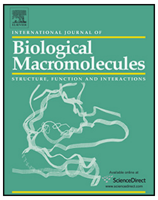
International Journal of Biological Macromolecules xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

International Journal of Biological Macromolecules

journal homepage: www.elsevier.com/locate/ijbiomac



Enhanced defluoridation and facile separation of magnetic nano-hydroxyapatite/alginate composite

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ARTICLE INFO

Article history:
Received 21 April 2015
Received in revised form 3 June 2015
Accepted 11 June 2015
Available online xxx

Keywords:
Magnetic
Nano-hydroxyapatite
Alginate
Biocomposite
Fluoride removal

ABSTRACT

In this research study, a new magnetic biosorbent namely Fe_3O_4@n-HAp/Alg composite was developed by the fabrication of Fe_3O_4 particles on nano-hydroxyapatite(n-HAp)/alginate (Alg) composite for defluoridation in batch mode. The synthesized Fe_3O_4@n-HAp/Alg biocomposite possess an enhanced defluoridation capacity (DC) of 4050 mgF$^-$/kg when compare to n-HAp/Alg composite, Fe_3O_4@n-HAp composite, n-HAp and Fe_3O_4 which possesses the DCs of 3870, 2469, 1296 and 1050 mgF$^-$/kg respectively. The structural changes of the sorbent, before and after fluoride sorption were studied using FTIR, XRD and SEM with EDAX techniques. There are various physico-chemical parameters such as contact time, pH, co-existing anions, initial fluoride concentration and temperature were optimized for maximum fluoride removal. The equilibrium data was well modeled by Freundlich, Langmuir and Temkin isotherms. The present system follows Langmuir isotherm model. The thermodynamic parameters revealed the feasibility, spontaneity and endothermic nature of fluoride sorption. To check the performance and efficiency of the adsorbent material was examined with water samples collected from a fluoride endemic area namely Reddiyarchatram and Ammapatti in Dindigul District of Tamil Nadu using standard protocols.

1. Introduction

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Fluoride is well desirable at lower concentration level, but harmful when it exceeds the tolerance limit as suggested by WHO (>1.5 mg/L) [1]. The presence of fluoride in groundwater is a serious human health trouble because consumption of drinking water with higher concentration of fluoride causes fluorosis. The drinking water is a major source for fluoride intake. Generally, fluoride is entered into the environmental system by both natural behaviors, including leaching of fluoride from contaminated soils and/or minerals and anthropogenic activities like glass, aluminum and semiconductor manufacturing industries [2]. India is one among the 23 nations around the world where health problems have been reported due to excessive fluoride in drinking water. In India, it was estimated that 62 million people, including 6 million children less than 14 years of age in 17 states are affected with dental, skeletal and/or non-skeletal fluorosis [3]. In rural area, groundwater is intended for drinking, cooking and other domestic purposes. So, it is a time to supply safe drinking water to the people who are consuming fluoride contaminated water.

Numerous conventional technologies exist for the removal of excess fluoride from water viz., chemical precipitation, electrocoagulation, nanofiltration, reverse osmosis, Donnan dialysis and ion-exchange [4–9]. Among them, adsorption is one of the commonly used techniques to remove excess fluoride from water, especially for small community systems and homes in rural areas in low income regions because the system is cost-effective and simple to operate [10]. In recent days, significant effort has been performed for the purpose of developing new and cost-effective sorbents for the removal of fluoride.

Biosorption is an eco-friendly technique for the removal of fluoride from aqueous medium. Alginate is one of the biopolymer have been studied extensively for the sorption of fluoride because of its low cost, biodegradability, biocompatibility and eco-friendly nature. However, it possesses limitations like low removal capacity, stability, etc. The biopolymer supported inorganic composites has significant attention in recent years for fluoride removal as it possess the high uptake capacity than the base components [11–18].

The nanocomposites have unique properties for the valuable applications in removal of fluoride from the environment. The extremely small size of nano-particles creates a large surface area in relation to their volume, which makes them highly reactive, compared to non-nano forms of the same sorbents. Usually it is difficult to separate nano-particles quickly from

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http://dx.doi.org/10.1016/j.ijbiomac.2015.06.019
0141-8130/© 2015 Published by Elsevier B.V.

Please cite this article in press as: K. Pandi, N. Viswanathan, Int. J. Biol. Macromol. (2015), http://dx.doi.org/10.1016/j.ijbiomac.2015.06.019

large volumes of solution, while magnetic adsorbents can circumvent this problem because they can be separated easily from solution by an external magnetic field. Therefore, adsorbents combining nanotechnology and magnetic separation technique would remove toxic ions in ideal presentation [19]. So far, there are several magnetic nanocomposites, including aluminum-type super paramagnetic, Fe/Al mixed hydroxides, Fe_3O_4@Al$(OH)_3$ magnetic nanoparticles, polypyrrole/Fe_3O_4 magnetic nanocomposite, magnetic magnesium–aluminum layered double hydroxides, sulfate-doped Fe_3O_4/Al_2O_3 nanoparticles and γ-AlOOH@CS magnetic nanoparticle adsorbents have been explored for the removal of fluoride [20–26]. These magnetic nanocomposites were found to be cost-effective, simple to use and environmentally friendly when compared to the other adsorbents. So far, there is no report available for utilizing alginate supported magnetic biocomposite materials for fluoride removal.

Hence in the present study, the authors have aimed to fabricate magnetic Fe_3O_4 particles over nano-hydroxyapatite/alginate biocomposite for defluoridation of water in batch mode. The sorption studies were carried out to optimize various equilibrating conditions like contact time, pH, presence of competitor anions, different initial fluoride concentrations and temperature. The thermodynamic parameters viz., ΔG°, ΔH° and ΔS° have also been calculated and interpreted. The application of the biocomposite at field conditions was also tested by collecting the field fluoride water sample in a nearby fluoride rife area namely Reddiyarchatram and Ammapatti in Dindigul District of Tamil Nadu.

2. Materials and methods

2.1. Materials

Sodium alginate was purchased from Himedia (India). Ammonium dihydrogen phosphate, calcium nitrate tetrahydrate, ferrous chloride tetrahydrate, ferric chloride hexahydrate, 25% of ammonia solution and sodium fluoride was purchased from Merck (India) were of analytical grade and used without further purification. A stock solution containing 1000 mg/L fluoride ion was prepared by dissolving the appropriate amount of NaF in 1 l of double distilled water. The working solutions were prepared by diluting the stock solution with double distilled water.

2.2. Synthesis of Fe_3O_4@n-HAp/Alg biocomposite

The synthesis of n-HAp/Alg composite was performed according to our previous report [12]. Fe_3O_4@n-HAp/Alg biocomposite was prepared by 2% (w/v) concentration of sodium alginate was dissolved in double distilled water at 40 °C and continuously stirred for 6 h. Then 20 mL of 1 M $(NH_4)_2PO_4$ solution was added dropwise 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 25% of 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 and then stirred for 2 h. Then a mixture of 10 mL of $FeCl_2{\cdot}4H_2O$ (1.85 mmol) and $FeCl_3{\cdot}6H_2O$ (3.7 mmol) solution was slowly added into above mentioned n-HAp/Alg medium over 10 min, during addition the pH of the medium was maintained at 10. The formed magnetic n-HAp/Alg biocomposite was aged for 24 h in mother liquor and then filtered, washed with plenty amount of distilled water to neutral pH and dried at 80 °C for 24 h in hot air oven. The magnetic nano-hydroxyapatite (Fe_3O_4@n-HAp) composite was prepared by without alginate. The dried Fe_3O_4@n-HAp, n-HAp/Alg and Fe_3O_4@n-HAp/Alg composites 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. Batch sorption experiments

Batch sorption experiments were performed in duplicate. A 50 mL of 10 mg/L initial concentration of fluoride was added to the 250 mL stopper conical flasks. A prefixed mass of Fe_3O_4@n-HAp/Alg biocomposite (0.1 g) was added to a flask and shaken in a thermostat shaker with a constant speed of 200 rpm at 30 °C. At a range of time intervals, the sorbent was separated and the concentration of fluoride was determined. The solution 0.1 M HCl/NaOH was used for pH adjustment. In isotherm studies, 50 mL of different initial fluoride concentrations (8, 10, 12 and 14 mg/L) was stirred with 0.1 g of sorbent dosage in a thermostat shaker in the temperature range of 30, 40 and 50 °C at neutral pH. The sorbent was separated by magnet and the fluoride concentration was analyzed. The defluoridation capacity (DC) can be calculated by

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

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. Analytical methods

The concentration of the fluoride ion was determined using Thermo Orion Benchtop multiparameter kit (Model: VERSA STAR92) 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 [27].

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. An X-ray diffraction (XRD) measurement was obtained using X'per PRO model-PANalytical to determine the crystalline phases present in the composite. The surface morphology of the composites was imagined 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 composites. 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 composites. The pH at zero point of charge (pH_{zpc}) of the sorbents was determined by pH drift method [28].

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 regression correlation coefficient (r), chi-square analysis (χ^2) and standard deviation (sd).

3. Results and discussion

3.1. Effect of contact time

The fluoride removal capacities of Fe_3O_4, n-HAp, Fe_3O_4@n-HAp, n-HAp/Alg and Fe_3O_4@n-HAp/Alg sorbents were carried out with

Please cite this article in press as: K. Pandi, N. Viswanathan, Int. J. Biol. Macromol. (2015), http://dx.doi.org/10.1016/j.ijbiomac.2015.06.019