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Adsorption of Lead and Cadmium on Ca-Deficient Hydroxyapatite

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A Ca-deficient hydroxyapatite(d-HAp) has been used to remove lead and cadmium from their mixed ions solution. The effect of pH, coexistent calcium and magnesium ions, and humic acid on the adsorption efficiency were investigated. The results showed that this d-HAp adsorbed both Cd^{2+} and Pb^{2+} efficiently within a wide pH range. The existence of humic acid reduced the removal efficiency of Cd^{2+} and Pb^{2+}. The addition of Ca^{2+} and Mg^{2+} with a concentration of 500 mg/L only slightly reduced the removal efficiency. The adsorption kinetics was described by pseudo-second-order reaction model and the adsorption isotherm followed the Langmuir model.

Keywords adsorption; Ca-deficient hydroxyapatite; cadmium; lead

INTRODUCTION

Lead and cadmium have been recognized as priority pollutants by USEPA and other organizations. They can result in serious damage to blood composition, lungs, kidneys, liver, and other vital organs or reduce mental and central nervous function by combining to enzyme inside. Thus, the removal of heavy metal ions such as lead and cadmium has become an important issue which is getting more and more attention in the world (1–4). In the past years, many methods such as precipitation (5), adsorption (6), ion-exchange (7), filtration (8), electrochemical technique (9), and reverse osmosis (10) have been used for the removal of toxic heavy metals from wastewaters. Adsorption is an efficient method for the removal of trace components from water. Over the last few years a number of investigations have been conducted to test the various adsorbents, such as activated carbon (11), agricultural waste (12,13), zeolite (14,15), clay (16), nonliving alga (17,18), for the removal of heavy metal ions. Throughout the world, there have been increasing interests in the utilization of waste materials as low-cost adsorbents rather than disposal in a landfill.

Hydroxyapatite (HAp, $Ca_{10}(PO_4)_6(OH)_2$), the main component of bones and teeth, attracts considerable interests in many areas because of its high adsorption capacity, biological compatibility, low solubility in basic and neutral media, excellent buffer property, high stability and low cost. A number of investigations on HAp have been carried out on the removal or immobilization of heavy metal ions (19–27) using synthetic or natural HAp. Generally, contaminated waters is a complex polluted system that contains various heavy metals. The adsorption removal of the targeted heavy metals is usually affected by natural organic matter (NOM) and other coexisting mineral ions which occur widely in soil and natural waters. However, most of the studies mentioned above were limitedly conducted with test solutions containing single kind of heavy metal ion. And what is more, few studies have evaluated the effect from the coexisting NOM and mineral ions on the removal capacity of HAp for heavy metal ions.

The purposes of this study were

(a) to evaluate the uptake of Cd^{2+} and Pb^{2+} ions by the Ca-deficient hydroxyapatite (d-HAp), a by-product of phosphate wastewater treatment from Japan Chem. Co. Ltd., in multi-metal systems;
(b) to examine the effect of humic acid (model NOM), Ca^{2+} and Mg^{2+} ions on the sorption of heavy metal ions by this d-HAp.

EXPERIMENTAL

Apparatus and Materials

Apparatus

The concentrations of Cd^{2+} and Pb^{2+} ions in solution were measured by an atomic adsorption spectrophotometer (AAS, SHIMADZU AA-6501F). Crystallization states of the d-HAp were detected by X-ray diffraction (XRD) analysis on a Bruker D8ADVANCE diffractometer. The morphological analysis was carried out using a scanning electron microscope (SEM, JEOL JSM EMP-800). The pH of the solution was measured using a glass electrode (Leici 3010 pH meter, Shanghai, China). An electronic

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temperature-controlled shaker (Yuejin THZ-82A, Shanghai, China) was used for shaking the water solution during the adsorption process.

Adsorbent

Ca-deficient hydroxyapatite (d-HAp), a by-product of phosphate wastewater treatment from Japan Chem. Co. Ltd. (28), had a P/Ca ratio of 0.65~0.825 and 19.2~19.8% of phosphorus. The d-HAp was dried at 60°C, ground in a mortar and sieved through a 100 μm mesh.

All chemicals were of analytical grade, from Sinopharm Chemical Reagent Co., Ltd, Shanghai without further purification.

Methods

Determination of Zero Charge Point

To a series of 100 ml polyethylene bottle that contained 40 ml of 0.01 mol/L $NaNO_3$, different volumes of either 0.1 mol/L HCl or 0.1 mol/L NaOH were added so as to obtain the solution with a wide pH range (pH 2–10). The total volume of the solution in each bottle was made up to 50 ml by 0.01 mol/L $NaNO_3$. After 2 h of equilibration, the pH values were measured and designated as initial pH or pH_i. A known amount of the absorbent was added in each bottle, which was then purged with nitrogen gas for 3–5 min and securely sealed. After 72 h of equilibration at room temperature with intermittent shaking, the pH values of the supernatant liquid in each bottle was noted and designated as final pH or pH_f. The difference between the pH_i and the pH_f ($\triangle pH$) was plotted against pH_i. The pH at the point of zero charge (pH_{pzc}) value for a specific adsorbent was at the pH_i value, where the curve intersects $\triangle pH = 0$. At this pH, the absorbent do not induce the release of either H^+ or OH^- ion in solution, the surface does not undergo or acquire any charge through acid-base dissociation.

Adsorption Studies

0.08 g of the d-HAp was equilibrated with Cd^{2+} and Pb^{2+} mixed solutions (100 ml) of different initial concentrations (10, 15, 20, 25, 30 mg/L for Cd^{2+} and Pb^{2+} respectively) in a series of 250 ml conical flasks at room temperature for 24 h. After filtration with cellulose acetate membrane (pore size 45 μm), the final concentrations of heavy metal ions in the solutions were measured using AAS.

The mixed solution (100 ml) containing 0.08 g d-HAp and 10 mg/L Cd^{2+} and 10 mg/L Pb^{2+} were stirred at room temperature for different time (2, 5, 10, 20, 40, 60, 90, 150, 180, 210, 240, 270, 300, 360, 420, 1440 min), and then separated and analyzed to determine the residual Cd^{2+} and Pb^{2+} concentration. The metal ions uptake q (mg metal ion/g d-HAp) was determined as follows: $q = (C_0 - C_t)V/m$, where C_0 and C_t are the concentrations of the initial and the final metal ions (mg/L), respectively; V is the volume of the solution (L); and m is the d-HAp weight (g) in dry form.

RESULTS AND DISCUSSION

Characterization of the Ca-deficient HAp

The mineralogical identity of the d-HAp powder was verified by XRD analysis (Fig. 1). The patterns are in agreement with those of JCPDS International Center for Diffraction Data (ICDD) Powder Diffraction File for this phase (file number 89-4405). The SEM images of the d-HAp is shown in Fig. 2. The SEM results showed that the morphology of the adsorbent was in spherical shape with a diameter of about 5 μm.

Effect of pH

The pH of the aqueous solution is an important controlling parameter in the adsorption process. The system pH controls the adsorption capacity due to its influence on the surface properties of the adsorbent and the ionic forms of heavy metal ions in solutions. The plot of the (pH_i–pH_f) against pH_i was shown in Fig. 3. There is a distinct common point of intersection at the $\triangle pH = 0$ line at pH_i 6.8, which is the pH_{pzc} of the d-HAp. Figure 3 also demonstrates the excellent buffering properties of d-HAp, since for initial pH in the range of 3 to 10, the final pH values were almost the same as the pH_{pzc}. In the lower initial pH range, the consumption of protons from the solution by the protonation of negatively charged and neutral surface groups results in final pH increase, while in the higher range of initial pH, OH^- consumption occurs due to deprotonation of positively charged surface sites, resulting in final pH decrease (26).

As the pH plays an important role in the adsorption processes, the experiments focusing on metals adsorption at different pH were performed, and the results are shown in Fig. 4. The experiments were carried out in the pH range of 2–9 by equilibrating 0.8 g/L of d-HAp with mixed metal

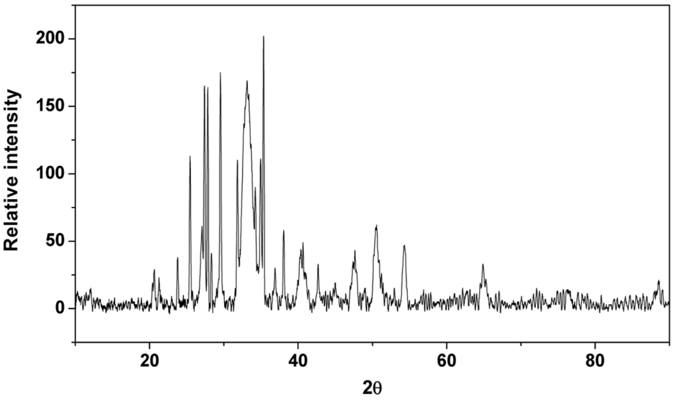


FIG. 1. XRD pattern for the Ca-deficient HAp (d-HAp).

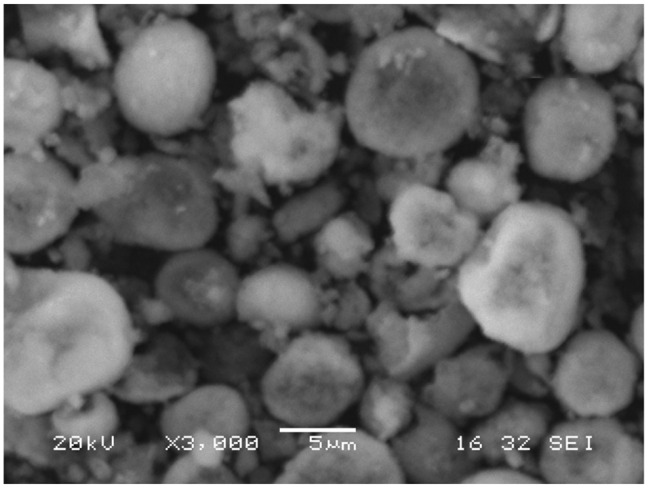


FIG. 2. SEM photographs of the Ca-deficient HAp (d-HAp).

solutions (Cd + Pb) at initial concentration of 10 mg/L for Cd^{2+} and Pb^{2+} respectively for 24 h at room temperature. As shown in Fig. 4, at low pH, the removal efficiency of both cadmium and lead ions were low. However, there was a sharp increase in metal removal as pH increased and the maximum adsorption were nearly complete (100%) for cadmium and above 80% for lead at pH 4.

This phenomenon can be explained as follows. At low pH, the surface of the adsorbent was surrounded by hydronium ions that compete with metal ions, which prevented the metal ions from approaching the binding sites on the adsorbent. The increase in metal removal as pH increases can be explained on the basis of a decrease in competition between hydronium ions and metal species for the surface sites and also by the decrease in positive surface charge on the adsorbent, which results in a lower electrostastic repulsion between the surface and the metal ions and hence uptake of metal ions increases. When the solution pH increased to above pH_{pzc}, the surface of the d-HAp was negatively charged, which was favorable for heavy metal ions adsorption. However, when $pH > pH_{pzc}$, both the ions precipitate as $Cd(OH)_2$ and $Pb(OH)_2$, preventing further adsorption of Cd and Pb. Hence pH 5–6 was selected as optimum pH in our further adsorption studies of Cd and Pb.

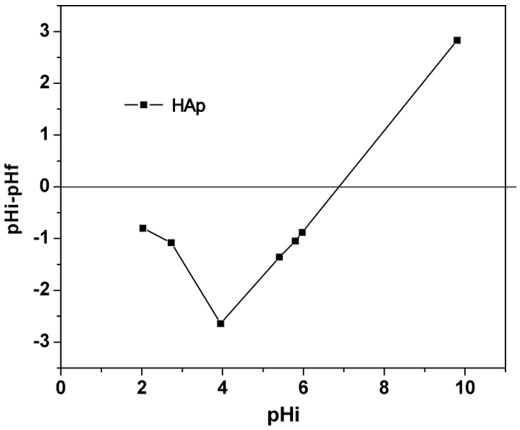


FIG. 3. pH change of the d-HAp as a function of pH_i.

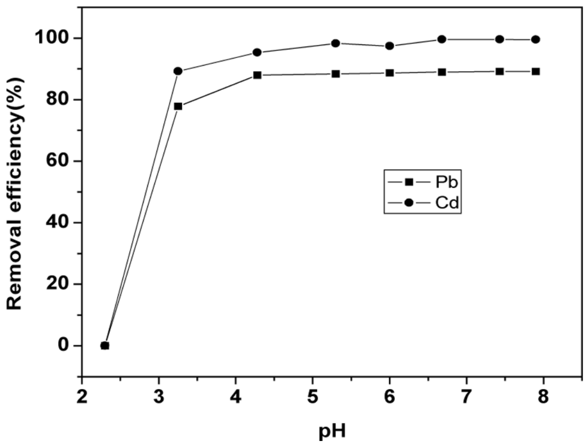


FIG. 4. Effect of pH on removal of cadmium and lead.

Effect of Humic Acid Addition

Natural organic matter (NOM) presents in environment ubiquitously. As far as we know, NOM can greatly influence the mobility and bioavailability of heavy metal ions. Humic acid, accounting for a significant portion (40–90%) of the NOM, has a negative effect on the water quality. As a model compound of NOM, humic acid, was used in our experiments to investigate its effect on cadmium and lead co-adsorption, and the results were shown in Fig. 5.

Figure 5 shows the adsorption of two heavy metals in the presence of different initial concentrations of humic acid. A slight decrease in cadmium adsorption onto the

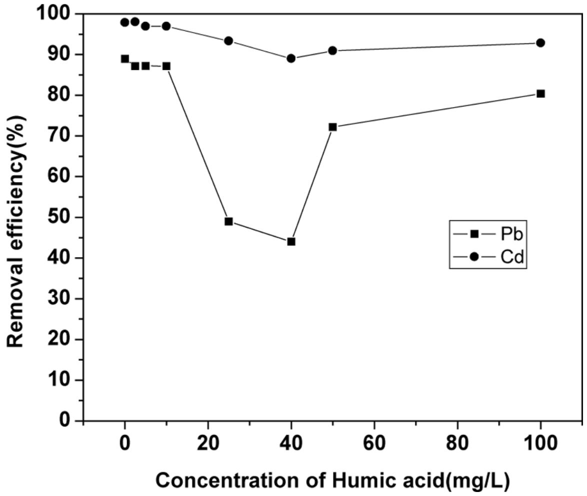


FIG. 5. Effect of different concentration of humic acid on the removal efficiency of Cd^{2+} and Pb^{2+}.

TABLE 1
The effect of coexisting cations (Ca^{2+} and Mg^{2+}) on Pb^{2+} and Cd^{2+} adsorption (Adsoption conditions: initial concentration of Cd^{2+} and Pb^{2+} was 10 mg/L respectively, dosage of the d-HAp = 0.8 g/L, reaction time = 24 h, and pH = 6)

	Initial concentration of Ca^{2+}/ Mg^{2+} (mg/L)							
	0	2.5/2.5	5/5	10/10	50/50	100/100	250/250	500/500
Pb^{2+} removal (%)	88.49	88.43	87.48	85.57	84.55	84.18	83.61	82.48
Cd^{2+} removal (%)	97.81	97.74	97.72	96.65	90.91	87.90	84.79	79.76

d-HAp was observed, which showed a negative effect of humic acid on it. However, for Pd^{2+}, as the humic acid concentration increases, humic acid first inhibits and then enhances the adsorption of lead ions.

However, when the humic acid concentration was above 40 mg/L, humic acid might form a new insoluble complexes that precipitate on the surface of the d-HAp, thus to enhance the lead ions uptake.

Effect of Coexisting Cations (Ca^{2+} and Mg^{2+})

As the most common minerals existed in surface water and groundwater, Ca^{2+} and Mg^{2+} ions are important parameters that influence the adsorption of cadmium and lead ions on HAp. The effect of different concentrations of Ca^{2+} and Mg^{2+} ions on the adsorption of cadmium and lead was shown in Table 1.

As shown in Table 1, there is a slight decrease in the adsorption efficiency of cadmium and lead ions with the increase of Ca^{2+} and Mg^{2+} concentration. At the initial Ca^{2+} and Mg^{2+} concentrations of 500 mg/L respectively, the removal of Pb^{2+} decreased by about 6% compared to the condition without Ca^{2+} and Mg^{2+}, while the removal of Cd^{2+} reduced more, that was by 18%. These results confirmed that the effect of $Ca^{2+}$and Mg^{2+} on cadmium adsorption was more obvious than that on lead ions. The possible reason was that the coexistence of Ca^{2+}, Mg^{2+} competed with other heavy metal ions during the adsorption process. Since no significant reduction of removal efficiency was observed because of the addition of $Ca^{2+}$and and Mg^{2+}, the d-HAp can be considered as an excellent adsorbent for Cd^{2+} and Pb^{2+} in hard water.

Adsorption Kinetics

The adsorption of cadmium and lead inos as a function of contact time was illustrated in Fig. 6.

The results in Fig. 6 showed that the removal took place in two different steps. The first involved a rapid removal and the second one exhibited a subsequent slow removal until equilibrium was reached. In addition, cadmium showed a higher adsorption rate compared to lead. The first rapid adsorption step was followed by a slow approach to equilibrium, which was 3 h for cadmium and 7 h for lead respectively.

Pseudo-second-order reaction model was applied to our experimental data. The linear form of pseudo-second-order rate expression (29) is

$$t/Q_t = 1/k_2 Q_e^2 + t/Q_e$$

where Q_e and Q_t are the amounts of solute sorbed at equilibrium and time t (mg/g), k_2 is the equilibrium rate constant of pseudo-second-order ($g \cdot mg^{-1} \cdot min^{-1}$). Figure 7a and 7b showed the plots t/Q_t versus t for cadmium and lead ions respectively. These figures clearly indicated that the pseudo-second-order rate equation yields an excellent fit and the correlation coefficients for the linear plots are very close to 1 ($R^2(Cd^{2+}) = 0.9999$, $R^2(Pb^{2+}) = 0.9983$), suggesting the kinetic adsorption can be described by the pseudo-second-order rate equation reasonably. Xu Huanyan et al. (30) also reported the similar results for the adsorption of cadmium on carbonate-hydroxyapatite. However, studies (27,31) on the adsorption of single metal Pb^{2+} in solution have revealed that the adsorption rate was much higher than that in mixed metal solution (Cd + Pb) in our study, which suggested that the coexistence of cadmium ions, to some extent, inhibited the adsorption of lead ions on the d-HAp.

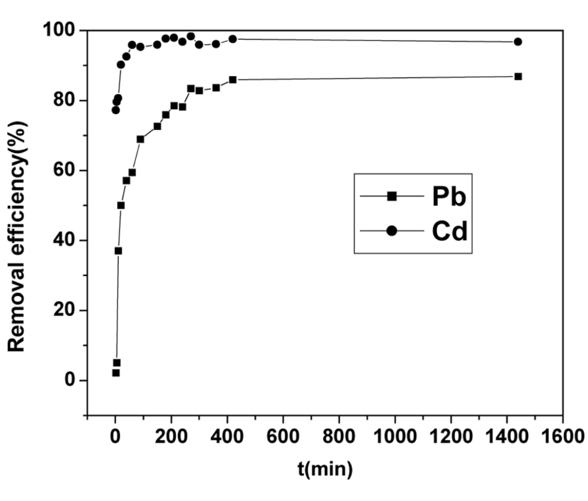
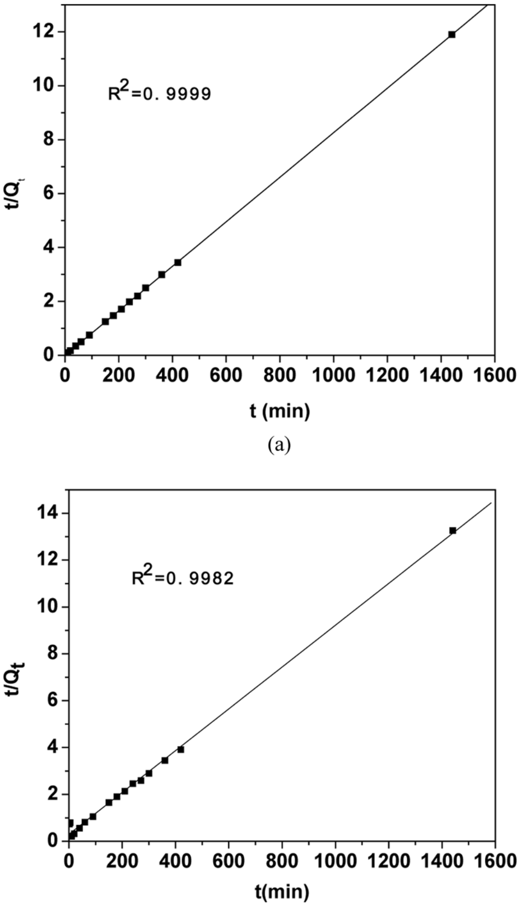


FIG. 6. Effect of contact time on the adsorption of Cd^{2+} and Pb^{2+} ions.



(a)

(b)

FIG. 7. (a) Pseudo-2nd-order plot for the adsorption of Cd^{2+} on the d- HAp. (b) Pseudo-2nd-order plot for the adsorption of Pb^{2+} on the d- HAp.

Adsorption Isotherms

Several mathematical adsorption isotherm models have been developed to quantitatively express the relationship between the extent of sorption and the residual solute concentration. The most widely used model is the Langmuir model, which is expressed as:

$$C_e/Q_e = 1/X_mK + C_e/X_m$$

Where C_e (mg/L) is the equilibrium concentration, Q_e (mg/g) is the amount adsorbed per amount of adsorbent at equilibrium, K is the Langmuir equilibrium constant (L/mg), and X_m is the amount of adsorbate adsorbed per unit mass of adsorbent corresponding to complete monolayer coverage. The linear plot of $C_e/Q_e \sim C_e$ based on the Langmuir equation gives a fairly good linear fit to the adsorption isotherms of Cd^{2+} and Pb^{2+} on the d-HAp, as shown in Fig. 8 and Fig. 9. The values of X_m and K from the slope and intercept of linear plots of C_e/Q_e versus C_e were calculated, together with the regression coefficients, as summarized in Table 2. In addition, the maximum sorption capacity calculated for Cd^{2+} is higher than that of Pb^{2+}, which is quite consistent with those obtained before.

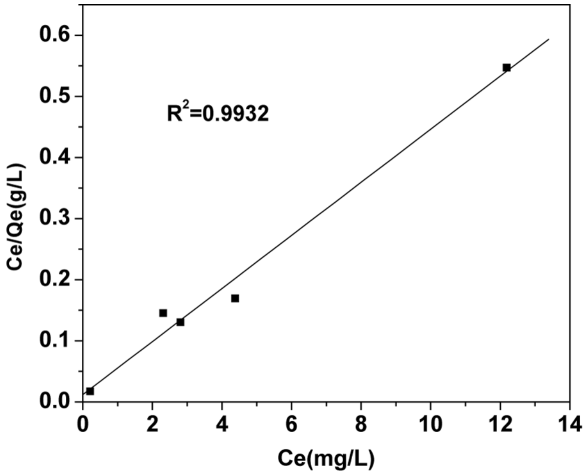


FIG. 8. Langmuir isotherm for the adsorption of Cd^{2+} ions on the d-HAp.

Adsorption Mechanism on Hydroxyapatite

Hydroxyapatite, with a relative complex composition and diverse characteristics, has been investigated as an adsorbent in different fields, such as protein adsorption, small organic molecules adsorption, and the removal of heavy metals. Several possible mechanisms for the adsorption of hydroxyapatite were proposed.

Gorbunoff et al. (32,33) has reported their investigation on the interaction of proteins with hydroxyapatite and put forward the mechanism of protein binding to and elution from hydroxyapatite. Both the nonspecific attraction between protein positive charges and HAp and specific complexing of protein carboxyls with calcium on HAp occurred in the interaction.

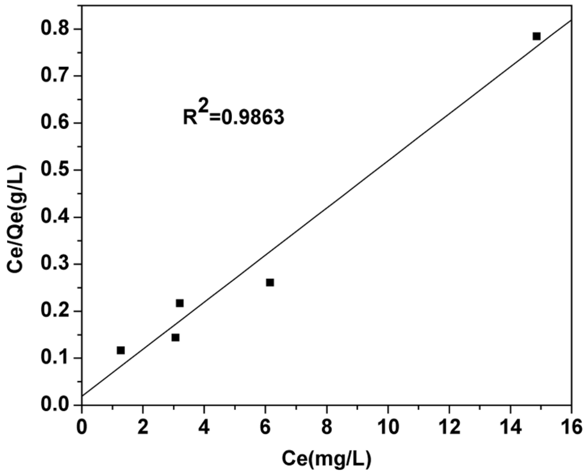


FIG. 9. Langmuir isotherm for the adsorption of Pb^{2+} ions on the d-HAp.

TABLE 2
Langmuir coefficients (X_m and K) for the adsorption of Cd^{2+} and Pb^{2+} on the d-HAp, together with the regression coefficient (R^2)

Adsorbate	Langmuir model	X_m (mg/g)	K (l/mg)	R^2
Cd^{2+}	$C_e/Q_e = 0.1196 + 0.0434Ce$	23.04	0.3629	0.9932
Pb^{2+}	$C_e/Q_e = 0.0191 + 0.0501Ce$	19.96	2.6233	0.9863

By combining X-ray absorption spectroscopy analysis and density function theory calculation, Tang and Li (34) have examined the mechanism for Zn incorporation in the hydroxylapatite structure, and discussed the mechanism from the angle of coordination chemistry. Their results suggest tetrahedral coordination and one dominant coordination environment for Zn ions.

For adsorption of divalent cations on hydroxyapatite, two dominant mechanisms have been proposed (31,35). The first mechanism is the adsorption of cations on the HAp surfaces and following ion exchange reaction between cations adsorbed and Ca^{2+} ions of HAp. This ion exchange reaction mechanism is expressed as:

$$Ca_{10}(PO_4)_6(OH)_2 + xM^{2+} \longrightarrow xCa^{2+} + Ca_{10-x}M_x(PO_4)_6(OH)_2$$

For the first mechanism, the coordination action of the ions in solution with the possible ligands from the solution or the surface of HAp is an important factor to affect the adsorption or release efficiency.

The second mechanism is the dissolution of HAp in aqueous solution containing cations followed by precipitation of $M_{10}(PO_4)_6(OH)_2$, Hpy, i.e., the dissolution-precipitation mechanism, which is described as:

$$\text{Dissolution: } Ca_{10}(PO_4)_6(OH)_2 + 14H^+ \longrightarrow 10Ca^{2+} + 6H_2PO_4^- + 2H_2O$$

$$\text{Precipitation: } 10M^{2+} + 6H_2PO_4^- + 2H_2O \longrightarrow 14H^+ + M_{10}(PO_4)_6(OH)_2$$

The two mechanisms coexist and compete with each other. The dominant removal mechanism of heavy metals by HAp is varied, depending on the pH values in aqueous solutions: the dissolution of HAp and following precipitation of HPy is the dominant removal mechanism at lower pH ($pH < 3$), whereas as the pH increases, such as $pH > 4$, the cation exchange reaction between Ca^{2+} of HAp and cations is increasingly dominant (26,35). As shown in Fig. 4, the removal efficiency of both cadmium and lead ions were low at $pH < 3$, but increased with increasing pH and reached the maximum adsorption efficiency above pH 4 ($pH = 4$–8), which implicated that the cation exchange mechanism was dominant in the adsorption of mixed ions of cadmium and lead.

With the aim of understanding the impact of ion exchange on the crystalline structure and properties of Hydroxyapatite, Pizzala and Caldarelli have used a Solid-State NMR technology to investigate the Lead and Vanadium Substitution into Hydroxyapatite to know the adsorption mechanism (36), which brings out very valuable structural information and the local coordination environmental of all the ions in hydroxyapatite.

As to the effect of humic acid addition, there are two possible roles of humic acid in the metal adsorption system. First, humic acid can inhibit cadmium and lead adsorption by forming non-adsorbable coordination compounds with the metal ions. Second, metal adsorption can be enhanced by the presence of humic acid, due to the coordination of metal ions in solution and the ligands such as phosphate and hydroxy anions on the adsorbent surface (37). It is assumed that at low concentration of humic acid, the hydrated lead ions were dominately adsorbed on the d-HAp because of the coordination action between lead ions and the ligands on d-HAp. At a concentration of 20–40 mg/L of humic acid, it formed soluble complexes with lead ions to increase the mobility of Pb^{2+}, and hence reduced the effectiveness of the sorption process.

CONCLUSIONS

In this study, adsorption of lead and cadmium on a Ca-deficient hydroxyapatite(d-HAp) from their mixed ions solution was investigated as a function of pH, coexistent calcium and magnesium ions, and humic acid. The results showed that this d-HAp adsorbed Cd^{2+} and Pb^{2+} efficiently within a wide pH range ($pH = 4 \sim 8$). The existence of humic acid in the solution reduced the removal efficiency of both heavy metal ions, and the effect mechanism on lead ions was complicated which needed to be further investigated. The addition of Ca^{2+} and Mg^{2+} with a concentration of 500 mg/L respectively only slightly reduced the removal efficiency of both Cd^{2+} and Pb^{2+} under the experimental conditions. The adsorption kinetics was described by the Pseudo-second-order reaction model and the correlation coefficient R^2 was more than 0.998. It was also found that the removal of Cd^{2+} and Pb^{2+} ions can be evaluated by using Langmuir adsorption isotherm model. The maximal adsorption capacity was calculated as 23.04 and 19.96 mg/g for Cadmium and Lead respectively. It was also referred that ion exchange was the main mechanism during the adsorptive process.

To avoid the possible second pollution of the adsorbed materials, more attention should be paid in the reuse of adsorbents including d-HAp used in our experiments. For the long-term objective to recycle the d-HAp and the separated heavy metals, further experiments are needed.

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