

Cation-exchanged hydroxyapatite for strontium separation from groundwater

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1. Introduction

Strontium-90 (^{90}Sr) is a typical fission product of nuclear fuel and released into the various environments, especially groundwater, as a result of nuclear accidents and weapon testing [1-3]. Numerous efforts have been made to separate ^{90}Sr from groundwater. Adsorption has been widely used in remediation of contaminated groundwater that remove contaminants by reactive adsorbents. Hydroxyapatite (HAP) is a natural mineral that consists of calcium and phosphate ($\text{Ca}_5(\text{PO}_4)_3(\text{OH})$) with hexagonal crystal structure. It is well-known cation adsorbent via ion-exchange with structural Ca^{2+} [4-6]. Previous HAP studies in Sr^{2+} adsorption have reported that major cations in groundwater such as Na^+ , Mg^{2+} , Ca^{2+} significantly decrease the Sr^{2+} adsorption efficiency by competing process. In this study, we have modified chemical composition of HAP surface to enhance its Sr^{2+} adsorption ability at the groundwater conditions. The modification has been carried out by post-exchange of surface Ca^{2+} with various cations including Na^+ , Mg^{2+} , Fe^{2+} , Cu^{2+} , Ba^{2+} , Al^{3+} , respectively. The modified HAPs were characterized using XRD, surface area, and zeta-potential analyzer. The Sr^{2+} removal efficiencies of modified HAPs were measured and compared by means of the batch adsorption experiments. The most effective adsorbent, Mg^{2+} -exchanged HAP (Mg-HAP), was evaluated in terms of the Sr^{2+} adsorption isotherm and kinetic. The Sr^{2+} adsorption performance of Mg-HAP in groundwater was demonstrated through the batch test with radioactive ^{90}Sr .

2. Methods and Results

2.1 HAP synthesis and modification

Nano-sized HAP (nHAP) was synthesized using a hydrothermal method. Briefly, 0.668 M calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 99%) was stirred and the solution pH was adjusted to 9 by adding NH_4OH (28-30%). A solution of 0.4 M $\text{NH}_4\text{H}_2\text{PO}_4$ ($\geq 98\%$) was dropped into Ca^{2+} solution at 0.1 mL/min resulting in a Ca/P molar ratio of 1.67. The obtained white suspension was stirred at 80°C for 24 h. The synthesized HAP particles were separated by ultra-centrifugation (100,000 rpm for 15 min.), washed with deionized water, and freeze-dried for 24h. The surface-modified HAP was obtained as follows; The exact amount (500 mg) of bare-HAP (Ca^{2+} -HAP) nanoparticles were immersed in 50 mL of 0.5 M cation

(Na^+ , Mg^{2+} , Fe^{2+} , Cu^{2+} , Ba^{2+} , Al^{3+}) solutions, respectively. It was magnetically stirred for 24 h at room temperature to induce the cation exchange process on the surface. The treated particles were collected by the identical separation procedure as aforementioned.

2.2 HAP characterization and Batch experiments

The surface area of synthesized HAP were measured using a ASAP 2420 Micrometrics surface analyzer. The estimated value was $117.6 \text{ m}^2/\text{g}$ that corresponding to the surface area of $< 30 \text{ nm}$ of HAP particle which was identified from SEM analysis (Figure 1(a)). The crystallographic structure of HAP were determined by XRD analysis using a Rigaku Smartlab X-ray Diffractometer with $\text{Cu K}\alpha$ radiation. The diffraction pattern of sample was obtained from 10 to $70^\circ 2\theta$ at a speed of $2^\circ 2\theta \text{ min}^{-1}$. Figure 1(b) represents the XRD patterns for the synthetic HAP and the peak positions were matched to JCPDS card no. 01-076-8436 (synthetic hydroxyapatite). The modified HAP with cations showed the identical XRD patterns except Cu^{2+} - and Al^{3+} -exchanged HAP. The immersion of HAP in 0.1M Cu^{2+} solution causes formation of secondary phase of $\text{Cu}_2\text{OHPO}_4(\text{s})$. In addition, exchange of Al^{3+} with surface Ca^{2+} have completely dissolved the HAP particles.

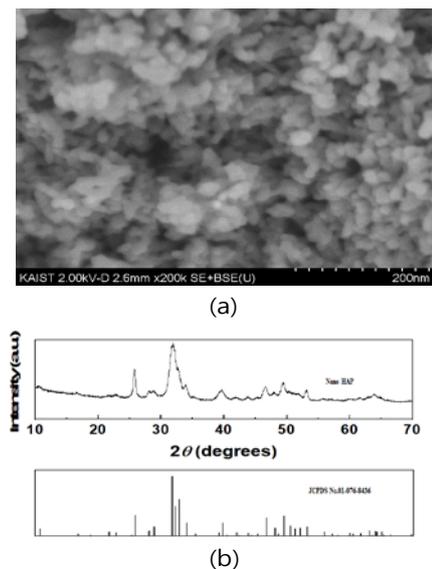


Figure 1. (a) SEM image of synthetic HAP nano-particles (b) XRD pattern of synthetic HAP.

The chemical composition of modified HAPs were determined by Atomic Absorption Spectrometry analysis. Exact amounts of HAPs were weighed and completely dissolved in 1M HCl to quantify the cation/phosphorous concentrations of HAPs (Table 1). Monovalent sodium ion did not occupy the Ca^{2+} site of HAP while divalent cations showed the 3 – 17% of exchange efficiency toward surface Ca^{2+} . The measured (Ca+cation)/P ratio proved that the modified HAPs have maintained its hexagonal structure after the cation-exchange process.

Table 1 Chemical composition of bare and modified HAP

Cation	Ca [mol]	Exchanged cation [mol]	P [mol]	(Ca+cation)/P	Exchange efficiency (%)
Ca^{2+}	41	0	26	1.56	-
Na^+	34	0.25	22	1.56	0.73
Mg^{2+}	30	0.91	20	1.55	2.96
Ba^{2+}	33	1.21	23	1.49	3.52
Fe^{2+}	25	5.48	20	1.52	17.87

The batch experiments of synthetic and modified HAPs were performed in duplicate at 25 °C. The initial concentration of Sr^{2+} was 10 ppm and the solid to liquid ratio was kept at 5 g/L.

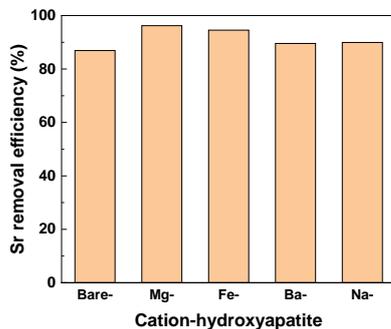
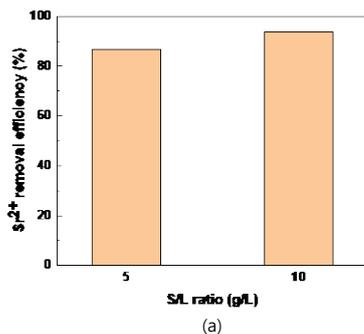
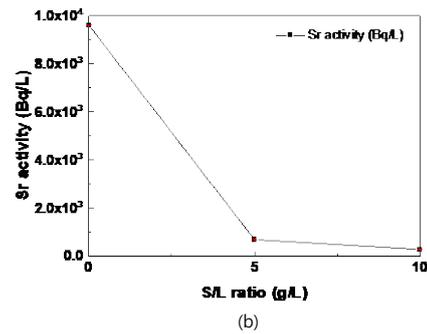


Figure 2. Sr^{2+} removal efficiencies of bare and modified HAP.

Figure 2 showed Sr^{2+} uptake capacities of bare and modified HAPs. The HAPs could remove >80% of Sr^{2+} in 24h and Mg^{2+} -exchanged HAP was the most reactive adsorbent ($\eta=96.7\%$).



(a)



(b)

Figure 3. Batch adsorption capacities of Mg^{2+} -HAP toward (a) Non-radioactive Sr^{2+} and (b) radioactive ^{90}Sr from simulated groundwater.

The adsorption performance of Mg^{2+} -HAP was confirmed at the simulated groundwater conditions containing 125 ppm of Na^+ , 25 ppm of Ca^{2+} , 10 ppm of Mg^{2+} , and 5 ppm of K^+ (Figure 3). The initial concentration of Sr^{2+} was 1 ppm and >80% of it was separated from the groundwater in 2h. The selective ^{90}Sr uptake by Mg^{2+} -HAP was also confirmed in which the activity of ^{90}Sr was successfully decreased from 9,500 Bq/L to <1,000 Bq/L in 2h.

3. Conclusions

The synthetic HAP was modified by various cations via cation-exchange process with surface Ca^{2+} . Among the modified HAPs, Mg^{2+} -HAP showed the most selective Sr^{2+} separation ability at the groundwater conditions. Its Sr removal ability was also proved in the radioactive ^{90}Sr adsorption test. The results indicated that the simple HAP modification technique in this study can improve the HAP performance toward Sr at the contaminated groundwater sites.

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