Enhanced fluoride adsorption using Al (III) modified calcium hydroxyapatite

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HIGHLIGHTS

- ▶ Al modified hydroxyapatite possessed a higher defluoridation capacity of 32.57 mg/g.
- ▶ Hydroxyl groups on the surface of Al-HAP was the adsorption sites for F⁻ removal.
- ▶ Enhanced F⁻ removal over Al-HAP was attributed to the modification with aluminum.

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ABSTRACT

Aluminum-modified hydroxyapatite (Al-HAP) was prepared and characterized using XRD and BET analyses. Al-HAP possessed higher defluoridation capacity (DC) of 32.57 mgF⁻/g than unmodified hydroxyapatite (HAP) which showed a DC of 16.38 mgF⁻/g. The effect of Al/Ca atomic ratio in Al-HAP, solution pH and co-existing anions was further studied. The results indicated that the adsorption data could be well described by the Langmuir isotherm model and the adsorption kinetic followed the pseudo-second-order model. The pH changes during the adsorption process suggested that the —OH on the surface of Al-HAP was the adsorption sites. The more adsorption sites were formed on Al modified HAP, which possessed abundant surface hydroxyl groups, resulting in higher efficiency of F⁻ removal. Thermodynamic parameters such as ΔG° , ΔH° and ΔS° were calculated in order to understand the nature of adsorption process. The results revealed that the adsorption reaction was a spontaneous and endothermic process.

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1. Introduction

Presence of fluoride in drinking water can be beneficial or harmful depending on its concentration [1]. Excess ingestion of fluoride with high concentration can induce mottling of teeth, softening of bones, even neurological damages [2]. So, fluorosis is an important public health problem all over the world, and an appropriate concentration of fluoride (0.5–1.5 mg/L) is required to prevent dental cavities [3–5].

Fluoride removal from drinking water could be achieved by chemical precipitation, adsorption, membrane and ion exchange [6]. Among these methods, membrane and ion exchange processes are not very common due to its high installation and maintenance cost, while chemical precipitation results in relatively higher residual fluoride concentration in the effluents [5,7]. Adsorption process is a widely accepted technique because of its ease of operation and cost-effectiveness [3]. Activated alumina is one of the most economical adsorbent for fluoride removal from drinking water. However, the slow rate of adsorption of commercially available

activated alumina limits its use for treating large quantity of water [8,9]. In recent years, many efforts have been devoted to investigate and develop new fluoride adsorbent using various synthetic, naturally occurring and waste materials, such as fly ash [10], clay [11], hydrotalcite [12], zeolite [13], etc.

Hydroxyapatite (HAP) is a calcium phosphate based bioceramic and used in the medical field as it is the main component of the hard tissues of living bodies such as bones, teeth, etc. [14]. It has been proven that nanoscale materials offer new possibilities to chemists and the surface properties, electronic structure, coordination etc. would be modified when material dimensions reach the nanoscale [1]. Nano-HAP was hence used as adsorbent material to remove fluoride from water and exhibited high performance for fluoride removal [1,15,16]. It has been reported that the surface hydroxyl groups are the active site for adsorbent material and the heavy metals removing by adsorption depends on the surface site [1,17]. Therefore, the fluoride removal efficiency should be greatly enhanced by increasing the amount of surface hydroxyl groups on the Nano-HAP.

In this paper, aluminum modified calcium hydroxyapatite (Al-HAP) nanoparticles were synthesized by co-precipitation method and defluoridation studies were carried out under various conditions such as the effect of Al/Ca atomic ratio in Al-HAP, solution pH

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and competitor anions. The results indicated that Al-HAP possessed higher defluoridation capacity (DC) of 32.57 mgF⁻/g than unmodified hydroxyapatite (HAP) which showed a DC of 16.38 mgF⁻/g. Moreover, the experimental data were fitted with isotherms and the kinetic models. The equilibrium and kinetic studies would definitely throw more light in understanding the defluoridation mechanism of Al-HAP. Moreover, the reasonable mechanism of fluoride removal by Al-HAP was also suggested.

2. Materials and methods

2.1. Materials

Ca(NO₃)₂·4H₂O, Al(NO₃)₃·9H₂O, H₃PO₄ and NH₄OH were purchased from the YiLi Company. NaF, NaOH, HCl and all other chemicals and reagents were all analytical grade and used as received without purification. The fluoride stock solution was prepared with deionized water using NaF. Fluoride working solutions were freshly prepared by diluting fluoride stock solution with deionized water. Deionized and doubly distilled water was used throughout this study. NaOH and HCl solutions were used to adjust the pH of the solution.

2.2. Adsorbent preparation

Al modified HAP particles were prepared by co-precipitation method. Ca(NO₃)₂ and Al(NO₃)₃ were dissolved in 1 L deionized-distilled water free from CO₂ at atomic ratios Al/Ca from 0 to 0.5. The total amount of Ca and Al in solution was held at 0.1 mol. 0.06 mol of H₃PO₄ was added to the solutions and the solution pH was adjusted to 9 by adding a 15 M NH₄OH solution. The suspension was aged in a capped Teflon vessel at 100 °C for 6 h. The resulting precipitates were filtered off, washed with 5 L deionized-distilled water, and finally dried at 70 °C overnight in air.

As a reference, HAP particles were synthesized by the same process.

2.3. Characterization of adsorbents

Powder X-ray diffraction of the adsorbents were recorded on a Scintag-XDS-2000 diffractometer with Cu Kα radiation (λ = 1.54059 Å). Nitrogen adsorption/desorption experiments were carried out using a Micromeritics ASAP2000 analyzer (Micromeritics Co., USA). TEM images of the catalyst were examined using a TEM Hitachi H-7500. The infrared spectra were recorded on Bruker Tensor 27 FTIR Spectrophotometer. The KBr pellet technique was used and the spectra data was recorded from 4000 to 400 cm⁻¹ with a resolution of 4 cm⁻¹. The Zeta potential of the adsorbents in the KNO₃ (10⁻³ M) solution was measured with a Zetasizer 2000 (Malvern, Worcestershire, UK) with three consistent readings.

2.4. Adsorption experiments

Stock solution of sodium fluoride containing 100 mg/L was prepared and this was used for fluoride sorption experiments. All batch fluoride adsorption studies were carried out in 250 mL Teflon flasks with a working volume of 100 mL. After adding the required amount of Al-HAP (0.5 g/L) to the fluoride solution (10 mg/L), the flasks were sealed and kept in an orbital shaker with thermostatic control at 180 rpm and 25 °C for specified contact time. The solution at pre-determined time intervals was filtered and the residual fluoride concentration was measured. The fluoride concentration in solutions was determined using expandable ion analyzer (Rex, PHS-3C) and the fluoride ion selective electrode pF-1.

The kinetic and thermodynamic parameters of the adsorption were established by conducting the experiments at 288, 298 and

Fig. 1. Fluoride removal onto Al-HAP with different Al/Ca atomic ratio (adsorbent, 0.5 g/L; [F⁻]₀ = 10 mg/L; pH = 7.0).

308 K in a temperature controlled mechanical shaker. Moreover, the defluoridation capacity was studied at different conditions like Al-HAP with different Al/Ca atomic ratio, contact time, pH of the medium and the effect of co-anions on defluoridation. Adsorption isotherms were obtained in batch equilibrium experiments with 0.05 g of HAP or Al-HAP in 100 mL solutions of fluoride (concentrations up to 50 mg/L at pH = 7.0, T = 25 °C).

3. Results and discussion

3.1. Selection and characterization of Al-HAP adsorbent

The effect of Al doping dose on the adsorption capacity of hydroxyapatite was evaluated by the fluoride removal and the results were shown in Fig. 1. Obviously, the sample with the ratio of Al to Ca 1:10 exhibited the highest efficiency for the removal of fluoride, which was then used for all the adsorption experiments (Al-HAP) unless otherwise specified.

Fig. 2 showed the X-ray diffraction patterns of Al-HAP with different Al/Ca atomic ratio. In comparison with the characteristic patterns of HAP (curve a), Al-HAP (1:10) had almost identical XRD patterns to that of pure HAP (curve b). There was a good match with standard both in terms of intensity and position of the peaks. The crystalline peaks at 2θ = 26°, 32°, 40°, 47° and 50° confirmed the formation of hydroxyapatite structure. No peaks that correspond to Al element were found. This may be due to the Al (III) incorporation into hydroxyapatite. While the main crystalline phase of HAP disappeared in 1:5 and 1:2 samples (curve c and d), indicating the higher Al doping dose did not favor the formation of HAP structure.

Fig. 2. XRD patterns of Al-HAP with different Al/Ca atomic ratio: (a) 0, (b) 1:10, (c) 1:5, (d) 1:2.

Fig. 3. TEM images of HAP and Al-HAP.

Moreover, the size and shape of HAP and Al-HAP was measured by TEM (Fig. 3). The HAP samples were cylindrical rod-like shape with homogeneous microstructure, 25–30 nm in diameter and 50–80 nm in length and several particles seem to aggregate together by melting their surfaces. However, the particle sizes of Al-HAP (5–15 nm in diameter and 20–50 nm in length) decreased significantly with the presence of Al element. In comparison with HAP, Al-HAP was more dispersible and fluffy, resulting in high defluoridation capacity.

Fig. 4 presented the nitrogen adsorption–desorption isotherms of different samples. Both the isotherms were the type IV with hysteresis loops in different sizes. Al-HAP had a surface area of 258.6 m²/g, which was almost 4 times larger than that of HAP (75.7 m²/g). This result also agreed well with the TEM analysis.

3.2. Adsorption kinetics and the effects of pH and co-existing anions on fluoride removal

The kinetics of adsorption is an important parameter for designing adsorption system and is required for selecting optimum operating conditions for full-scale batch process. Fig. 5 illustrated the kinetics of fluoride adsorption onto Al-HAP as a function of reaction time. Obviously, most of the removal took place during the first 5 h. From the shape of the kinetic curve, it was evident that the fluoride adsorption onto Al-HAP is a two-step process, i.e. initial rapid adsorption during the first 5 h and slow rate of adsorption until the equilibrium was reached. The kinetics of any sorption process is a function of different parameters, such as the structural properties of adsorbent, nature and concentration of sorbate, and

adsorbent-sorbate interactions. The results indicated that non-linear method is more suitable to obtain the kinetic parameters. In our study, the kinetic data fitted well with pseudo-second-order equation.

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \rightarrow \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

where q_t is the amount of fluoride on the surface of Al-HAP at any time (mg/g), k_2 is the pseudo-second-order rate constant (g/mg min), q_e is the amount fluoride adsorbed at equilibrium (mg/g) and the initial adsorption rate.

The pH of the medium is one of the important variables which significantly affect the extent of adsorption of fluoride. Fig. 6 showed the effect of the initial solution pH on the fluoride adsorption onto Al-HAP at given conditions. Obviously, the maximum fluoride removal (75%) was recorded at pH = 5.0 and showed gradual decreasing trend with increase in the solution pH. This was in agreement with fluoride removal studies on synthetic HAP by other report [1,18]. The reduction of fluoride removal in alkaline pH range should be attributed to competition of hydroxyl ions with fluoride for adsorption sites because of similarity in fluoride and hydroxyl ions in charge and ionic radius. Similar findings have also been reported earlier [19,20].

Moreover, the concentration of Ca²⁺ and Al³⁺ in solution after the adsorption experiments at different pH was measured using ICP-AES to confirm the degree of dissolution of Ca²⁺ and Al³⁺ from Al-HAP. From the results in Fig. 7, the maximum amount of Ca²⁺ and Al³⁺ was 21.1 and 0.19 mg/L at pH = 5.0, while Al-HAP was insoluble

Fig. 4. Nitrogen adsorption–desorption isotherms of HAP and Al-HAP.

Fig. 5. Pseudo-second-order adsorption rate of F[−] adsorption onto Al-HAP (adsorbent, 0.5 g/L; [F[−]]₀ = 10 mg/L; pH = 7.0).

Fig. 6. Fluoride removal onto Al-HAP at various initial pH values (adsorbent, 0.5 g/L; $[F^-]_0 = 10 \text{ mg/L}$).

Fig. 7. Ca^{2+} and Al^{3+} dissolution from Al-HAP at various initial pH values (adsorbent, 0.5 g/L; $[F^-]_0 = 10 \text{ mg/L}$).

or dissolved the least in the initial pH of 7–9. This indicated that Al-HAP in the pH range was stable enough and was appropriate for use as a fluoride adsorbent.

The contaminated ground water contains several other co-existing ions along with fluoride, which may compete with fluoride for the active adsorption sites. Hence, it is important to investigate the interference of co-existing ions of fluoride adsorption onto Al-HAP. Fig. 8 showed the effect of various co-existing ions of different concentrations on fluoride adsorption by Al-HAP. Except CO_3^{2-} and PO_4^{3-} , Cl^- , NO_3^- and SO_4^{2-} have shown negligible effect on fluoride adsorption. Interference was observed on fluoride adsorption by CO_3^{2-} and PO_4^{3-} ions above a concentration of 0.2 mM. Fluoride

Fig. 8. Effect of co-existing anions on the F^- adsorption onto Al-HAP (adsorbent, 0.5 g/L; $[F^-]_0 = 10 \text{ mg/L}$; pH = 7.0).

Fig. 9. Langmuir (A) and Freundlich (B) isotherms for F^- adsorption by Al-HAP (adsorbent, 0.5 g/L; $[F^-]_0 = 5\text{--}50 \text{ mg/L}$; pH = 7.0).

adsorption capacity was reduced by 10% for an initial CO_3^{2-} and PO_4^{3-} concentration of 5 mM. The reduction in fluoride removal observed by the presence of CO_3^{2-} and PO_4^{3-} may be due to competition from these ions for active site [1,3,7].

3.3. Adsorption isotherm and the mechanism of fluoride removal over Al-HAP

Analysis of equilibrium data is important for developing an equation that can be used to compare different adsorbents under different operational conditions and to design and optimize an operating procedure. The adsorption isotherms of HAP and Al-HAP were shown in Fig. 9. Data from the adsorption isotherms were modeled using the Langmuir and Freundlich isotherm models with the resulting isotherm constants presented in Table 1.

$$\frac{C_e}{q_e} = \frac{1}{Q_{\max}b} + \frac{C_e}{Q_{\max}} \quad \text{Langmuir model}$$

$\log q_e = \log K_F + \frac{1}{n} \log C_e$ Freundlich model where C_e is equilibrium concentration (mg/L), q_e is the amount adsorbed at equilibrium (mg/g), $Q_{\max}$ is adsorption capacity for Langmuir isotherms and 'b' is an energy term which varies as a function of surface coverage strictly due to variations in the heat of adsorption. 'n' indicates the degree of favorability of adsorption and K_F is the isotherm constant for Freundlich model.

As seen in Fig. 9, Table 1 and S1, fluoride adsorption onto HAP and Al-HAP was well described by the Langmuir model with the correlation coefficients of $R^2 > 0.99$. The calculated maximum adsorption capacity $Q_{\max}$ for Al-HAP was 32.57 mg/L at 25 °C, which was twice larger than that of HAP (16.38 mg/L). Results from the Freundlich analysis indicated that the standard deviation was significantly higher than the Langmuir analysis in describing the adsorption of fluoride onto the HAP and Al-HAP. The fact that the Langmuir isotherm fitted the experimental data very well

Table 1
Langmuir and Freundlich isotherm constants for F[−] adsorption by Al-HAP and HAP.

Adsorbent	Temperature	Langmuir model			Freundlich model		
		$Q_{\max}$ (mg/g)	b (1 g ^{−1})	R^2	K_F (1 g ^{−1})	n	R^2
HAP	25 °C	16.38	0.0688	0.9898	2.528	2.178	0.9810
	15 °C	26.95	0.0800	0.9914	3.884	2.169	0.9815
Al-HAP	25 °C	32.57	0.0859	0.9917	3.690	1.813	0.9846
	35 °C	42.37	0.0802	0.9875	4.504	1.875	0.9908

Table 2
Thermodynamic parameters for F[−] removal on Al-HAP.

Temperature	15 °C	25 °C	35 °C
ΔG° (kJ/mol)	−1.279	−1.586	−2.842
$\ln K_C$	0.232	0.278	0.482

ΔH° : 18.1 kJ/mol, ΔS° : 67.2 J/mol K.

may be due to homogeneous distribution of active sites on the adsorbents surface and the adsorption of fluoride took place in a monolayer adsorption manner [21]. Furthermore, as the temperature increased from 15 to 35 °C, a positive effect was observed on the adsorption of fluoride (Table 1). This phenomenon was because of the increased tendency of fluoride attached to Al-HAP, which might also indicated that the adsorption of fluoride onto Al-HAP was endothermic in nature. In order to study the feasibility of the process, the thermodynamic parameters were obtained from the following equations:

$$K_C = \frac{C_{Ae}}{C_e}$$

$$\Delta G^\circ = -RT \ln K_C$$

$$\log K_C = \frac{\Delta S^\circ}{2.303R} - \frac{\Delta H^\circ}{2.303TR}$$

where C_e is the equilibrium concentration in solution in mg/L and C_{Ae} is the equilibrium concentration on the adsorbent in mg/L and K_C is the equilibrium constant.

The values of ΔH° and ΔS° can be obtained from the slope and intercept of a plot of $\ln K_C$ vs. $1/T$ and the results were represented in Table 2. The adsorption of fluoride onto Al-HAP was endothermic in nature.

To further study the mechanism for fluoride adsorption to Al-HAP, the pH changes of Al-HAP suspension without/with fluoride was measured and the results were shown in Fig. 10. Apparently, the pH of Al-HAP suspension increased with the reaction time and

Fig. 10. The pH changes of Al-HAP suspension: (a) without F[−], (b) with F[−] (adsorbent, 0.5 g/L; [F[−]]₀ = 10 mg/L; pH = 7.0).

reached to 8.5 during the F[−] adsorption process. While the pH of suspension without F[−] was only 7.5. Moreover, Zeta potential and FTIR spectra (Fig. S1 and S2) of Al-HAP before and after F[−] adsorption were further investigated. Obviously, after the F[−] adsorption, the zeta potential of Al-HAP was greatly decreased and the —OH stretching vibrations at 3420 cm^{−1} also shifted to higher frequencies. The result indicated that the surface M—OH was active sites and the quantitative substitution of the M—OH groups by F[−] played a key role in F[−] adsorption.

4. Conclusion

Al-modified hydroxyapatite was prepared and used for the adsorption of F[−] from aqueous solution. It showed higher efficiency for the removal of F[−] (32.57 mg/g) than that of unmodified HAP (16.38 mg/g). The adsorption data could be well described by the Langmuir isotherm model and the adsorption kinetic followed the pseudo-second-order model. It has been suggested that the —OH on the surface of Al-HAP was the adsorption sites. The more adsorption sites were formed on Al modified HAP, which possessed abundant surface hydroxyl groups, resulting higher efficiency for F[−] removal.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jhazmat.2012.07.020>.

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