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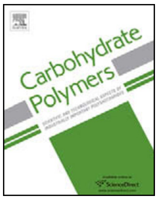

Synthesis of alginate bioencapsulated nano-hydroxyapatite composite for selective fluoride sorption

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.

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., $(1 \rightarrow 4)\beta$-D-mannuronate and $(1 \rightarrow 4)\alpha$-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

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* 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