Removal of Co^{2+} and Sr^{2+} from aqueous solution by hydroxyapatitie nanoparticle

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1. Introduction

Hydroxyapatite (HAP, $Ca_{10}(PO4)_6(OH)_2$), one of apatite minerals, is a sparingly soluble, stable and inexpensive salt which can be easily produced by precipitation from calcium phosphate solution. The structure of HAP allowed many substitutions of divalent cations and retained them for long time because of its high adsorption capacity, low solubility, high redox conditions, availability and low cost. Many researches have reported the ability of HAP to bind divalent cations and previous studies have shown that synthetic HAP has a high removal capacity for Pb, Zn, Cu, Cd, Co and Sr from aqueous solutions. In present study, synthetic HAP nanoparticle was prepared by precipitation in simulated body fluid (SBF) solution. The adsorption ability of HAP nanoparticle for Co^{2+} and Sr^{2+}in single and binary solutions was investigated.

2. Methods and Materials

2.1 preparation of HAP nanoparticle

The HAP nanoparticle was synthesized by precipitation in growth medium of simulated body fluid (SBF) solution. SBF was prepared by dissolving NaCl, $NaHCO_3$, KCl, K_2HPO_4, $MgCl_2$, $CaCl_2$ and Na_2SO_4 in 1 L distilled and deionized water at 37℃ It is noted that these reagents should be added one by one after each reagent was completely dissolved. Thereafter, 4.4 g $CaCl_2$ and 4.14 g K_2HPO_4 were added to the SBF solution with stirring. The suspension stands still for 24 hours at 37℃ and centrifuged and the precipitate was washed with distilled and deionized water for three times and with ethanol for two times. After all washing steps, 1 wt% of polyethylene glycoland ethanol were added to the precipitate in 50 mL centrifuge tube. After that the precipitate in the centrifuge tube was treated with ultrosonication for 10 min at 30 kHz. The resulting solid was dried at 50℃ for 24 hours and pulverized using a mortar.

2.2 Adsorption experiment

The single-solute adsorption of Co^{2+} and Sr^{2+} by HAP nanoparticle was carried out in batch system at 25℃ 0.1 g HAP nanoparticle was mixed with 15 mL Co^{2+} or Sr^{2+} stock solution in 15 mL conical centrifuge tube and the pH of the system was maintained at 5 by using 0.05 M MES buffer solution. The initial Co^{2+} and Sr^{2+}concentration varied from 1 to 20 mM, in some case, to 30 mM. The samples were placed in a rotary shaker and shaken for 24 h at 200 rpm to reach equilibrium and centrifuged at 3000 rpm for 20 min and filtered through 0.2-μm nitrate cellulose membrane filter. The adsorbed amounts of Co^{2+} and Sr^{2+} were calculated by the difference between initial and final concentration remaining in equilibrium solution after adsorption. The binary adsorption experiments were performed in same manner as were in the single-solute adsorption experiments with equimolar concentration of metal ions.

3. Results and discussion

3.1 Single-solute adsorption

The single-solute adsorption isotherms of Co^{2+} and Sr^{2+} onto HAP nanoparticle were illustrated in Fig. 1. The metal uptake capacity increased as increasing initial metal ion concentrations until it reach equilibrium state. This is a result of the increase in driving force because of concentration gradient. The experimental data were fitted by Langmuir, Freundlich and Dubinin-Radushveich (DR) models as shown in Fig. 1 and their parameters were presented in Table 2.

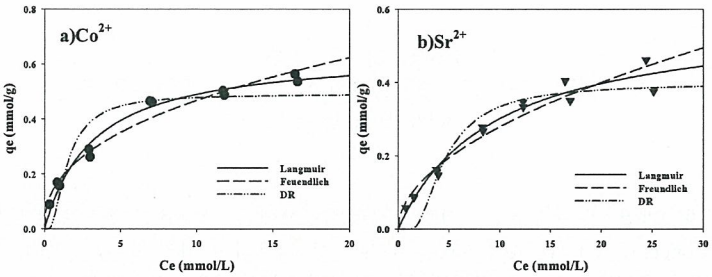

Fig. 1. Single-solute adsorption isotherms of Co^{2+} and Sr^{2+} onto HAP nanoparticle

Table 1. Single-solute adsorption parameters determined from Langmuir, Freundlich and DR models

Metal	Freundlich				Langmuir				DR			
ions	K_F	N_F	R^2	SSE	q_{mL}	b	R^2	SSE	q_{mD}	E	R^2	SSE
Co^{2+}	0.180	0.413	0.9934	0.011	0.645	0.315	0.9958	0.0073	0.49	1.05	0.9679	0.056
Sr^{2+}	0.084	0.519	0.9887	0.012	0.582	0.107	0.9934	0.0072	0.397	0.402	0.9702	0.032

3.2 Bi-solute adsorption

The simultaneous removal of Co^{2+} and Sr^{2+} by HAP nanoparticle from aqueous solution was studied with equimolar concentration and the result is given in Fig. 2 along with prediction by Langmuir model. The value of q^*_{mL}/q_{mL} for Co^{2+} and Sr^{2+} are less than unity indicating the adsorption of both metals were suppressed and the adsorption of $Sr^{2+}$was more hindered (0.767 < 0.910).

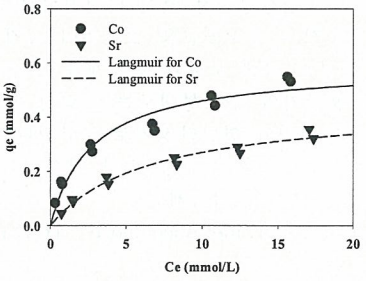

Fig. 2. Bi-solute adsorption isotherms of Co^{2+} and Sr^{2+} onto HAP nanoparticle

Table 2. Langmuir model parameters from bi-solute adsorption system

metal	q^*_{mL}	b^*	q^*_{mL}/q_{mL}	R^2	SSE
Co^{2+}	0.587	0.359	0.910	0.9903	0.014
Sr^{2+}	0.446	0.152	0.767	0.9947	0.003

4. Conclusions

The single-solute adsorption data was fitted by Langmuir, Freundlich and DR models. The maximum adsorption capacities obtained by Langmuir model are found to be 0.646 mmol/g and 0.582 mmol/g for Co^{2+} and Sr^{2+}, respectively. In binary system, the adsorption of Sr^{2+} was more affected than Co^{2+} by the simultaneous presence of both metal ions in solution.

5. Acknowledgement

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