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Removal of Cd^{2+} from aqueous solutions by hydroxyapatite

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ABSTRACT

A study on the removal of cadmium ions from aqueous solutions by synthetic hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HAP) with different morphologies was conducted in batch conditions. The influence of different sorption parameters, such as equilibration time, initial concentration of metal ion, the amount of HAP, pH value of solution and the specific surface area on the sorption amount of Cd^{2+} were studied and discussed. Our experimental results are in agreement with pseudo-second-order kinetic equation. The Freundlich and Langmuir adsorption isotherms, often used to describe the sorption of solutes from a liquid phase, can be applied to our experimental results. The Langmuir adsorption isotherm constant corresponding to adsorption capacity, X_m, was found to be 260.42 mg/g. The sorption amount of Cd^{2+} increased as the pH value enhanced from 5 to 8. The ion-exchange mechanism and surface complex mechanism may both exist in the adsorption process. Nearly linear dependence between Cd^{2+} sorption amount and specific surface area within a certain range has been confirmed. Cd^{2+} desorption amount decreased with the increasing pH value of the extracting solution.

1. Introduction

Cadmium is an element that occurs naturally in the earth's crust and usually present in the environment as a mineral combined with other elements such as oxygen (cadmium oxide), chlorine (cadmium chloride), or sulfur (cadmium sulfate, cadmium sulfide). Although it occurs naturally in the environment, due to anthropogenic activity excessive amounts of cadmium are released to the environment. Cadmium and its compounds have variety of applications: active electrode materials in nickel–cadmium batteries, pigments used mainly in plastics, engineering coatings on steel and some nonferrous metals, components of various specialized alloys and so on [1].

As far as we know, there are no good effects from taking in cadmium. Cadmium is a highly toxic element and considered as a carcinogen. It can enter the human body by eating food, drinking water, breathing or smoking. Most of the cadmium that enters the body goes to kidney and liver and can remain there for many years and can cause serious damage to kidney and bones [1,2].

A good number of technologies are available for removal of heavy metals from solution, such as reverse osmosis, chemical precipitation, ion exchange and solvent extraction. However, sorption is recognized as a preferred method for removal, recovery and recycling of toxic heavy metals from waste water. Many kinds of sorbents have been reported for removal of Cd^{2+}, such as activated carbon, mesoporous materials, clay, zeolite, chitosan and apatite [2–4].

The general formula of apatite is $M_{10}(XO_4)_6Y_2$ ($M = Ca^{2+}$, Sr^{2+}, Pb^{2+}, Cd^{2+}, Ba^{2+}, Zn^{2+}, Mg^{2+}, ...; $XO_4 = PO_4{}^{3-}$, $VO_4{}^{3-}$, $AsO_4{}^{3-}$,...; $Y = F^-$, OH^-, Cl^-,...) [5]. Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HAP) is a member of apatite mineral family. It is an ideal material for long-term containments because of its high sorption capacity for heavy metals, low water solubility, high stability under reducing and oxidizing conditions, availability and low cost [6]. There are many reports on using HAP to stabilize a variety of metals, such as Co, Pb, Cu, Zn, Cd, Sb, Cr [5–10]. The mechanisms of the metal cations retention are different and include: ion exchange, adsorption, dissolution/precipitation, and formation of surface complexes [8,11,12].

The interaction between cadmium and apatite was studied by Dalas and Koutsoukos, they found that the interaction cannot be explained by simple adsorption [13]. Recently, many studies were concentrated on the mechanism of cadmium sorption. Rocha et al. have investigated the synthesis of HAP in different conditions and found that the maximum sorption capacity is 0.631 mmol/g (70.67 mg/g) [12]. Srinivasan et al. have used HAP with three-dimensionally ordered macropores to capture cadmium and lead and the ion-exchanged mechanism was confirmed [11].

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Recently, the morphology control of HAP has attracted a great attention, and different properties and applications of HAP with different morphologies have been studied extensively. HAP nanofibers are particularly promising for being used as a variety of implantable materials, for example, directly as porous bone blocks and defect fillers or through formulation with degradable biopolymers in order to support cell functions and stimulate regeneration of new tissues [14]. HAP spheres can be used as fillers in high-performance liquid chromatography (HPLC) for separating biopolymers such as proteins [15].

So far, there is no report about the influence of morphology of HAP on the sorption of Cd^{2+}. Therefore, this study was aimed to clarify the role of morphology on sorption, and the factors influencing Cd^{2+} immobilization by HAP such as: contact time, aqueous Cd^{2+} concentration, HAP amount, solution pH, specific surface area as well as the leaching ability of Cd-sorbed HAP in liquid phases with different pH and calcium contents.

2. Experimental

2.1. Preparation and characterization of HAP sorbent

HAP powders were prepared according to the following reaction [16]:

$$6(NH_4)_2HPO_4 + 10Ca(NO_3)_2 + 8NH_3{\cdot}H_2O = Ca_{10}(PO_4)_6(OH)_2 + 20NH_4NO_3 + 6H_2O \quad (1)$$

The concentration of $Ca(NO_3)_2$ is 0.528 mol/dm^3, and the mole ratio of $Ca(NO_3)_2$ and $(NH_4)_2HPO_4$ is 1.67. The mixed solution was sealed in Teflon-lined stainless autoclave and heated at 200 °C for 24 h (sample A). The mixed solution stirred for 48 h at 80 °C, 98 °C and 60 °C were named as samples B, C and E, respectively. Using $Sr(NO_3)_2$ to partly substitute $Ca(NO_3)_2$ (the mole ratio of Sr/(Ca + Sr) is 0.1) can get Sr-substituted HAP (sample D).

The phase identification was performed by an X-ray diffractometer (X' Pert Pro, Panalytical, The Netherlands). The morphologies of the samples were observed by a field emission scanning electron microscope (SEM, JSM-6700F, JEOL, Japan). The specific surface areas of the samples were measured from nitrogen adsorption–desorption isotherms measured on an automatic surface area and pore size analyzer (Quantachrome ASIMP).

2.2. Sorption experiments

In order to determine the sorption capacity of HAP for Cd^{2+} as well as the influence of the contact time, aqueous Cd^{2+} concentration, the amount of HAP, solution pH and morphology, sorption experiments were performed by batch equilibration technique. Cd^{2+} solutions were prepared from $Cd(NO_3)_2{\cdot}4H_2O$ salt and deionized water. A typical experiments was performed at room temperature, in glass beaker, containing HAP (sample C) at a solid to solution ratio of 1:1000, magnetic stirring, and after a specific time, the HAP was separated from the solutions by centrifugal separation. The final Cd^{2+} concentration was determined by a Perkin-Elmer Analyst 200 AAS.

2.2.1. Effects of equilibration time

The suspensions containing HAP and 30 mg/dm^3 Cd^{2+} solution were stirred at room temperature with different times from 2 min to 120 min, separated and analyzed to determine the residual Cd^{2+} concentration.

According to the literature, several models, such as first-order, pseudo-first, pseudo-second-order reaction model, can be used to express the kinetics of the sorption processes. Our studies showed best correlation with the pseudo-second-order model. Pseudo-second-order reaction model was applied to our experimental data in order to determine the sorption rate constant, at room temperature. The linear form of pseudo-second-order rate expression is

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right)t \quad (2)$$

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/mg min). The following expression denotes the initial sorption rate h (mg/g min):

$$h = k_2 q_e^2 \quad (3)$$

2.2.2. Effect of initial Cd^{2+} concentration

HAP was equilibrated with Cd^{2+} solutions of different initial concentrations (5–1000 mg/dm^3) for 24 h. After separation, the final concentrations of Cd^{2+} in the residual solutions were measured.

The Freundlich and Langmuir adsorption isotherms, often used to describe the sorption of solutes from a liquid phase, were applied to our experimental results. Linear form of the Freundlich equation can be expressed as follows:

$$\ln Q_e = \ln K_f + n \ln C_e \quad (4)$$

where Q_e (mg/g) and C_e (mg/dm^3) are the equilibrium concentrations of sorbate in the solid and liquid phase, K_f and n being Freundlich coefficients [4]. Linear form of the Langmuir equation can be expressed as follows:

$$\frac{C_e}{Q_e} = \frac{1}{X_m K} + \left(\frac{1}{X_m}\right)C_e \quad (5)$$

where Q_e (mg/g) and C_e (mg/dm^3) denote the equilibrium concentrations of sorbate in the solid and the liquid phase, X_m (mg/g) is the maximum sorption capacity, and K (dm^3/g) is the Langmuir constant related to the energy of adsorption [4,17].

2.2.3. Effect of HAP amount

The suspensions containing different amount of HAP (from 0.5 g/dm^3 to 10 g/dm^3) and 500 mg/dm^3 Cd^{2+} solution were stirred at room temperature for 24 h, separated and analyzed to determine the residual Cd^{2+} concentration.

2.2.4. Effect of pH

The effect of pH was studied in the pH range of 5–8. The initial metal concentration was 500 mg/dm^3, while the initial pH values were adjusted by adding KOH or HNO_3 solutions. After 24 h of contact, the suspensions were separated, and analyzed for final pH and residual Cd^{2+} concentrations.

2.2.5. Effect of specific surface area

The effect of specific surface area was studied. The initial metal concentration was 500 mg/dm^3 Cd^{2+} solution. After 24 h of contact at room temperature, the suspensions were separated, and analyzed for final pH and residual Cd^{2+} concentrations.

2.3. Desorption experiments

In order to estimate the reversibility of Cd^{2+} sorption, desorption experiments using solutions with different pH and calcium contents were performed. Firstly, HAP was loaded with Cd^{2+} by equilibrating with the 500 mg/dm^3 cadmium solution (at a solid to solution ratio of 1:1000). Solid residue was thoroughly washed several times with deionized water, and dried at 105 °C over night. Secondly, 0.0250 g of the obtained solid phase was treated with the 25 cm^3 of each leaching solution for 24 h. Six extracting solutions were prepared. Two acidic solutions were prepared from acetic acid at pH 2.88 and 5.00 following the technique for the preparation of extraction fluids for toxicity characteristic leaching procedure [18]. The other two solutions were deionized water and NaOH solution with pH values of 7.01 and 11.85, respectively. The last two solutions used in this study were prepared using different amounts of $Ca(NO_3)_2$ salt [5,19].

3. Results and discussion

3.1. Characteristics of sorbent

The XRD patterns of all the samples are pure HAP without any other phase. SEM images of the prepared samples are shown in Fig. 1. The SEM results show that the morphology of sample A is rod-like shape with length of about 200 nm, the morphology of samples B, C and D is spherical shape with diameter of 8.5 μm, 4 μm and 8 μm, respectively, sample E is irregular shape. The specific surface area of samples A–E are 65.4 m^2/g, 80 m^2/g, 100 m^2/g, 115 m^2/g, and 121.7 m^2/g, respectively.

3.2. Sorption study

3.2.1. Sorption kinetics

Sorption of Cd^{2+} by HAP as a function of contact time is illustrated in Fig. 2. The result revealed that a removal takes place in two different steps (Fig. 2(a)). The first involves a rapid Cd^{2+} removal (first 40 min). The second one exhibits a subsequent removal until equilibrium is reached, which is slow and quantitatively insignificant step. Since there is no significant increase on Cd^{2+} sorption when the time is 120 min, the reaction time of 24 h was enough for further experiments.

In order to investigate the rate of Cd^{2+} sorption, the linear form of pseudo-second-order kinetic equation was applied to our result (Fig. 2(b)). By plotting t/q_t versus time, the second-order constant k_2 and q_e can be obtained from the interception and slop of the line. Excellent agreement exists between our result and the equation ($R = 0.99997$, S.D. = 0.01072). The values of k_2 and q_e are 0.09476 g/(mg min) and 28.579 mg/g, respectively. The value of initial sorption rate h is 77.40 mg/(g min), which shows the sorption in the first step is very fast.

3.2.2. Sorption isotherms

The plot of Cd^{2+} sorbed by HAP against initial metal concentration is shown in Fig. 3(a). It can be seen that with the increasing of the initial metal concentration, the amount of Cd^{2+} sorbed by HAP increased. Specially, when the initial Cd^{2+} concentration is below 5 mg/dm^3, Cd^{2+} can be completely sorbed by HAP and there is no residue in the solution.

At low initial metal ion concentration, the ratio of Cd^{2+} to the number of available adsorption sites or ions exchange site is small and consequently the adsorption is independent of the initial concentration. At high concentration of metal, a unit mass of the adsorbent is exposed to a large number of metal ions and progressively higher number of metal ions is taken up with the gradual filling up of the appropriate binding sites. This gives rise to an increase in the amount of Cd^{2+} sorption while the percent adsorption decreased from 100% to 26%.

The empirical Freundlich isotherm yields linear plot ($R = 0.991$, Fig. 3(b)) and the values of the coefficients ($K_f = 26.3$, $n = 0.33$) indicate that HAP have a good potential to be used as adsorbent for Cd^{2+}. As is well known, Freundlich isotherm applies to adsorption on nonspecific and heterogeneous sites on solid surfaces, so the isotherm is valid for weak van der Waals' type adsorption as well as for strong chemisorption.

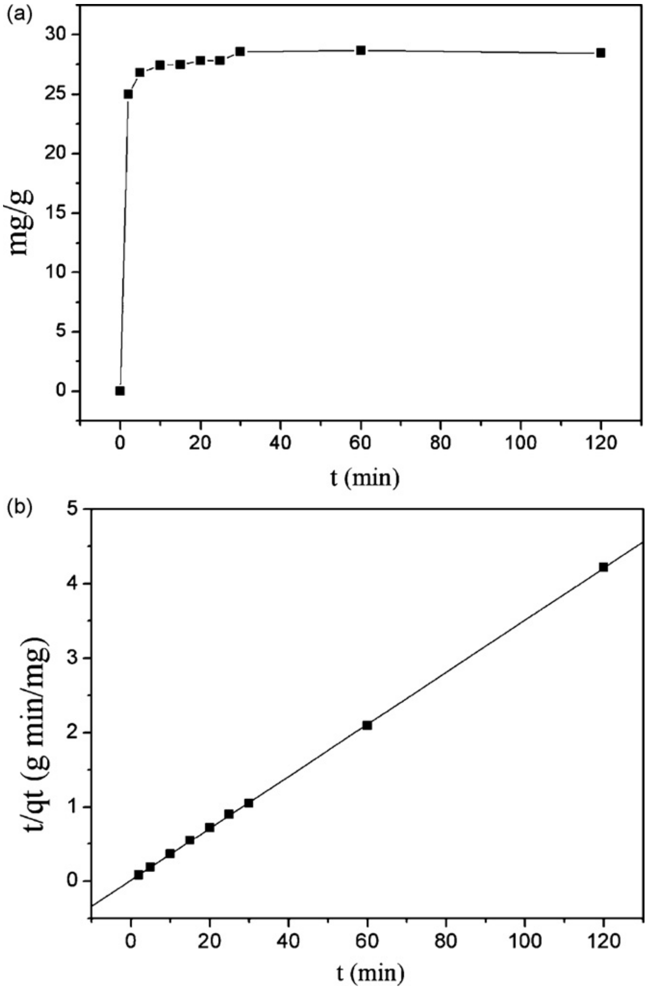

Fig. 2. (a) Effect of contact time on sorption of Cd^{2+} onto HAP and (b) linear fit of experimental data obtained using pseudo-second-order kinetic equation.

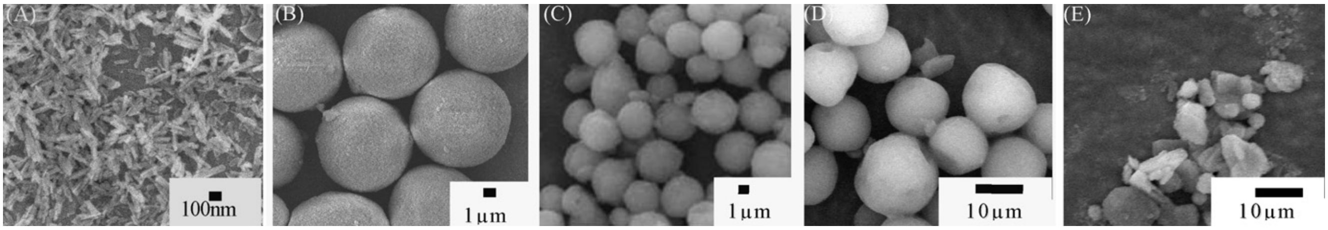

Fig. 1. SEM images of the prepared samples.

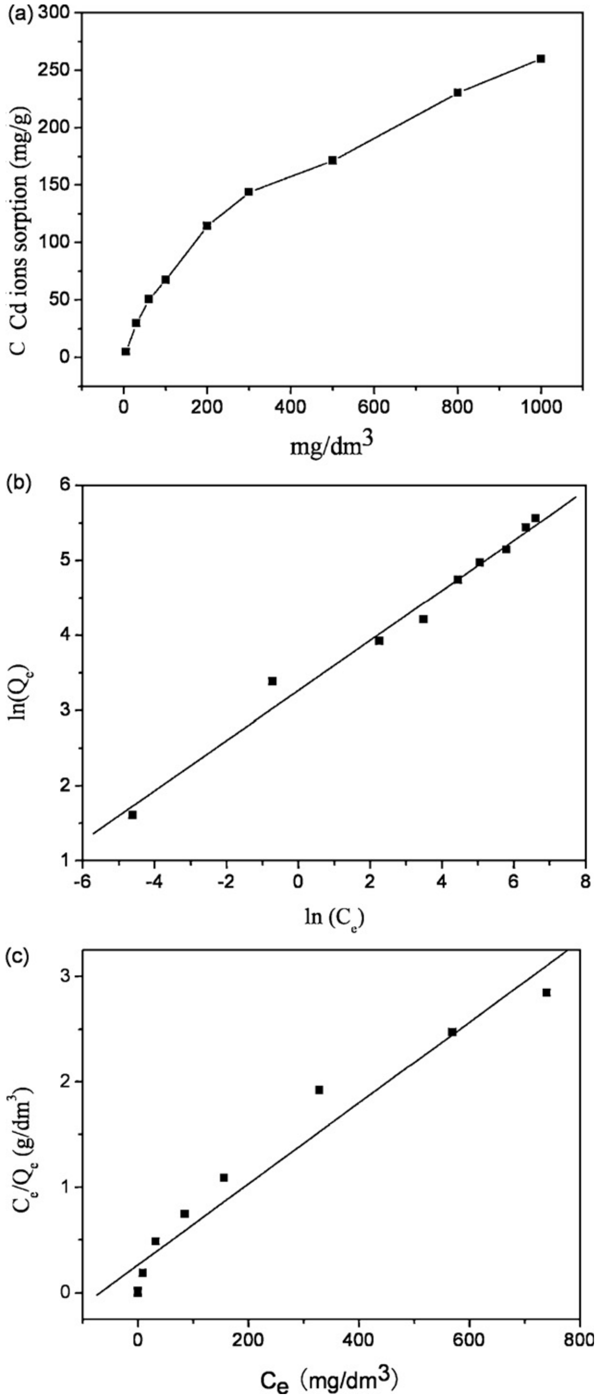

Fig. 3. (a) Relationship between equilibrium metal concentration and initial Cd^{2+} concentration, (b) linear fit of experimental data obtained using Freundlich isotherm model and (c) linear fit of experimental data obtained using Langmuir isotherm model.

The linear fit of our experimental data obtained with Langmuir isotherms is shown in Fig. 3(c) with correlation factor $R = 0.97$. The maximum sorption capacity, X_m, calculated from Langmuir isotherm is 260.42 mg/g [12], while Langmuir constant K is 0.0145 dm^3/g. The Langmuir model is basically developed to describe the sorption processes where no interaction between sorbate species occur on sites having the same sorption energies independent of surface coverage. Maximum sorption capacity represents the monolayer coverage of sorbent with sorbate.

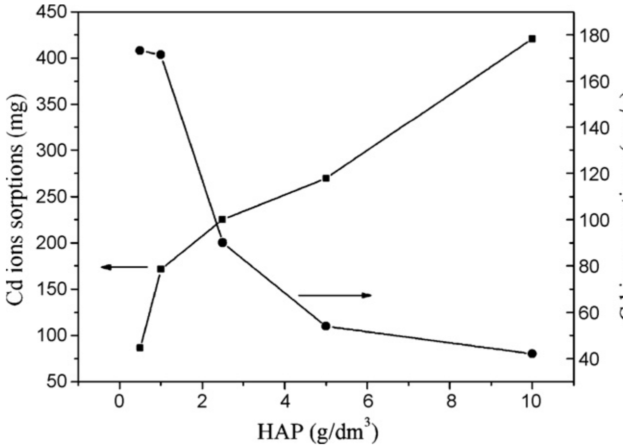

Fig. 4. The relationship between HAP amount and the Cd^{2+} sorption.

3.2.3. *Effect of HAP amount*

The relationship between HAP amount and the Cd^{2+} sorption is shown in Fig. 4. In our experiments, the amount of Cd^{2+} sorption increased rapidly with the increasing HAP amount. The phenomenon is to be expected, for a fixed initial concentration, increasing HAP amount provides greater sorption sites. While a large amount of HAP effectively reduces the unsaturation of such sites of the per unit mass, resulting in the great reduction of per unit mass adsorption at higher HAP amount [4].

The amount of Cd^{2+} adsorption per unit mass of HAP decreased from 173.2 mg/g to 42.1 mg/g, as the HAP amount was changed from 0.5 g/dm^3 to 10 g/dm^3. The corresponding extent of adsorption increased from 17.32% to 84.16%. Similar results have been reported earlier [4,19,20].

3.2.4. *Effect of pH*

Sorption of Cd^{2+} by HAP was studied using the pH range from 5 to 8 based on the reason that, when the pH value is lower than 4, HAP partly dissolved and when the pH value is higher than 8, Cd^{2+} started to precipitate which introduce uncertainty into the adsorption results. The relationship between the initial pH value and the Cd^{2+} sorption is presented in Fig. 5. The final pH values of the experiments are almost the same around 6.02 which could be ascribed to the buffering properties of HAP. The buffering characteristics of HAP are the result of acid–base reactions of

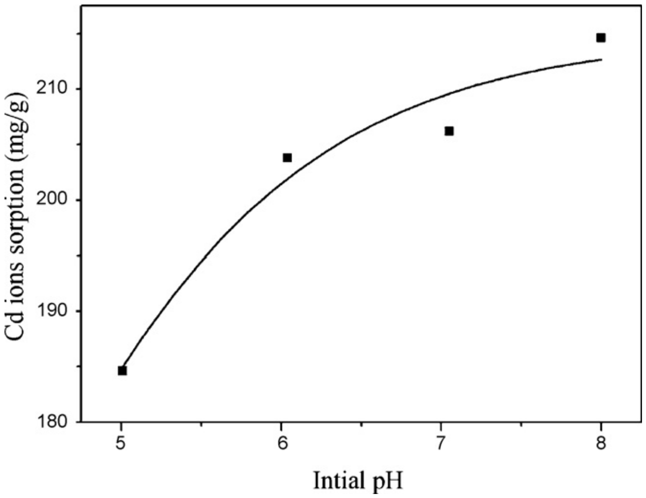

Fig. 5. Relationship between initial pH values and the Cd^{2+} sorption.

the reactive surface sites. Wu et al. [21], mentioned that the reactions responsible for the surface properties of HAP in aqueous solutions are:

$$\equiv\mathrm{P{-}O^-} + \mathrm{H^+} \rightleftarrows \equiv\mathrm{P{-}OH} \tag{6}$$

$$\equiv\mathrm{Ca{-}OH_2}^+ \rightleftarrows \equiv\mathrm{Ca{-}OH} + \mathrm{H^+} \tag{7}$$

In the lower range of initial pH value (5.01), protons in the solution were consumed by protonation of the surface $\equiv$P–O$^-$ and $\equiv$Ca–OH result in final pH value increase. The positively charged $\equiv$Ca–OH$_2{}^+$ and neutral $\equiv$P–OH sites prevail on HAP surface in acidic solutions, making surface charge of HAP in this pH region positive. On the other hand, final pH decrease takes place in the range of higher initial pH (6.04–8) due to OH$^-$ consumption via deprotonation of surface $\equiv$Ca–OH$_2{}^+$ and $\equiv$P–OH sites. Thus, neutral $\equiv$Ca–OH and negatively charged $\equiv$P–O$^-$ species predominate in alkaline solutions, causing HAP surface to become negatively charged in solutions with high pH value [8].

As reported, cadmium present in aqueous solution is mainly in the form of Cd^{2+} in the pH range of 5–8 [22]. Therefore, the sorption amount increased with the increasing pH value can be ascribed to the electrostatic. At low pH value (5.01), the significant amount of cadmium sorption occurred suggesting other sorption mechanisms may existed.

It is well known that the Ca^{2+} ions in HAP can be easily ion-exchanged with many other metal ions [11]. The ionic radius of Cd^{2+} (0.095 nm) is smaller than that of Ca^{2+} (0.099 nm), so we think that Ca^{2+} can be easily substituted in the HAP crystal lattice. Comparing with the XRD pattern of the original HAP (Fig. 6(a)), the corresponding peaks in Fig. 6(b) shifted to high degree, which indicated that the lattice parameters decreased. And the possible changes in the lattice parameters were quantified [23]. The space group of HAP is $P_6{}^3/m$. The lattice parameters (a and c) of original HAP are 9.422 Å and 6.870 Å. After sorption, the lattice parameters of HAP are 9.401 Å and 6.851 Å. The lattice parameter for both a and c slightly decreased, which further demonstrated the above conclusion. In addition, the intensity of XRD pattern in Fig. 6(b) was apparently lower than that of the original HAP, which showed the degree of crystallinity decreased after cadmium sorption. These results support the ion-exchange mechanism.

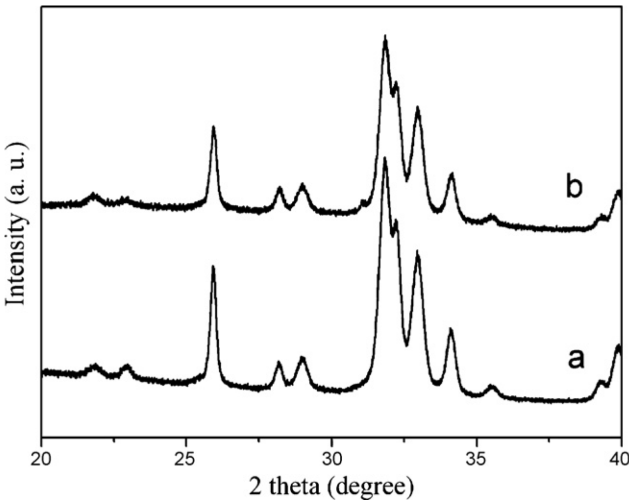

Fig. 6. XRD patterns of (a) original HAP and (b) HAP after sorption of Cd^{2+}.

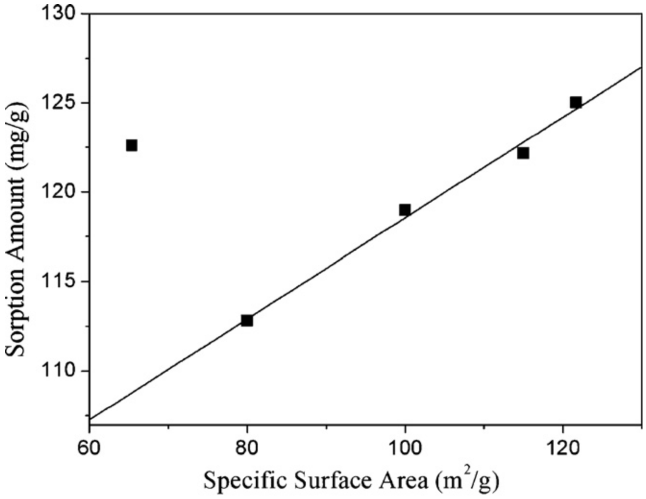

Fig. 7. Relationship between specific surface area and the Cd^{2+} sorption.

The decrease of final pH value for some of the experiments suggest that H^+ ions are released into the aqueous solution as a result of the exchange with Cd^{2+}

$$\mathrm{HAP{-}OH} + \mathrm{Cd^{2+}} \rightleftarrows \mathrm{HAP{-}O{-}Cd^+} + \mathrm{H^+} \tag{8}$$

$$\mathrm{2HAP{-}OH} + \mathrm{Cd^{2+}} \rightleftarrows \mathrm{(HAP{-}O)_2Cd} + \mathrm{2H^+} \tag{9}$$

which suggest the contribution of surface complexes formation [5,8,10,18].

The above discussion suggested that the mechanisms of electrostatic, ion exchange and surface complexes may be co-applicable to our experiment. The mechanism taking the main part needs further study.

3.2.5. Effect of specific surface area

When Cd^{2+} sorption amount was plotted against the samples specific surface area, a nearly linear dependence was observed (except for the sample with specific surface area of 65.4 m^2/g), the slope of rectilinear is 0.282 and the intercept is 90.3 mg/g (shown in Fig. 7).

The interception of the rectilinear (90.3 mg/g) may be considered as the sorption amount when considering the samples specific surface area is zero. So that value can be thought to be the sorption by ion exchange and the sorption amount higher than the intercept can be ascribed to the surface complex and electrostatic [12]. This reinforces the previous discussion of Cd sorption mechanisms.

When the sample's specific surface area is 65.4 m^2/g, the sorption amount is greatly departed from the above-described line. As this sample was prepared by hydrothermal process (other samples were prepared by precipitation method), the crystalline degree and the mole ratio of Ca to P should be considered. Higher crystalline degree and Ca/P ratio is favored for the ion exchange with Ca^{2+} and Cd^{2+}, so the sorption amount is higher.

Table 1
Desorption of Cd^{2+} from loaded HAP

Eluants	Initial pH	Final pH	Desorbed Cd^{2+} (%)
HAc	2.88	3.58	26.53
HAc + NaOH	5	5.13	13.83
H_2O	7.01	6.81	0.41
NaOH	11.85	11.57	0.13
$Ca(NO_3)_2$ 0.01 M	5.59	6.11	10.32
$Ca(NO_3)_2$ 0.001 M	5.63	6.32	4.6

3.3. Desorption

Results on the efficiencies of different eluants to release Cd^{2+} from loaded HAP are shown in Table 1. The desorbed amount of cadmium decreased continuously with the increasing initial pH values. The amount desorbed from the acetic acid solution was the highest while the NaOH solution was the lowest. This is because that HAP can exist stably in alkaline solution rather than in acidic solution. With the increase of the Ca^{2+} concentration, the amount of cadmium desorbed increased and this phenomenon may partly support the mechanism of ion exchange [5,19].

4. Conclusions

In this study, sorption of Cd^{2+} on spherical hydroxyapatite was investigated as a function of equilibration time, initial metal concentration, HAP amount, pH and specific surface area. The experiments have proved that:

1. Sorption in our investigated system follows pseudo-second-order kinetics. The rate of uptake of the Cd^{2+} by the HAP is very high initially, followed by a low rate.
2. The Freundlich and Langmuir adsorption isotherms can both be applied to our experimental results.
3. The amount of Cd^{2+} sorption increased rapidly with increasing HAP amount while the per unit mass adsorption reduced greatly at higher HAP amount.
4. The sorption of Cd^{2+} increases as pH value enhanced from 5 to 8.
5. Cd^{2+} sorption amount is related to the specific surface area, crystalline degree and Ca/P ratio.
6. The desorbed amount of Cd^{2+} decreased continuously with increasing pH, only trace amounts being desorbed at neutral or alkaline solutions, and increased with increasing Ca^{2+} concentration.

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References

[1] P.H.S., U.S. Department of Health and Human Services, Agency for Toxic Substances and Disease Registry (Editor), Toxicological Profile for Cadium, 1999, p. 1.
[2] S.S. Gupta, K.G. Bhattacharyya, J. Hazard. Mater. 128 (2006) 247.
[3] M. Ziagova, G. Dimitriadis, D. Aslanidou, X. Papaioannou, E.L. Tzannetaki, M. Liakopoulou-Kyriakides, Bioresour. Technol. 98 (2007) 2859.
[4] K.G. Bhattacharyya, S.S. Guptaa, J. Colloid Interf. Sci. 310 (2007) 411.
[5] I. Smiciklas, S. Dimovic, I. Plecas, M. Mitric, Water Res. 40 (2006) 2267.
[6] A. Krestou, A. Xenidis, D. Panias, Miner. Eng. 17 (2004) 373.
[7] A. Coramia, S. Mignardi, V. Ferrini, J. Hazard. Mater. 146 (2007) 164.
[8] Y. Xu, F.W. Schwartr, Environ. Sci. Technol. 28 (1994) 1472.
[9] Q.Y. Ma, S.J. Tralna, T.J. Logan, J.A. Ryan, Environ. Sci. Technol. 28 (1994) 1219.
[10] B. Sandrine, N. Ange, B.-A. Didierb, C. Eric, S. Patrick, J. Hazard. Mater. 139 (2007) 443.
[11] M. Srinivasan, C. Ferraris, T. White, Environ. Sci. Technol. 40 (2006) 7054.
[12] N.C.D. Rocha, R.C.D. Campos, A.M. Rossi, E.L. Moreira, A.D.F. Barbosa, G.T. Moure, Environ. Sci. Technol. 36 (2002) 1630.
[13] E. Dalas, P.G. Koutsoukos, J. Chem. Soc., Faraday Trans. 85 (1985) 3159.
[14] H.-W. Kim, H.-E. Kim, J. Biomed. Mater. Res. Part B 77 (2006) 323.
[15] V.S. Komlev, S.M. Barinov, E.V. Koplik, Biomaterials 23 (2002) 3449.
[16] S.W.K. Kweh, K.A. Khor, P. Cheang, J. Mater. Process. Technol. 89–90 (1999) 373.
[17] I. Langmuir, J. Am. Chem. Soc. 40 (1918) 1361.
[18] C.Y. Jing, S.Q. Liu, G.P. Korfiatis, X.G. Meng, Chemosphere 64 (2006) 379.
[19] R.R. Sheha, J. Colloid Interf. Sci. 310 (2007) 18.
[20] C.K. Jain, M.K. Sharma, Water Air Soil Pollut. 137 (2002) 1.
[21] L. Wu, W. Forsling, P.W. Schindler, J. Colloid Interf. Sci. 147 (1991) 178.
[22] P. Srivastava, B. Singh, M. Angove, J. Colloid Interf. Sci. 290 (2005) 28.
[23] Z.Y. Li, W.M. Lam, C. Yang, B. Xu, G.X. Ni, S.A. Abbah, K.M.C. Cheung, K.D.K. Luk, W.W. Lu, Biomaterials 28 (2007) 1452.