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Immobilization of lead and copper in aqueous solution and soil using hydroxyapatite derived from flue gas desulphurization gypsum

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ABSTRACT

Flue gas desulphurization (FGD) gypsum is an abundant waste generated from coal-fired power plants. This study evaluated the potential application of hydroxyapatite (F-HAP) derived from FGD gypsum for immobilization of lead (Pb) and copper (Cu) in water and soil. MINTEQ software was employed to determine the species distribution of Pb(II) and Cu(II) at different solution pH conditions. The factors that affect sorption behavior such as pH effect, sorption kinetics, thermodynamics, and isotherms were investigated using batch tests. Various kinetics and isotherms models were used to fit the obtained data. The experimental results showed that the amount of Pb(II) and Cu(II) adsorbed on F-HAP increased as the pH increased from 2.0 to 6.0, and adsorption was enhanced with the rise in temperature. The predicted maximum adsorption capacities were found to be 1.376 and 0.460 mmol/g for Pb(II) and Cu(II), respectively. The values of mean free energy (E) obtained from Dubinin–Radushkevich (D-R) model implied that the chemical reaction, which was stronger than ion exchange governed the process of Pb(II) adsorption, while the adsorption of Cu(II) was mainly ascribed to ion exchange. XRD analysis revealed that the final solid obtained after Pb(II) immobilization was mainly mixed of pyromorphite and F-HAP, while the final solid acquired after Cu(II) immobilization still consisted of a single phase of F-HAP. On the other hand, application of F-HAP in contaminated soil effectively reduced the leachable and exchangeable Pb and Cu, reflecting that F-HAP is a potential material for remediating environmental pollution with Pb and Cu. This study realized the potential of a modified geochemical waste material towards remediation of metal contaminated soils, providing very useful and valuable information for other similar solid wastes, such as paper sludge and phosphogypsum.

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1. Introduction

With rapid development of industrialization, toxic heavy metals such as lead (Pb) and copper (Cu) are ubiquitous in water and soil, posing serious threats to plants, animals and even human beings. Pb has been widely used for different purposes such as battery manufacturing, paints, ceramics, metal plating, ammunition (Ahmad et al., 2012; Shahat et al., 2015). The accumulation of Pb or its compounds in living organisms can damage the central nervous system, brain, kidney, and circulatory system, which may cause severe poisoning that may lead to intellectual disability, anemia, mental deficiency or cancer (Huang and

Pan, 2016; Ma et al., 2015). Cu has been widely used in processing of ores and oil, paper and paper board mills, manufacture of ceramics, electroplating, glass making, production of fertilizers, etc. (Dean et al., 1972; Gandhi and Meenakshi, 2011). Exposure to higher concentrations (>5 mg Cu/L) has been linked to serious kidney failure and liver diseases (Pawar et al., 2016). Hence, developing technologies to efficiently immobilize Pb and Cu thereby reducing their mobility and availability in environment are urgently and universally required.

Recently, utilization of phosphate for adsorption and immobilization of heavy metal ions has been considered as a cost-effective and environmentally positive technology for treating heavy-metal contaminated water and soil (Cao et al., 2004; Liu and Zhao, 2007; Seshadri et al., 2016). Liang et al. (2011) found that hydroxyapatite derived from the porous glass strongly adsorbed Pb(II) and Cu(II). Matusik et al. (2008) compared the effectiveness of different phosphate compounds (K_2HPO_4 , $NH_4H_2PO_4$ and “Polifoska 15” fertilizer) on Cd(II) immobilization. The

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results showed that all used forms of phosphates presented >99% reduction for Cd(II) removal from aqueous solution, and the process was mainly influenced by pH condition rather than source of phosphates. Yang and Mosby (2006) demonstrated that the application of H_3PO_4 significantly reduced the risk of Pb mobility in smelter-contaminated urban soil. Hamon et al. (2002) assessed the remediation effect of $CaCO_3$, KH_2PO_4 , red mud, and a kaolin byproduct on Cd and Zn in a polluted soil. The results showed that immobilization of both Cd and Zn was greatest in KH_2PO_4 treated soil, and this treatment was also found to be resistant to soil acidification. Mignardi et al. (2012) used synthetic hydroxyapatite and natural phosphate rock to immobilize Cd, Cu, Pb, and Zn in mine waste soils. The results showed that both materials effectively reduced the heavy metal water solubility generally by about 84–99%, and synthetic hydroxyapatite was slightly superior to natural phosphate rock for immobilizing heavy metals. Ogawa et al. (2015) used hydroxyapatite and ferrihydrite both individually and in combination to immobilize Pb in shooting range soil and observed marked increase in Pb immobilization for the combined treatment. However, the stability of immobilized Pb was similar for hydroxyapatite alone and the combined treatment. Although soluble phosphate (e.g., K_2HPO_4 , $NH_4H_2PO_4$) was highly effective in immobilization of heavy metals, excess phosphate in soil is still a potential risk to the environment (Cao et al., 2004; Jiang et al., 2012). Hydroxyapatite (HAP, $Ca_{10}(PO_4)_6(OH)_2$) is a less soluble phosphate, furthermore, it is environmentally friendly and possesses high stability under reducing and oxidizing conditions, which would be an ideal amendment for the immobilization of heavy metals.

In order to reduce the production costs of HAP, many scientists attempted to develop low-cost source of calcium to replace expensive reagents. Sanosh et al. (2009) synthesized nano-HAP powder from biowaste chicken eggshells. Piccirillo et al. (2013) immobilized the special bacterial strains on fish bones based HAP for water treatment. Muhammad et al. (2016) extracted HAP from the waste fish scales with the yield of ~32%. However, these attempts are based on biowastes and the research involving industrial by-products is limited.

In our previous work, flue gas desulphurization (FGD) gypsum, a second largest solid waste in coal-fired power plants has been successfully transformed to hydroxyapatite (F-HAP) (Yan et al., 2014). The overall goal of this study is to evaluate the feasibility of using F-HAP to immobilize Pb(II) and Cu(II) in aqueous solution and soil. The specific objectives are to: (1) investigate the adsorption behavior of Pb(II) and Cu(II) in aqueous solution based on pH impact, sorption kinetics, thermodynamics, and isotherms; (2) compare the leachability of Pb and Cu in unamended and amended soils via toxicity characteristics leaching procedure (TCLP) method; and (3) study the effect of F-HAP addition on the distribution of Pb and Cu in soil.

2. Materials and methods

2.1. Materials and soil collection

Chemical reagents used in this work are all analytical grade. FGD gypsum samples were collected from a coal-fired power plant in Nanjing, China. F-HAP with a Ca/P molar ratio of 5:3 was prepared by the stoichiometric reaction between FGD gypsum and KH_2PO_4 solution as described by Yan et al. (2014) with a minor modification.

The stock solutions of Pb(II) and Cu(II) were prepared by dissolving $Pb(NO_3)_2$ and $Cu(NO_3)_2$ in Milli-Q water, respectively. The required concentrations in adsorption experiments were prepared by diluting the stock solutions. KNO_3 (0.01 M) was used to maintain the ionic strength of all solutions. NaOH (0.1 M) and HNO_3 (0.1 M) were used to adjust the pH of all solutions.

Soil samples contaminated with Pb and Cu were collected from a small firing range in Nanjing, China at a depth of 0–20 cm. The samples were air-dried and sieved through a 10-mesh sieve to remove the large bullet fragments and provide homogeneous fractions. The total Pb and Cu concentrations based on extraction by the mixed concentrated acid

(HNO_3 – $HClO_4$ –HF) (Lu, 1999) were approximately 3715 and 284 mg/kg, respectively.

2.2. Adsorption experiments

Batch experiments were carried out by mixing 0.1 g F-HAP with 100 mL diluted stock solutions of Pb or Cu in conical flasks, and the mixtures were shaken in an air bath oscillator at a speed of 200 rpm. After adsorption, the mixtures were filtered through 0.22 μm membrane filter for analysis of the residual metals concentration by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, Optima 7000DV). The adsorption capacity (q_e , mmol/g) were calculated from the following equations:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where C_0 and C_e (mmol/L) are initial and equilibrium concentrations of adsorbate, respectively, V (L) is the volume of solutions, and m (g) is the dosage of adsorbent.

The experiments on pH impact were performed at 25 °C, the pH values of the solutions with 1.0 mmol/L concentration of Pb and Cu solutions were adjusted to 2.0, 3.0, 4.0, 5.0, and 6.0. Kinetic experiments were carried out at different periods (0, 5, 10, 15, 30, 45, 60, 90, 120, 150, 180, 240, and 300 min) for three temperatures (25, 35 and 45 °C) using 1.0 mmol/L concentration of Pb and Cu solutions. Adsorption isotherms were obtained using various Pb (0.5, 1.0, 1.5, 2.0, and 3.0 mmol Pb/L) or Cu (0.1, 0.5, 1.0, 1.5, and 2.0 mmol Cu/L) concentrations.

2.3. Theories

2.3.1. Kinetic models

Two well-known kinetic models, pseudo-first order (Ho, 2004) and pseudo-second order models (Ho, 2006) were usually used to study the controlling mechanism of the adsorption process such as mass transfer, diffusion control or chemical reaction. Their non-linear forms are expressed as:

$$\text{Pseudo-first order equation : } q_t = q_e(1 - e^{-k_1 t}) \quad (2)$$

$$\text{Pseudo-second order equation : } q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (3)$$

where q_e and q_t (mmol/g) represent the amount of adsorbate adsorbed at equilibrium and at time t , k_1 (min^{-1}) and k_2 ($\text{g}/(\text{mmol min})$) are the rate constants for the pseudo-first order and pseudo-second order models, respectively.

In addition, when $t \rightarrow 0$, the initial adsorption rate, h (mmol/(g min)), can be calculated by:

$$h = k_2 q_e^2 \quad (4)$$

2.3.2. Thermodynamic studies

The thermodynamic parameters including Gibbs free energy change (ΔG° , kJ/mol), enthalpy change (ΔH° , kJ/mol) and entropy change (ΔS° , kJ/mol/K) were determined by (Wang et al., 2012):

$$\Delta G^\circ = -RT \ln K \quad (5)$$

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (6)$$

where K is the adsorption equilibrium constant, R is the ideal gas constant, 8.314 J/mol/K, and T (K) is the temperature.

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