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La(III)-loaded bentonite/chitosan beads for defluoridation from aqueous solution

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Abstract: Developing low-cost and effective materials for excess fluoride removal is important for providing safe water. A novel adsorbent, La(III)-loaded bentonite/chitosan beads (La-BCB) was prepared for defluoridation from aqueous solution. The effects of various parameters such as dosage of La(III), pH, temperature, contact time, initial fluoride concentration and presence of co-existing anions were investigated to examine the defluoridation behavior. The maximum defluoridation capacity of La-BCB was 2.87 mg/g at pH 5, 30 °C. Scanning electron microscopy (SEM), energy dispersive spectroscopy (EDX) and Fourier transform infrared spectroscopy (FTIR) were employed to analyze the characteristics of La-BCB. The equilibrium fluoride adsorption data fitted well with both Langmuir and Freundlich isotherm models. The R_L value revealed that the defluoridation process using La-BCB was favorable. The adsorption kinetics followed pseudo-second order kinetic as well as particle and intraparticle diffusion models. The presence of carbonate and bicarbonate reduced defluoridation capacity of La-BCB while sulphate, nitrate and chloride showed slight effect. The exhausted La-BCB was regenerated using sodium hydroxide with only 17% loss. The reasonable defluoridation mechanism could be interpreted as adsorption and ion exchange.

Keywords: La(III); bentonite; chitosan beads; defluoridation; adsorption; fluoride; rare earths

Presence of fluoride dissolved in water is due to natural processes as well as anthropogenic activities[1]. Drinking water and food with low concentrations are beneficial for health; however, long-term exposure to excess fluoride level can cause dental and skeletal fluorosis[2]. Around 200 million people living in 25 nations worldwide[3] consume drinking water with excess fluoride concentration which exceeds 1.5 mg/L recommended by WHO[4]. In China, endemic fluorosis, associated with high fluoride concentration in drinking water and brick tea liquor, has affected approximately 2 million people in 29 provinces, municipalities or autonomous regions[5]. In some rural areas ground water with fluoride concentration above 10 mg/L[5–7] is the main source of drinking water. Therefore, it is extremely important to prevent fluorosis by developing more cost effective materials for excess fluoride removal from water.

Various methods based on adsorption[8], ion exchange[9], precipitation[10], electro coagulation[11], and membrane separation[12,13] have been investigated for defluoridation. Among these methods, adsorption still seems to be a widely used one. Recent research work mainly focuses on low-cost adsorbents such as red mud[14], clay[15], mesoporous alumina[16], granular bentonite[17] and fly ash[18]. Bentonite is a major and low-cost aluminosilicate clay group containing SiO_2, Al_2O_3 and oxides of Mg, Fe, Ca, K. Because of the large surface areas and high cation exchange capacity, the bentonite possesses sorption ability for fluoride. However, bentonite typically displays drawbacks like dimensional instability and low permeability[19], which limits its application for fluoride removal. Thus, it is important to modify bentonite to improve its adsorption capacity for fluoride. It has been well reported that granular acid-treated bentonite[17], La-incorporated bentonite[20], MgO-incorporated bentonite[15], etc., show an enhancement in defluoridation and acid-treated bentonite was confirmed to be accessible and effective.

Chitosan is a polysaccharide obtained by partial or total N-deacetylation of chitin which is abundant in nature[21]. In order to improve its defluoridation capacity, much effort has been devoted to modify chitosan either physically or chemically. Chitosan beads[22–24] or particles[25] showed desirable stability and could be regenerated compared with the natural flakes or powder chitosan. Chitosan-based composites with minerals (mixed rare

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earth oxides[26], silica[27], zeolite[28], etc.) have been studied as successful fluoride adsorbents. Chitosan chelated with polyvalent metal cations such as La(III)[22,23], Fe(III)[24], Ce(III)[29] effectively utilize the amino groups of chitosan as well as the high affinity of metal cations to adsorb electronegative fluoride ions. Viswanathan et al.[22] and Thakre et al.[23] have developed La(III) incorporated carboxylated chitosan beads using complexation mechanism and La(III) incorporated chitosan beads in method of chemical precipitation, respectively, which showed good adsorption capacity for fluoride. However, the mechanical performance and reusability are low, which reduce their application value. In this work, adsorbent was prepared using inverse suspension polymerization in the steps of mixing bentonite and chitosan, chelating with La(III) and crosslinking. This method theoretically ensures the better mechanical stability, higher resistance to acid solution and less release of loaded La(III) of the beads.

The objective of the study was to: (i) synthesize a novel fluoride adsorbent namely La(III)-loaded bentonite/chitosan beads (La-BCB), (ii) examine the defluoridationcapacity of La-BCB by adsorption experiments, (iii) investigate the defluoridation behavior and mechanism of La-BCB by isotherm models and kinetics models.

1 Experimental

1.1 Adsorbent preparation

Natural bentonite powder was activated by hydrochloric acid and then calcined in a muffle furnace at 500 °C for 5 h.

The preparation mechanism of the adsorbent is shown in Fig. 1(a). 10.0 g chitosan (MW 5.1×10^5 Da, DD 95.4%), 1.0 g activated bentonite and a certain quantity of lanthanum nitrate (1.0, 2.0 and 3.0 g) were mixed in 100 mL deionized distilled water (DDW) with stirring for 3 h. The resulting solution was then added to100 mL acetic acid solution (4 vol.%) for 24 h. Liquid paraffin was added to form a dispersion phase. Formaldehyde and epoxy chloropropane were added as crosslinking agents[30]. Chitosan beads (CB) and bentonite/chitosan beads (BCB) were prepared under identical experimental conditions and served as control. The La(III)-loaded bentonite/chitosan beads with optimal dosage of La(III) was referred to La- BCB.

1.2 Defluoridation experiments

Fluoride stock solution of 100 mg/L was prepared using anhydrous sodium fluoride. Fluoride solutions of required concentrations were prepared by appropriate dilution of the stock solution.

Defluoridation experiments were carried out in PVC conical flasks shaken in a horizontal rotary shaker at a constant speed of 160 r/min at 30 °C for 8 h. 0.1 g adsorbent was added into 50.0 mL of 10 mg/L fluoride solution. After adsorption equilibration and filtration separation, fluoride concentration in filtrates was measured using a fluoride ion selective electrode (PF-1, Shanghai Leici, China). The amount of fluoride adsorbed was calculated from the following equation

$$q_e=\left(\frac{c_0-c_e}{W}\right)V \tag{1}$$

where q_e is the adsorption capacity of adsorbent at equilibrium (mg/g), c_0 is the initial fluoride concentration (mg/L), c_e is the equilibrium fluoride concentration (mg/L), V is the volume of solution (L), and W is the mass of the used adsorbent (g).

The effect of solution pH ranging from 3.0 to 9.0 on defluoridation was conducted by adjusting pH with 1.0 mol/L NaOH or 1.0 mol/L HCl. The adsorption kinetics was studied with contact time of 30, 60, 120, 240 and 480 min. The adsorption isotherm was investigated with initial fluoride concentrations of 2.0, 5.0, 10.0 and 20.0 mg/L at temperatures of 20, 30, 40 and 50 °C. The study of co-existing anions was carried out in the presence of sulphate, carbonate, nitrate, chloride and bicarbonate respectively with concentration of 200 mg/L by keeping initial fluoride concentration as 10 mg/L.

1.3 Regeneration studies

To retrieve La-BCB, sodium hydroxide aqueous solution was used to desorb fluoride ions from the exhausted beads, which is shown in Fig. 1(c). The fluoride- treated La-BCB was regenerated in 0.5 mol/L NaOH for 12 h and was washed with DDW to the neutral pH followed by drying in oven at 50 °C for 24 h. The regenerated La-BCB was reused in the next defluoridation experiments and the procedure was repeated for 10 times.

1.4 Characterization of La-BCB

The surface microstructure of La-BCB was observed with a scanning electron microscope (SEM, Inspect F50, USA). The element composition of La-BCB before and after fluoride adsorption was determined by energy dispersive X-ray analysis (EDX, USA EDAX Company). In order to confirm the functional groups present in adsorbents, FTIR spectra of CB, BCB, La-BCB and fluoride-treated La-BCB were recorded on a Nexus 470 FTIR spectrometer. The powder of adsorbent was mixed with spectrophotometric grade KBr in 1:100 ratios. The spectra of the tablets were scanned within spectral range of 400–4000 cm^{-1}.

2 Results and discussion

2.1 Optimization of La(III) loading dosage

From the data shown in Fig. 2, La-BCB possessed better defluoridation capacity than BCB and CB. As for