone charcoal (Mahramanlioglu, Kizilcikli, & Bicer, 2002), chitosan beads (Viswanathan, Sairam Sundaram, & Meenakshi, 2009), clays (Tor, 2006), layered double hydroxides (Lv, He, Wei, & Duan, 2006), mixed metal oxides (Biswas, Gupta, Goswami, & Ghosh, 2010) and ion-exchange resins (Meenakshi & Viswanathan, 2007), etc., for defluoridation studies. Recent days, biosorption plays an imperative role in the environmental concern. Alginate is a biopolymer isolated from brown seaweeds, which is composed of two monomers viz., (1 → 4)β-D-mannuronate and (1 → 4)α-L-guluronate. This polycarbohydrate possess precious properties such as biocompatible, biofunctional, non-toxic, non-immunogenic and biodegradable.

Hydroxyapatite (HAp) is a biomineral which shows excellent potential towards water pollution control, due to its low cost, availability, eco-friendly nature and rich in presence of exchangeable hydroxyl groups. Advanced studies of n-HAp have received extensive attraction because of their high surface area and reactivity. Research works have been carried out for the removal of toxic ions using hydroxyapatite (HAp) (Sairam Sundaram, Viswanathan, & Meenakshi, 2008; Sheha, 2007; Stotzel et al., 2009). However, the application of HAp is very limited due to its brittleness. In addition, HAp powder cannot be directly used in fixed bed columns, because it cause excessive pressure drop during field applications. To triumph such technological problems, polymeric composites were tried. In recent times, the preparation of biopolymer supported inorganic composites has attracted much attention owing to their unique structure and properties. The synergistic effect of biopolymer and inorganic material will improve the mechanical properties of the composite. Biopolymer supported composites will be utilized for toxic ions removal (Hassan, Abdel-Mohsen, & Fouda, 2014; Lakouraj, Mojerlou, & Zare, 2014).

The goal of the present investigation is to develop a low cost, eco-friendly, biocompatible and biodegradable composite with high DC. Based on the above aspire, the authors have synthesized alginate

* Corresponding author. Tel.: +91 451 2554066; fax: +91 451 2554066.
E-mail address: drnviswanathan@gmail.com (N. Viswanathan).

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bioencapsulated nano-hydroxyapatite, a new biocomposite which have been utilized for fluoride removal. Sorption studies were carried out to optimize various equilibrating conditions like contact time, pH, presence of competitor anions, different initial fluoride concentrations and temperature. Adsorption data have been fitted to various isotherms and kinetic models. The thermodynamic parameters viz., ΔG°, ΔH° and ΔS° have also been calculated and interpreted. The aptness of the biocomposite at field conditions was also tested by collecting fluoride water in nearby fluoride prevalent village.

2. Materials and methods

2.1. Materials

Sodium alginate with a molecular weight of 70,000–80,000 was purchased from Himedia (India). $Ca(NO_3)_2$, $(NH_4)_2PO_4$, ammonia and all other chemicals were of analytical grade and used without further purification.

2.2. Synthesis of n-HApAlg composite

The biocomposite, n-HApAlg composite was synthesized by in situ co-precipitation method (Sairam Sundaram et al., 2008). About 2 g of sodium alginate was dissolved in 100 mL of distilled water at 40 °C and stirred continuously for 6 h at the same temperature. Then 20 mL of 1 M $(NH_4)_2PO_4$ solution was added drop wise into the polymer solution over 15 min and stirred for 1 h at 40 °C. The pH of the medium was adjusted to 10 using ammonia solution. Thereafter, 20 mL of 1.67 M of $Ca(NO_3)_2$ solution was added to the above mixture over 20 min at the same temperature, the n-HAp was precipitated into the alginate polymeric matrix and stirred for 2 h. The resulting composite was aged for 24 h in mother liquor and then filtered, washed several times with distilled water to neutral pH, and dried at 80 °C for 24 h in hot air oven. The dried n-HApAlg composite were crushed to fine powder using ball mill (IKA, Germany). The fine composite powder was sieved to get uniform size and then used for fluoride sorption studies.

2.3. Sorption studies

Sorption experiments were performed by the batch equilibration method in duplicate. About 0.1 g of the composite was added into 50 mL of 10 mg/L initial fluoride solution. The mixture was shaken in a thermostated shaker with a constant speed of 200 rpm at room temperature and the filtrate was analyzed for fluoride. The pH of the medium was adjusted with 0.1 M HCl/NaOH solution. The various influencing parameters like contact time, pH and presence of co-ions were optimized. For temperature studies, the effect of different initial fluoride concentrations, viz., 8, 10, 12 and 14 mg/L of 50 mL solution and in the temperature range of 303, 313 and 323 K at neutral pH. The solution was filtered and the fluoride ion concentration was measured. The defluoridation capacity can be calculated by

$$\text{Defluoridation capacity(DC)} = \frac{C_i - C_e}{m} V \times 1000 \text{ mg } F^-/\text{kg}$$

where C_i is the initial fluoride concentration (mg/L), C_e is the equilibrium fluoride concentration (mg/L), m is the mass of the sorbent (g) and V is the volume of the solution (L).

2.4. Analysis

The concentration of the fluoride ion was determined using Thermo Orion Benchtop multiparameter kit (Model: VERSA STAR 92) with the fluoride ion selective electrode with the relative accuracy of ±1 significant digit, detection limit of 0.02 mg/L and the reproducibility of ±2%. The pH measurements were made with the same instrument using pH electrode. All other water quality parameters were investigated using standard methods (APHA, 2005).

2.5. Characterization studies

Fourier transform infrared (FTIR) spectra of the composite were carried out on a JASCO-460 plus spectrometer operated at 1 cm^{-1} resolution in the 400–4000 cm^{-1} region using the KBr pellets. The surface morphology of the composite was imagining by scanning electron microscopy (SEM) with Vega3 Tescan model. The SEM facilitates the direct observation of the surface microstructures of the fresh and fluoride sorbed composite. Elemental spectra of the composite were obtained using an energy dispersive X-ray analyzer (EDAX) with Bruker Nano GMBH model during SEM observations which allows a qualitative detection and localization of elements in the composite. The pH at zero point charge (pH_{zpc}) of the composite was determined by pH drift method (Lopez-Ramon, Stoeckli, Moreno-Castilla, & Carrasco-Marin, 1999).

2.6. Statistical tools

The computations were done using Microcal Origin (Version 8.0) software. The goodness of fit and best model was discussed using the error bar plot, regression correlation coefficient (r), chi-square analysis and standard deviation (sd).

3. Results and discussion

3.1. Effect of contact time

Defluoridation studies of both CaAlg and n-HApAlg composites were carried out with different period of contact time in the range of 10–60 min at 303 K with initial fluoride concentration of 10 mg/L with a sorbent dosage as 0.1 g. As is evident from Fig. 1a, both the sorbents reached saturation at 30 min. Therefore, 30 min of equilibrium time was chosen as contact time for the subsequent experiments. Among the sorbents, n-HApAlg composite possess enhanced DC when compare to CaAlg composite which posses DC of 680 mg F^-/kg. The reported DC of n-HAp is 1296 mg F^-/kg (Sairam Sundaram et al., 2008). So, further studies limited to n-HApAlg composite.

3.2. Influence of solution pH

Fluoride removal depends on the solution pH, so the sorption experiments were carried out with the different initial pH levels viz., 3, 5, 7, 9 and 11, by keeping all other parameters as constant which is shown in Fig. 1b. The fluoride uptake decreases with increase in pH. Reason is at lower pH ranges, the n-HApAlg composite surface acquires positive charge, F^- ion adsorbs more and the DC was found to be the maximum whereas in the higher pH ranges the decrease in DC is due to the competition of OH^- ions with F^- ions in the active sites of the composite.

3.3. Effect of challenger anions

The challenger anions like Cl^-, NO_3^-, SO_4^{2-} and HCO_3^- are normally present in water. The effects of the DC of the composite with the fixed initial concentration of challenger anions are 200 mg/L, 10 mg/L as the initial fluoride concentration and by keeping all other parameters as constant. Fig. 2 shows there is no significant change in the DC of the composite in the presence of co-anions like Cl^-, NO_3^- and SO_4^{2-}, except HCO_3^- ion. The decrease in the

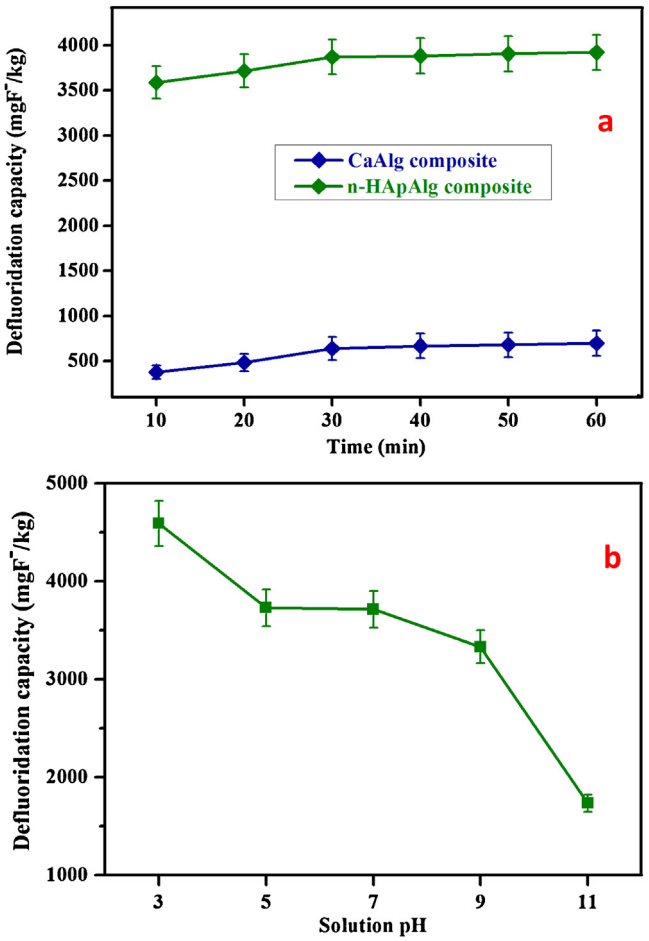

Fig. 1. (a) Effect of contact time on the DC of the sorbents. (b) Effect of pH on DC of n-HApAlg composite.

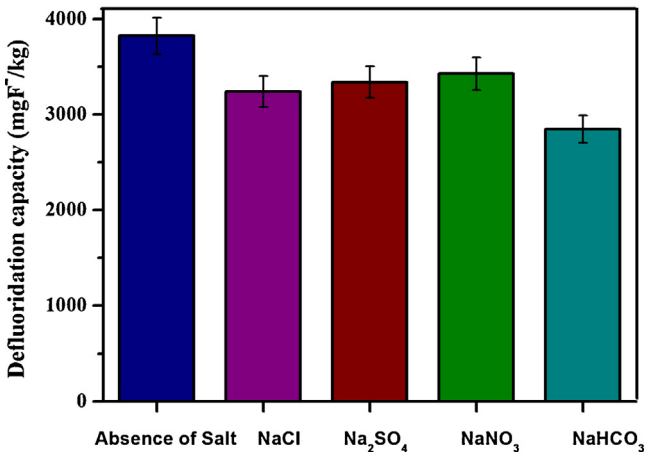

Fig. 2. Influence of co-anions on DC of n-HApAlg composite.

DC of the composite in presence of HCO_3^- ion is due to increase in solution pH which reduces the active sites for fluoride sorption (Viswanathan & Meenakshi, 2010).

3.4. Characterization of the composite

Fig. 3 illustrates the FTIR spectra of synthesized n-HApAlg composite and fluoride treated n-HApAlg composite. The strong absorption band observed at 552 and 1035 cm^{-1} which are

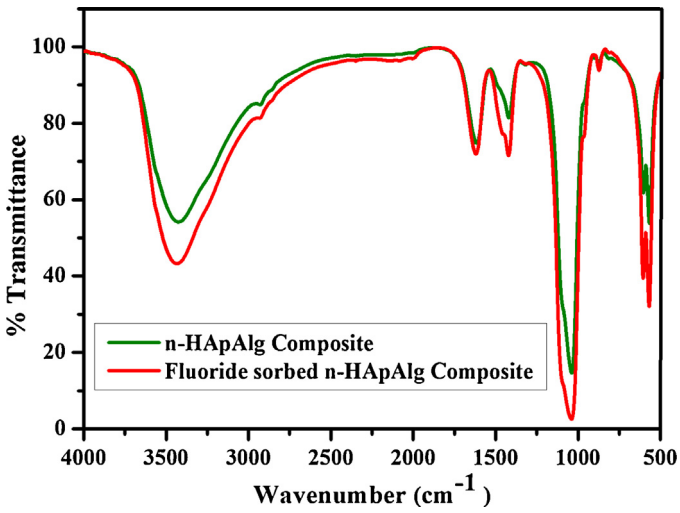

Fig. 3. FTIR spectra of n-HApAlg composite and fluoride-sorbed n-HApAlg composite.

attributed to the bending and stretching of PO_4^{3-} of n-HAp (Ma, Zhu, & Chang, 2006). In addition, alginate also has a strong band at 1035 cm^{-1} (Jin et al., 2008). Thus, the observed broad band at 1035 cm^{-1} is attributed to the overlap of C—O—C stretching of Alg and PO_4^{3-} stretching of n-HAp. In n-HApAlg composite, the observed band at 1607 and 1418 cm^{-1} suggests that the formation of a chemical bond between the mineral phase and the organic polymeric matrix; i.e., the interaction between the positive charge of calcium and the negative charge of the carboxyl group in alginate (Wang, Li, & Li, 2009). The presence of intermolecular interactions between inorganic minerals and alginate chains in the polymer network could be used to control nucleation and the growth of inorganic phases (Rajkumar, Meenakshisundaram, & Rajendran, 2011). The band at 3446 cm^{-1} in the spectrum of n-HApAlg composite is assigned to stretching of the —OH groups of Alg and n-HAp. The broadening band at 3446 cm^{-1} in the fluoride sorbed n-HApAlg composite is due to electrostatic adsorption between the composite and the fluoride ion (Viswanathan & Meenakshi, 2010).

The change in the surface morphology of n-HApAlg composite with respect to n-HAp was supported by shifting of pH_{zpc} values from 7.88 (n-HAp) to 7.2 (n-HApAlg composite). SEM pictures of n-HApAlg composite and fluoride sorbed n-HApAlg composite are presented in Fig. 4a and b, respectively. The surface of the sorbent is rough with abundant bump and many pores are present on the surface, which facilitates the diffusion of fluoride ions into the n-HApAlg composite for its sorption. The change in the SEM micrographs of the sorbent before and after fluoride treatment facilitates the structural changes in the sorbent. This is further supported by EDAX analysis which provides the direct confirmation for the sorption of fluoride ions onto n-HApAlg composite. The EDAX spectra of n-HApAlg composite confirm the presence of respective ions in the composite (cf. Fig. 4c). The fluoride sorption has occurred onto n-HApAlg composite was confirmed by the presence of fluoride peaks in the EDAX spectra of fluoride treated n-HApAlg composite (cf. Fig. 4d).

3.5. Sorption isotherms

The fluoride uptake capacity of the composite was determined using Freundlich (1906) and Langmuir (1916) isotherms. The linear plot of $\log q_e$ vs. $\log C_e$ indicates the applicability of Freundlich isotherm. The k_F and n values are presented in Table 1. The values of $1/n$ lying between 0 and 1 and the n value lying in the range of 1 to 10 confirm the favourable conditions for adsorption. The values of b

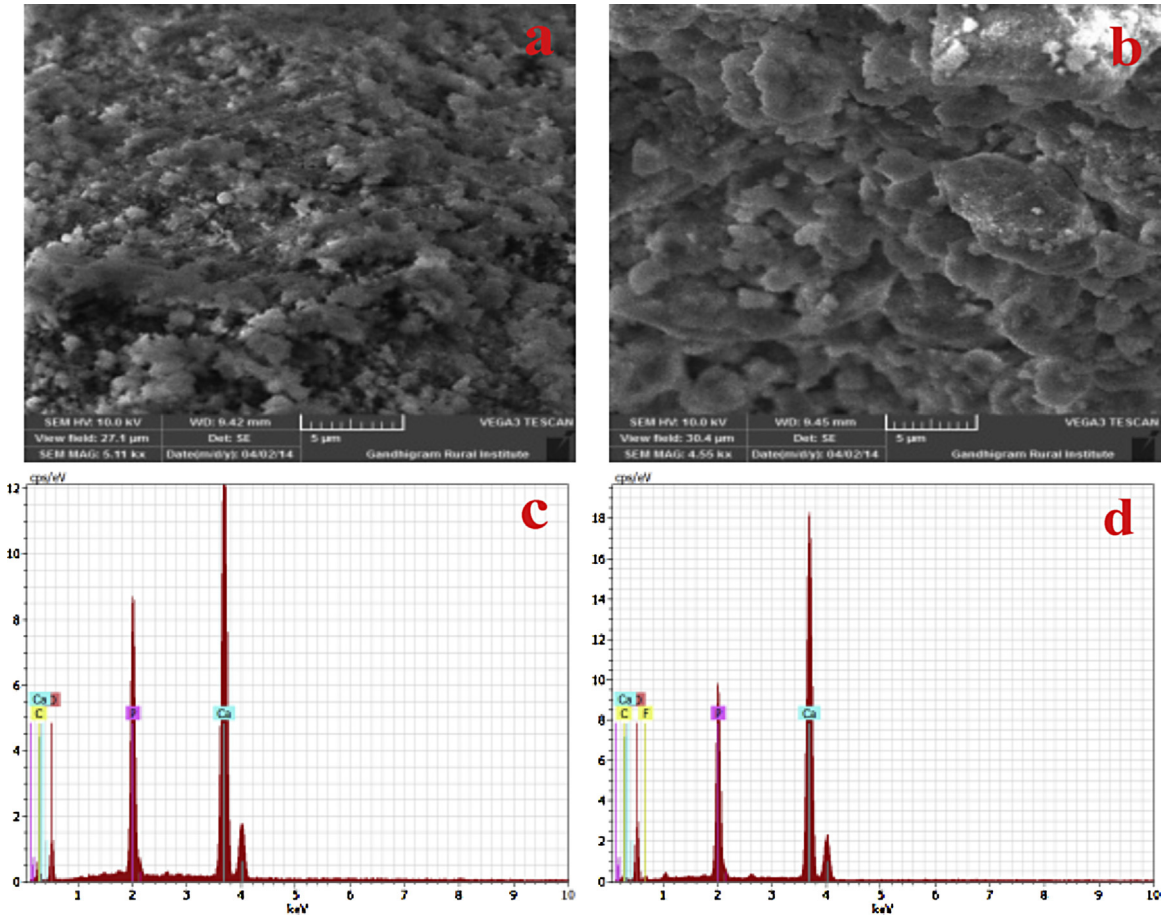

Fig. 4. SEM images of (a) n-HApAlg composite and (b) fluoride sorbed n-HApAlg composite, EDAX spectra of (c) n-HApAlg composite and (d) fluoride treated n-HApAlg composite.

and Q° can be calculated from the intercept and slope of the plot of C_e/q_e vs. C_e. The values of Q° and b are listed in Table 1. The characteristics of Langmuir sorption isotherm can be represented in terms of dimensionless separation factor (R_L) values. The experimentally calculated values of R_L lie in the range between $0 < R_L < 1$, thereby indicating that the sorption process was favourable. Moreover, the low values of R_L reveal that there is a strong interaction between the fluoride and the composite. The results of chi-square analysis are presented in Table 1. The χ^2 values of Langmuir isotherm are lower than Freundlich isotherm, indicating that Langmuir isotherm is more suitable for the sorption of fluoride onto n-HApAlg composite.

3.6. Thermodynamic parameters

The thermodynamic parameters of n-HApAlg composite viz., ΔG°, ΔH° and ΔS° are shown in Table 1. The negative values of ΔG° and positive values of ΔH° indicate that the fluoride sorption process is spontaneous and endothermic in nature. The positive value of ΔS° suggests the increased randomness at the solid–solution interface during the sorption of fluoride onto n-HApAlg biocomposite.

3.7. Sorption kinetics

The sorption kinetics describes the sorbate uptake rate that can determine the residence time of sorbate at the solid–solution interface. The sorption processes are analyzed by using reaction-based models, including pseudo-first order (Lagergren, 1898) and pseudo-second-order (Ho, 2006) models. The linear plots of $\log(q_e - q_t)$ against t give straight line indicate the applicability of pseudo-first-order model. The slope of the straight line plot of $\log(q_e - q_t)$ against t sorption at different temperatures viz., 303, 313 and 323 K give the value of the pseudo-first-order rate constant (k_{ad}) and r values are listed in Table 2. The pseudo-second-order equation can be found out experimentally by plotting t/q_t against t. The values of q_e, k, h and r of the pseudo-second-order model were obtained from the plots of t/q_t vs. t

Table 1
Isotherms and thermodynamic parameters of n-HApAlg composite.

Temp. (K)	Freundlich isotherm					Langmuir isotherm					Thermodynamic parameters		
	$1/n$	n	k_F (mg/g) (L/mg)$^{1/n}$	r	χ^2	Q° (mg/g)	b (L/g)	R_L	r	χ^2	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/(mol K))
303	0.178	5.605	3.187	0.974	0.0009	0.123	1.728	0.055	0.983	0.0006	−3.25	4.19	0.0031
313	0.187	5.352	3.300	0.894	0.0050	0.113	1.811	0.052	0.903	0.0040	−3.20		
323	0.221	4.520	3.404	0.877	0.0070	0.121	1.532	0.061	0.896	0.0060	−3.18		

Table 2
Kinetic models of n-HApAlg composite on fluoride removal.

Kinetic models	Parameters	303 K				313 K				323 K			
		8 mg/L	10 mg/L	12 mg/L	14 mg/L	8 mg/L	10 mg/L	12 mg/L	14 mg/L	8 mg/L	10 mg/L	12 mg/L	14 mg/L
Pseudo-first-order	k_{ad} (min^{-1})	0.158	0.153	0.155	0.200	0.146	0.107	0.157	0.183	0.158	0.153	0.155	0.153
	r	0.912	0.886	0.766	0.943	0.974	0.989	0.850	0.953	0.912	0.886	0.766	0.886
	sd	0.322	0.364	0.591	0.320	0.154	0.073	0.443	0.260	0.322	0.364	0.591	0.364
Pseudo-second-order	q_e (mg/g)	3.446	3.663	4.292	4.330	3.521	3.861	4.484	4.545	3.521	4.000	4.673	4.975
	k (g/mg min)	0.237	0.384	0.137	0.246	0.236	0.315	0.181	0.177	0.349	0.248	0.129	0.114
	h (mg/g min)	2.809	5.155	2.532	4.608	2.924	4.695	3.636	3.610	4.320	3.968	2.817	2.817
	r	0.999	0.999	1.00	1.00	0.999	0.999	1.00	0.999	0.999	0.999	0.999	0.999
	sd	0.075	0.052	0.082	0.043	0.022	0.017	0.092	0.069	0.058	0.066	0.164	0.087
Particle diffusion	k_p (min^{-1})	0.189	0.038	0.129	0.112	0.141	0.106	0.163	0.176	0.149	0.166	0.156	0.212
	r	0.871	0.996	0.978	0.979	0.978	0.989	0.844	0.960	0.924	0.870	0.764	0.937
	sd	0.489	0.326	0.174	0.159	0.352	0.322	0.166	0.291	0.364	0.447	0.172	0.279
Intraparticle diffusion	k_i (mg/g $min^{0.5}$)	0.133	0.085	0.213	0.133	0.154	0.125	0.151	0.176	0.088	0.127	0.199	0.243
	r	0.997	0.996	0.991	0.996	0.961	0.956	0.984	0.977	0.977	0.966	0.948	0.986
	sd	0.013	0.011	0.039	0.015	0.059	0.052	0.036	0.052	0.009	0.015	0.090	0.055

for fluoride sorption at different temperatures viz., 303, 313 and 323 K of the composite are presented in Table 2. The values of q_e increase with the increase in temperature indicating the fluoride sorption increases with increase in temperature. The higher r values obtained for pseudo-second-order model than pseudo-first-order model indicate the applicability of the pseudo-second-order model.

For a solid–liquid sorption process, the solute transfer is usually characterized either by particle diffusion (Chanda, O'Driscoll, & Rempel, 1983) or by intraparticle diffusion (Weber & Morris, 1964) control. The respective 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, respectively. The k_p, k_i and r values at three different temperatures viz., 303, 313 and 323 K for both particle and intraparticle diffusion models are illustrated in Table 2. The r values obtained for both particle and intraparticle diffusion models are almost comparable and suggest that the fluoride diffusion on n-HApAlg composite follows both the models. The sd values were often used to evaluate the conformity between experimental data and modelled values. Based on the sd values shown in Table 2, it is clear that the lower sd values of pseudo-second-order and intraparticle diffusion model is suitable for describing the sorption kinetics of fluoride on composite.

3.8. Defluoridation mechanism of n-HApAlg composite

The fluoride removal by n-HApAlg composite was governed by both adsorption and ion-exchange mechanism as shown in Fig. 5.

Table 3
Field trial results of n-HApAlg composite.

Water quality parameters	Treatment	
	Before	After
F^- (mg/L)	3.07	0.94
pH	8.38	8.00
Cl^- (mg/L)	284	253
Total hardness (mg/L)	313	266
Total dissolved solids (mg/L)	736	704

The positively charged Ca^{2+} present in the composite attracted negatively charged fluoride ions by means of electrostatic attraction. In addition to this the OH^- ions of the n-HAp lattice are replaced by the F^- ions by means of ion-exchange.

3.9. Field study

The synthesized n-HApAlg composite used in the present study was also tested with a field sample taken from a nearby fluoride prevalent village. About 0.1 g of sorbent was added to 50 mL of fluoride field water sample and the contents were shaken with constant time at room temperature and the results are presented in Table 3. The treated field water contains fluoride concentration which is less than the tolerance limit (1.5 mg/L) which shows the selectivity of the composite towards fluoride. There is a significant reduction in the levels of other water quality parameters in addition to fluoride indicates, n-HApAlg composite can be effectively employed as promising defluoridating agent.

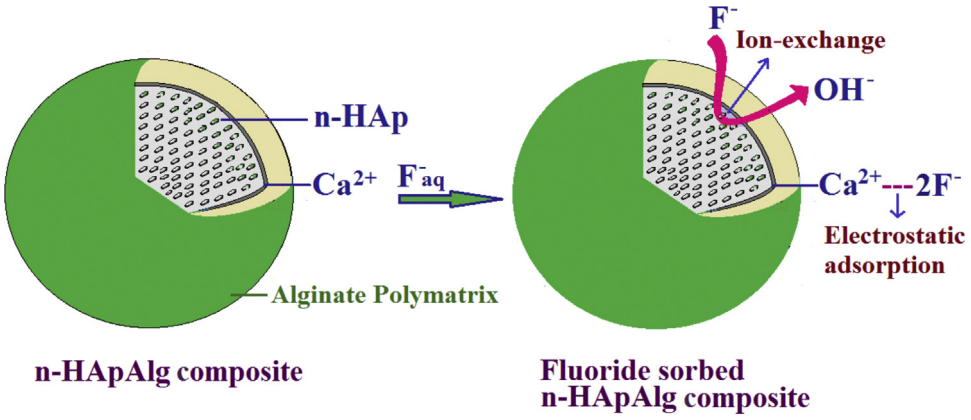

Fig. 5. Feasible fluoride removal mechanism of n-HApAlg composite.

4. Conclusions

The present study highlights the fluoride uptake capacity of n-HApAlg composite. The DC of n-HApAlg composite was influenced by the solution pH and slightly in the presence of bicarbonate ions. The sorption of fluoride on n-HApAlg composite follows Langmuir isotherm. The nature of fluoride sorption is spontaneous and endothermic. Kinetic studies revealed that fluoride sorption process was controlled by pseudo-second-order and intraparticle diffusion model. Field trial results indicate that n-HApAlg composite could be effectively employed as selective and promising defluoridating agent. The developed n-HApAlg composite is an eco-friendly, low cost, non-toxic, biocompatible and biodegradable material for the technology development.

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