Adsorption of aqueous Cd$^{2+}$, Pb$^{2+}$, Cu$^{2+}$ ions by nano-hydroxyapatite: Single- and multi-metal competitive adsorption study

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Being an inexpensive but efficient adsorbent, hydroxyapatite is extensively used for decontaminating wastewater and soils polluted by heavy metals. However, its solubility and grain size can affect its remediation effectiveness. This study investigated the ability of nano-hydroxyapatite (nano-HAP) to adsorb aqueous Cd, Pb and Cu ions from single-metal and multi-metal ions reaction systems. Langmuir and Freundlich isotherm equations were employed to study the sorption constants. Based on the sum of squares errors (SSE), results showed that the Langmuir isotherm better fits sorption data than the Freundlich equation. The sorption affinity of nano-HAP for Pb(II) is always higher than that for Cu(II) and for Cd(II); the sorption maxima for the Cd, Pb and Cu follow the order Pb$^{2+}$ > Cu$^{2+}$ > Cd$^{2+}$. This could be inversely proportional to the hydrated ionic radii as Pb$^{2+}$ (4.01 Å) > Cu$^{2+}$ (4.19 Å) > Cd$^{2+}$ (4.26 Å). The measured selectivity coefficients in multi-metal (Cd–Pb–Cu) reaction systems shows that Pb has the highest sorption selectivity on nano-HAP among the metals investigated. This sorption selectivity coincided well with the sorption affinity order in mono-metal reaction systems. The pH of the solution is an important parameter in controlling Cd, Pb and Cu ions sorption on nano-HAP. Indeed, the nano-HAP sorption capacity increases with increasing pH up to a value of 6.25. This implies that the removal of metals from the solution is recommended for pH $\approx$ 6.25 or below, during remediation using nano-HAP as a sorbent.

Keywords: nano-hydroxyapatite (nano-HAP), Cd, Pb, Cu, competitive adsorption, selectivity coefficients

INTRODUCTION

Toxic heavy metals present in wastewater, effluents and soils are a major environmental problem. Efforts have been made on remediation of soils and wastewater polluted by heavy metals, and several remediation practices have been proposed, such as physical and chemical extraction, chemical stabilization/solidification (S/S) and electrochemical methods (Khan et al., 2004; Zhu et al., 2004; Chen et al., 2007; Zhou et al., 2007). Among the in-situ remediation treatments, the use of phosphatic materials (e.g., phosphate clay, apatite, phosphorus fertilizer etc.) as a stabilizing agent to immobilize Pb in soils has received much attention in past years. Nriagu (1974) firstly suggested phosphate for removing soluble Pb from the aqueous phase. Since then, several studies on phosphate as an effective additive have been carried out, especially for Pb-contaminated media (Cheung et al., 2002; Zhu et al., 2004; Chen et al., 2006; Singh et al., 2006; Agnieszka et al., 2009). More recently, hydroxyapatite, has been proposed as an inexpensive but efficient adsorbent for removal/remediation of soils polluted by Pb (Hashimoto et al., 2009; Slobodan, 2009), Zn and Cd (Chen et al., 2007; Zhu et al., 2008) and Cu-, Zn-polluted wastewater (Qian et al., 2008; Wang et al., 2009). Besides phosphates, activated carbons are considered also an efficient treatment for the removal of many organic compounds and metals from both liquid and gas phases (Cheung et al., 2002; Danny et al., 2004; Xiao and Thomas, 2004; Chen et al., 2006), but expensive. Though cheaper, little information is available on the efficiency of hydroxyapatite as an additive to adsorb aqueous metals in single- and multi-metal reaction systems. The adsorption of aqueous metal ions is strongly influenced by the competition of those metal ions to occupy the limited number of sorption sites. This, in turn, will decrease the removal efficiency of adsorbent for the metals of interest. It is of critical importance to evaluate the overall performance of hydroxyapatite on adsorption of metals, especially competitive adsorption in multi-metal reaction systems. The main objective of this study is to examine...
the potential use of nano-hydroxyapatite as an efficient adsorbent in the treatment of wastewater or remediation of multi-metal polluted soils. This will be made by 1) comparing quantitatively the efficiency of aqueous Cd, Pb and Cu adsorption on nano-hydroxyapatite and evaluate the impacts of pH on metals sorption in a single-metal reaction system; 2) evaluating the competitive sorption of Cd, Pb and Cu in multi-metal reaction systems with the developed selectivity coefficient measurement combined with isotherm equations.

**EXPERIMENTAL**

The nano-hydroxyapatite (nano-HAP) used for this study was provided by the Xinjiang Center for Disease Control and Prevention of China. Surface area of the sample was measured by single point Brunauer, Emmett and Teller N₂ sorption procedure (BET-N₂), mineralogical analysis (X-ray diffraction, XRD) and grain size distribution (Laser diffraction analysis, LDA). Total metal concentration in nano-HAP was determined by atomic absorption spectroscopy (AAS) following microwave-assisted aqua regia acid digestion following the method of Lu (1999). All digestions were conducted in triplicate and each batch included a standard reference material (GSS-6, China National Center for Standard Materials) and blank to validate the digestion procedure. The main composition of the nano-hydroxyapatite includes: SiO₂ = 23.1 wt%; CaO = 40.2 wt%; P₂O₅ = 16.7 wt%, acid insoluble ash = 3.1 wt%. The measured average grain size is 97.3 nm, with a surface area of 71.8 m²g⁻¹. The nano-HAP material did not contain toxic metals except 1.87 ppm of Pb.

Adsorption study was conducted in batch experiments: cadmium, lead and copper stock solution of 5,000 mg L⁻¹ was prepared from their nitrate salts Cd(NO₃)₂, Pb(NO₃)₂ and Cu(NO₃)₂. Deionized water was used for making metal solutions and washing, and the chemicals used were all of reagent grade. 30 ml- aliquots of 0.05 M KNO₃ background electrolyte solution, containing a known amount of Cd, Pb and Cu concentration ranging from 0 to 180 mg L⁻¹ were equilibrated with 0.20 g of nano-HAP in 50 mL polycarbonate centrifuge tubes. The slurries were shaken on an over-to-over shaker (~12 rpm) at room temperature (25 ± 2°C) for 24 hours. After stabilized the pH, metal concentration was raised equivalent from 0 to 180 mg L⁻¹ by adding a concentrated stock solution. After addition of the stock solution of metals, the rest of experimental procedure including shaking, centrifugation and metal analysis remained similar to the previous sorption experiment.

To study and compare the adsorption of aqueous Cd, Pb and Cu on nano-HAP, the sorption data were fitted to the following Eqs. (1) and (2):

**Conventional Langmuir**

\[
\frac{C_e}{x/m} = \frac{1}{kb} + \frac{C_e}{b}
\]  

**Freundlich equation**

\[
\log\left(\frac{x}{m}\right) = \log(K_f) + \frac{1}{n} \log(C_e)
\]

where \(C_e\) is the concentration of metals (Cd²⁺, Pb²⁺ or Cu²⁺) in equilibrium in the solution (mg L⁻¹), \(x/m\) is the amount of the metal ions (mg kg⁻¹) adsorbed on the HAP, \(b\) is adsorption maxima (mg kg⁻¹) and \(k\) is the adsorption

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**Table 1. The percent of mole ratio of Cd, Pb, Cu added to solution in multi-metal reaction system (X_i*)**

<table>
<thead>
<tr>
<th>Percent of mole ratio added in solution</th>
<th>Cd(I)</th>
<th>Pb(II)</th>
<th>Cu(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>0.70</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>0.10</td>
<td>0.60</td>
<td>0.35</td>
<td></td>
</tr>
<tr>
<td>0.15</td>
<td>0.50</td>
<td>0.45</td>
<td></td>
</tr>
<tr>
<td>0.20</td>
<td>0.50</td>
<td>0.55</td>
<td></td>
</tr>
</tbody>
</table>

*Total concentration of metal added to suspension was 0.0025 mol L⁻¹.
Table 2. Langmuir and Freundlich isotherm constants and the corresponding sum of squares errors (SSE) values for Cd(aq), Pb(aq), Cu(aq) at single-metal reaction systems

<table>
<thead>
<tr>
<th></th>
<th>Cd</th>
<th>Pb</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>b</td>
<td>66.7</td>
<td>80.6</td>
<td>73.5</td>
</tr>
<tr>
<td>k</td>
<td>0.46</td>
<td>2.12</td>
<td>1.37</td>
</tr>
<tr>
<td>SSE</td>
<td>$2.36 \times 10^{-3}$</td>
<td>$1.86 \times 10^{-3}$</td>
<td>$1.76 \times 10^{-3}$</td>
</tr>
<tr>
<td>Freundlich</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_f$</td>
<td>64.5</td>
<td>43.0</td>
<td>57.4</td>
</tr>
<tr>
<td>$1/n$</td>
<td>0.73</td>
<td>1.85</td>
<td>1.46</td>
</tr>
<tr>
<td>SSE</td>
<td>$4.61 \times 10^{-1}$</td>
<td>$2.96 \times 10^{-3}$</td>
<td>$2.56 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

where $Q_e$ is the amount of metals sorbed by nano-HAP in solution (mg g$^{-1}$), $C_0$ and $C_e$ are the concentrations (mg L$^{-1}$) of the metals in the initial solution and the equilibrium solution after the experiment, respectively, $v$ (L) is the volume of the solution and $m$ (g) the amount of HA used.

Fig. 1. Langmuir sorption isotherms of Pb, Cd, Cu on nano-HAP (A) and their linear fittings (B) after the transformation by the Langmuir Eq. (1). The data are from 24 hrs adsorption experiment and nine final concentrations were used in this adsorption study.

RESULTS AND DISCUSSION

For sorption isotherms, several sorption equilibrium equations are available for data analysis. In this study, two isotherm equations, i.e., the Langmuir equation (Eq. (1)) and the Freundlich equation (Eq. (2)) were employed to study the adsorption process. The results showed that the Langmuir and Freundlich models apparently fit the isotherms for all the M$^{2+}$(aq) species investigated with regression coefficients $R^2 > 0.931$(data not shown) and acceptable square errors. The isotherm constants derived from Eqs. (1) and (2) and the corresponding sum of squared errors (SSE) values are given in Table 2. The results of Fig. 1 and Table 2 showed that the sorption affinity and sorption maximum on nano-HAP for the Pb(II) in single-metal sorption systems were always higher than Cu$^{2+}$ and Cd$^{2+}$ ions. The sorption maxima (m mol kg$^{-1}$)
for the Cd, Pb and Cu ions followed the order Pb$^{2+} >$ Cu$^{2+} >$ Cd$^{2+}$, with a sorption maximum of 80.6, 73.5, 66.7 (mg mol$^{-1}$) for Pb$^{2+}$, Cu$^{2+}$ and Cd$^{2+}$ respectively. Danny et al. (2004) investigated the ability of bone char clay and reported a similar result for the ability of calcium hydroxyapatite to adsorb Cu$^{2+}$ and Cd$^{2+}$ in solution. The sorption maxima seems to be inversely proportional to the hydrated ionic radii of the metals, being Pb$^{2+}$ (4.01

Fig. 2. Effect of pH on aqueous Cd, Pb, Cu adsorption on nano-HAP in single-metal reaction systems. The data are from 24 hrs sorption experiment and nine final concentrations were used in this adsorption study.

Fig. 3. Selectivity coefficients $K_{ij}$ plots with the varying mole ratio of metal ($X_i$) addition in multi-metal reaction systems (initial solution pH $= 6.20$, $\sum X_i = 0.0025$ mol L$^{-1}$).
Table 3. Langmuir parameters for the adsorption of Pb, Cd and Cu at various pHs by nano-HAP in single-metal reaction system

<table>
<thead>
<tr>
<th>pH</th>
<th>b</th>
<th>k</th>
<th>R²</th>
<th>b</th>
<th>k</th>
<th>R²</th>
</tr>
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<tr>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.52</td>
<td>35.25</td>
<td>0.892</td>
<td>0.999</td>
<td>60.12</td>
<td>1.891</td>
<td>0.999</td>
</tr>
<tr>
<td>4.60</td>
<td>36.58</td>
<td>0.881</td>
<td>0.998</td>
<td>71.58</td>
<td>1.542</td>
<td>0.999</td>
</tr>
<tr>
<td>5.45</td>
<td>49.36</td>
<td>0.812</td>
<td>0.992</td>
<td>87.47</td>
<td>1.275</td>
<td>0.991</td>
</tr>
<tr>
<td>6.25</td>
<td>56.37</td>
<td>0.782</td>
<td>0.987</td>
<td>92.20</td>
<td>1.155</td>
<td>0.968</td>
</tr>
<tr>
<td>7.20</td>
<td>39.04</td>
<td>0.655</td>
<td>0.912</td>
<td>79.25</td>
<td>0.887</td>
<td>0.867</td>
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</table>

Adsoption of aqueous Cd^{2+}, Pb^{2+} and Cu^{2+} by nano-hydroxyapatite.
able to the more weakly adsorbed species (B or C). Selectivity coefficient \( (K_{ij}) \) can be calculated as:

\[
K_{ij} = X^i (C^j)^{1/2} X^j (C^i)^{1/2} (i, j = 1, 2, 3)
\]

where \( X \) is the mole ratios of metals (Cd\(^{2+}\), Pb\(^{2+}\) or Cu\(^{2+}\)) in equilibrium solution, \( C^i \) and \( C^j \) are the concentrations of metal \( i \) and metal \( j \) respectively, with \( i, j = 1 \) (Cd), 2 (Pb), 3 (Cu); \( z \) is the chemical valence of metal ion and \( T \) represents the ternary metal ions reaction system.

The results (Fig. 3) indicate that the selectivity coefficients \( (\log K_{12}) \) for adsorption of Cd on nano-HAP in multi-ion system decreased sharply with increasing Pb concentration \( (X_{Pb}) \) in solution. However, the selectivity coefficients \( (\log K_{13}) \) for adsorption of Cd on nano-HAP only has a sharp decrease when the addition of mole ratio of Cu \( (X_{Cu}) \) is less than 0.40, then it continued decreased with a very slow rate when the addition of mole ratio of Cu \( (X_{Cu}) \) is more than 0.40. The difference between adsorption selectivity coefficients of Cd \( (\log K_{12}-\log K_{13}) \) shows the competitive impacts of Pb and Cu on Cd adsorption on nano-HAP in solutions. As indicated in single-metal adsorption system, Pb has the highest adsorption affinity on nano-HAP among the metals investigated, followed by Cu and Cd. In the multi-adsorption systems, competitive adsorption took place on the adsorbent surface sites that can be occupied by all species, that is, sites available to B and C, while non-competitive adsorption occurred on sites only available to A. The sharp decrease selectivity coefficients \( (\log K_{13}) \) showed that the Cd adsorbed on sites of nano-HAP was intensively displaced with increasing Pb\(^{2+}\) concentration in solution. In case of selectivity coefficients \( (\log K_{12}) \), it sharply decreased with the addition of Cu in solution when Cu mole ratio less than 0.40 and then continued decrease with a slow rate with continuous addition of Cu in solution, this result indicated that Cu has a strong competitive impact on the Cd adsorption at low concentration (Fig. 3), however, the impact of Cu on Cd adsorption becomes insignificant when most of the sites are not available for competitive adsorption after higher Cu\(^{2+}\) addition in solution. The plot of selectivity coefficients \( (\log K_{12}) \) vs. \( X_{Cu} \) showed also a competitive adsorption between Cu\(^{2+}\) and Pb\(^{2+}\) on nano-HAP. Generally, the selectivity coefficients follow the order \( \log K_{23} > \log K_{13} > \log K_{12} \). This result coincides well with the adsorption result found for mono-metal system which showed the Pb\(^{2+}\) has the highest competitive adsorption capacity among the metals investigated.

**Conclusions**

The adsorption of aqueous Cd\(^{2+}\), Pb\(^{2+}\) and Cu\(^{2+}\) on nano-HAP was investigated in mono- and multi-metal reaction systems. Sorption behaviour was predicted with Langmuir and Freundlich isotherm equations. For mono-metal reaction systems, results showed that the sorption of metals on nano-HAP are well fitted both using the Langmuir and Freundlich equations. The adsorption maximum and the sorption affinity of the metals on nano-HAP follows the order Pb\(^{2+}\) > Cd\(^{2+}\) > Cu\(^{2+}\), possibly related to the inverse of their hydrated ionic radii. The solution pH is an important parameter in controlling metals sorption onto the nano-HAP. The sorption maximum \( (b) \) and sorption affinity parameter \( (k) \) derived from the Langmuir equation increased with increasing the pH in solution with a deviation for pH = 7.2. A meaningful positive relation between adsorption potential \( (K_d) \) and solution pH was observed except the treatments at pH = 7.2. The deviation of sorption maximum \( (b) \) at pH 7.20 for nano-HAP showed a possible mechanism for the metals adsorption, that is a solubility-controlled reaction in system, the decreased sorption maximum \( (b) \) at pH 7.20 for nano-HAP probably related to its lower solubility at pH 7.20 than that at lower pHs. The higher capability of nano-HAP to adsorb aqueous Pb than other metals indicated its potential as promising way to remediate Pb-contaminated effluent, sediment and soils.

In multi-metal ions reaction systems, the competitive adsorption of the metals on nano-HAP was also investigated using the developed selectivity coefficient measurement combined with the isotherm equation. The result indicated that the competitive adsorption of multi-mixtures of Cd\(^{2+}\), Pb\(^{2+}\) and Cu\(^{2+}\) on nano-HAP decreased the adsorption capacity of nano-HAP for individual metal ions. The extent of the decrease depended on the adsorption affinity of nano-HAP to other metal ions present in mono-metal system (i.e., Pb\(^{2+}\) > Cu\(^{2+}\) > Cd\(^{2+}\)). Although the adsorption of aqueous metal ions is influenced by many factors, the ratios of metal ion displaced by other competitive metal ions in multi-metal ion mixtures were quite consistent over a wide concentration range.

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**References**


Adsorption of aqueous Cd²⁺, Pb²⁺ and Cu²⁺ by nano-hydroxyapatite 239


