



# Removal of Pb(II) from aqueous solution using hydroxyapatite/calcium silicate hydrate (HAP/C-S-H) composite adsorbent prepared by a phosphate recovery process



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## HIGHLIGHTS

- The phosphate recovery process from wastewater was used as a material modification method.
- HAP/C-S-H can remove Pb(II) from aqueous solution effectively at a wider pH range compared with C-S-H.
- HAP/C-S-H provides a double environmental benefit for resource recovery and pollution control.
- The compound mechanism of Pb(II) adsorption on HAP/C-S-H is proposed.

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## ABSTRACT

In this study, phosphate was recovered from wastewater by C-S-H, and its phosphate-rich product HAP/C-S-H was reused as a composite adsorbent to remove Pb(II) from aqueous solution. The samples were characterized by scanning electron microscope (SEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), zeta potential and specific surface areas analysis. The adsorption of Pb(II) on C-S-H and HAP/C-S-H were investigated at different pH, ionic strength, contact time, initial concentration and temperature. The results showed that the adsorption capacities of Pb(II) were heavily dependent on pH and slightly dependent on ionic strength. The adsorption kinetics and adsorption isotherms were well described by pseudo-second-order model and Langmuir model, respectively, and the thermodynamic parameters indicated that the adsorption process was endothermic and spontaneous. The adsorption capacities of Pb(II) on C-S-H and HAP/C-S-H could reach 543.5 mg/g and 946.7 mg/g, respectively, when the pH was 5.0, the temperature was 298 K and the ionic strength was 0.01 M. All the results indicate that HAP/C-S-H, recovered from phosphate wastewater, is an effective material for Pb(II) removal from aqueous solution, providing double environmental benefits for resource recovery and pollution control.

## 1. Introduction

Lead (Pb) is one of the major heavy metal pollutants in the natural environment, which mainly comes from the wastewater in many industries such as metal mining, metal smelting and storage battery manufacturing [1]. Because of its non-biodegradable and bioaccumulative properties, low concentrations of lead can damage the central nervous system, reproductive system, liver and kidney, particularly for pregnant women and children [2,3]. Therefore, the lead-contained wastewater must be properly treated before it is discharged into the water environment.

There are several typical techniques for Pb(II) removal from aqueous solution, such as chemical precipitation, complexation, ion exchange, adsorption, electrochemical treatments and membrane processes [4]. Among them, growing attention has been paid to the adsorption, because of its cost-effectiveness, good feasibility and wide adaptability [5]. Over the past decade, a lot of work has been devoted to the development of low-cost adsorbents for Pb(II) removal such as zeolite [6], clay minerals [7], phosphate materials [8], biochar [9] and synthetic polymers [10].

Some studies have shown that Pb(II) removal from aqueous solution by phosphate materials is particularly effective even in an acidic

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environment because of the high chemical stability of lead phosphate compounds [11]. However, phosphorus as a kind of non-renewable and limited resource are increasingly depleted on a global scale [12]. In order to make up for the lack of phosphorus resource, the phosphate recovery from wastewater by the crystallization of struvite [13] or hydroxyapatite [14] has become a hot topic. However, it is not easy to separate the product of fine phosphate crystal from aqueous solution [15], and the recovered product also lacks a high-value utilization mode because it contains a large amount of impurities and even harmful substances [16].

Some studies have shown that calcium silicate hydrate (C-S-H), as the combinations of seed crystal, calcium provider and pH regulator, can recover phosphate easily by forming hydroxyapatite (HAP) in a single crystallization process, and the recovered product is readily separated from the solution [17,18]. Besides, C-S-H is also an effective adsorbent for most heavy metal ions [19]. Therefore, C-S-H not only simplifies the phosphate recovery process, but the recovered product HAP/C-S-H is expected to be an effective composite adsorbent for Pb(II) removal from aqueous solution.

This study aims to use the recovered phosphate product HAP/C-S-H as an adsorbent for Pb(II) removal from aqueous solution, which provides double environmental benefits for resource recovery and pollution control. In this work, C-S-H was prepared by using a simple ultrasound-assisted sol-gel method at room temperature, and it was used for phosphate recovery from wastewater to prepare HAP/C-S-H. The adsorption behavior of Pb(II) on C-S-H and HAP/C-S-H were investigated by batch equilibrium experiments, and the effects of pH, ionic strength, contact time, initial concentration and temperature were considered. Adsorption kinetic model, adsorption isotherm model and thermodynamic parameters were used to fit the experimental data, and the adsorption mechanisms were discussed. It is worth noting that the term “adsorption” is used here loosely as a general term to describe the attachment of heavy metal ions from the solution to the adsorbent, because of the complicated mechanisms of Pb(II) removal on HAP/C-S-H.

## 2. Materials and methods

### 2.1. Chemicals

All chemicals used in this study were of analytical grade obtained from Sinopharm Chemical Reagent Co., Ltd. Simulated phosphate wastewater (60 mg-P/L) was prepared by dissolving the appropriate quantity of  $\text{KH}_2\text{PO}_4 \cdot 6\text{H}_2\text{O}$  into deionized water. The stock solutions of Pb(II) and supporting electrolyte were prepared by dissolving the appropriate quantity of  $\text{Pb}(\text{NO}_3)_2$  and  $\text{NaNO}_3$  into deionized water, respectively. All working solutions for Pb(II) removal experiments were obtained by mixing appropriate the stock solutions of lead and supporting electrolyte.

### 2.2. Preparation of C-S-H and HAP/C-S-H

C-S-H was prepared by a simple ultrasound-assisted sol-gel reaction. First, the calcium chloride solution was added dropwise into the sodium silicate solution under ultrasound (300 W) with Ca/Si ratio of 1.2 and liquid/solid ratio of 10. Then, a white sol was generated and gradually hardened and the sample was taken out and incubated in a plastic container at room temperature for 24 h. Afterwards, the gel was gently mixed into deionized water (10 g/L) to remove free  $\text{Ca}(\text{OH})_2$ . The mixture was filtered through a 0.45  $\mu\text{m}$  membrane filter, and the cake was dried in an oven at 80 °C for 24 h. Finally, C-S-H was collected by screening 80–150  $\mu\text{m}$  powder after grinding.

HAP/C-S-H was prepared by recovering phosphate from wastewater with C-S-H. 0.6 g C-S-H was added into 1 L simulated phosphate (60 mg-P/L) wastewater, and the mixture was shaken in a thermostatic shaker at 25 °C and a speed of 180 rpm for 24 h. Phosphate recovery efficiency

and pH changes with different initial pH (3.0, 5.0, 7.0, 9.0, 11.0) were studied with the contact time. The pH was adjusted by adding 0.01 M  $\text{HNO}_3$  or NaOH solutions. The remaining phosphate concentration was determined by molybdenum blue method with Spectrophotometers (Shimadzu UV-2550, Japan), and the pH of solution was monitored by a pH meter (Mettler Toledo Seven2Go, Switzerland). The phosphate recovery efficiency ( $R_e$ , %) was calculated by the following equation:

$$R_e = \frac{(C_0 - C_e)}{C_0} \times 100\% \quad (1)$$

where  $C_0$  and  $C_e$  are the initial and equilibrium phosphate concentrations (mg/L), respectively. When the initial pH was 5.0, the HAP/C-S-H sample was collected after the phosphate recovery process for further application.

### 2.3. Characterization of C-S-H and HAP/C-S-H

The surface morphology of samples were obtained by a field emission scanning electron microscopy (FE-SEM) (Zeiss Ultr55, Germany). XRD patterns of samples were identified by an X-ray powder diffractometer (Bruker D8 ADVANCE, Germany) equipped with Ni-filtered Cu K $\alpha$  radiation (40 kV, 40 mA) in a scanning range of 10–60° (2 $\theta$ ). FT-IR spectra were recorded by an infrared spectrometer (Nicolet Nexus 470, Germany) using a KBr pellets method in a scanning range of 500–4000  $\text{cm}^{-1}$ . The quantitative chemical compositions of samples were identified using an X-ray fluorescence spectrometer (XRF) (Shimadzu XRF-1800, Japan). XPS analyses were performed with a Scanning ESCA Microprobe (Perkin Elmer PHI 5300, USA) spectrometer equipped with a concentric hemispherical analyzer using Mg K $\alpha$  X-ray source. Data were extracted from the spectra via peak fitting using XPS Peak software, and spectra were corrected for charging effects using the adventitious carbon peak at 284.8 eV. Zeta potentials of samples were measured by Malvern Zetasizer Nano system (ZS 90, UK) with irradiation from a 633 nm He-Ne laser at various pH from 3.0 to 11.0. The specific surface areas and pore-size distributions of samples were analyzed by a  $\text{N}_2$  adsorption-desorption analyzer (JWGB BK112, China). The Brunauer-Emmett-Teller (BET) method was used to calculate the specific surface areas ( $\text{m}^2/\text{g}$ ). The pore size distributions were derived from desorption branch by using the Barrett-Joyner-Halenda (BJH) model. The total pore volume ( $\text{cm}^3/\text{g}$ ) was determined by the adsorbed amount of  $\text{N}_2$  at a relative pressure of  $p/p_0 = 0.99$ .

### 2.4. Batch adsorption experiments

The adsorption properties of Pb(II) on C-S-H and HAP/C-S-H were investigated by batch equilibrium experiments in polyethylene centrifuge tubes. The experiments were initiated by the addition of 0.4 g/L C-S-H or HAP/C-S-H to working solutions. During the experiments, the pH was maintained stable at initial pH by adding 0.01 M  $\text{HNO}_3$  or NaOH solutions. The tubes were shaken in a thermostatic shaker at 25 °C and a speed of 180 rpm for 4 h. After the reaction, the solution was separated from the mixture by filtering through a 0.22- $\mu\text{m}$  membrane filters, and the remaining concentration of Pb(II) was measured by an Inductive Coupled Plasma Emission Spectrometer (ICP-OES) (Agilent 720ES, USA). All the experiments were performed in triplicate and the average data were accepted. The standard deviations were found to be within  $\pm 3\%$ . The adsorption efficiency of Pb(II) ( $A_e$ , %), the adsorption capacities of Pb(II) on adsorbents ( $Q_e$ , mg/g) and the distribution coefficient ( $K_d$ , L/g) were calculated by the following equations:

$$A_e = \frac{(C_0 - C_e)}{C_0} \times 100\% \quad (2)$$

$$Q_e = \frac{(C_0 - C_e)V}{m} \quad (3)$$

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