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Lead cations immobilization by hydroxyapatite with cotton-like morphology

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ABSTRACT

Hydroxyapatite (HAP) in cotton morphology was first prepared by co-precipitation method using cotton as templates. The effect of contact time, initial concentration, and temperature on HAP immobilization of Pb^{2+} ions was studied using a batch technique. It was remarked that the maximum amount of Pb^{2+} immobilization by HAP was 1690.2 mg/g with a minimum contact time of 50 min. The pseudo-second-order kinetic model has been proposed to fit the data. Thermodynamic parameters such as ΔG^0, ΔH^0, and ΔS^0 were calculated to understand the nature of sorption. Original HAP and immobilization products were characterized using SEM, TEM/EDAX, XRD and BET. In the presence of Cl^-, the dissolution of HAP followed by precipitation of chloropyromorphite was found to be the main operating mechanism for Pb^{2+} immobilization by HAP.

1. Introduction

Heavy metals are of great concern because of their extreme toxicity even at low concentration and easy accumulation in food chain [1]. As a result of worldwide accumulation, lead presents a more serious environmental and health hazard than any other element [2]. Lead can cause central nervous system damaged, and also damage the kidney, liver, reproductive system, basic cellular processes and brain functions [3]. How to effectively and deeply immobilize lead from water systems is a very important but still challenging task for environmental engineers.

Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HAP) has been of interest because of it is similar to the mineral components of bone and teeth of human body, which means it is nontoxic to human body [4]. It is an ideal materials for long-term immobilizing heavy metals because of its high sorption capacity for heavy metals, low water solubility, high stability under reducing and oxidizing conditions, availability, and low cost [5]. HAP has been utilized in the immobilization of a wide variety of metals such as Pb [6,7], Cd [8,9], Zn [6,10,11], Cu [6,11,12], Co [13] by many investigators. HAP with improved immobile performance has become a hotspot of this field. Templated morphologies such as mesoporous usually show higher surface areas and much more uniform and controllable pore size and pore morphologies compared with randomly organized forms. Nowadays, the design and synthesis of materials with specific templated morphologies have attracted considerable attention because the performance characteristics of nanomaterial have particular relevance with the shape and structure of template [14]. Specifically, fabrication of materials with plant morphology have been proposed and partially realized in recent years [15]. The advantages of using plants as templates to fabricate materials are as follows: simple, mild, high-yield, and environmental friendly [16]. The potential benefits for biotemplated materials include a facile diffusion pathway for waste liquor transport and greater access to active site [17]. Since HAP is used mostly as powders and its usefulness depends on the powder properties such as particle size, surface area and morphology, the biotemplated HAP possessed controllable morphology and special structure could fabricate high surface area which can facilitate mass transferring [18]. Hollow structures have higher surface areas and hence could improve the immobile properties. Cotton as a biotemplate has more uniform morphology than other fibers, what's more, it is a nontoxic,

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economical, environmental-friendly, safe candidate in directing the fabrication of hollow architectures. Recently some researchers reported nanomaterials synthesized by simple method using cotton as biotemplate [19–22]. However, to our best knowledge, the HAP in cotton morphology has not been synthesized to immobilization the lead from the aqueous solution.

In this paper, biomorphic hydroxyapatite with hollow structures was used to immobilization the lead from water. The objective of this study was to investigate the feasibility of lead immobilization from water using hydroxyapatite with cotton morphology through a laboratory scale study in an open system. The effects of contact time, initial lead concentration, and temperature on the adsorption process were investigated and attention was given to evaluate the kinetic constants and thermodynamic parameters.

2. Materials and methods

2.1. Materials

The reagents used in this work included $Pb(NO_3)_2$ (99%, Beijing Hongxing chemical factory, China), $Ca(NO_3)_2{\cdot}4H_2O$(99%, Guangdong chemical reagent engineering-technological research and development center, China), $(NH_4)_2HPO_4$(Shantou Xilong chemical factory, Guangdong, China), HCl (36–38%, Chongqing Dongchuan Chemical Co., Ltd.), HNO_3(65–68%, Chengdu Kelong chemical factory, China), cotton (absorbent cotton, Nanchang Leiyi medical apparatus Co., LTD), and filter membrane (pore size 0.45 μm, Tianjin Hengao technology development Co., LTD). All chemicals are of analytical grade. Deionized water was used for all the experiments.

2.2. Synthesis of HAP with cotton morphology

HAP nanocrystalline was synthesized using co-precipitation method and cotton as templates. The co-precipitation was carried out with $Ca(NO_3)_2{\cdot}4H_2O$ and $(NH_4)_2HPO_4$ as the Ca and P sources respectively at temperature of 85 °C. The obtained templated hybrids were rinsed with deionized water for several times. Finally, the templated hybrids were dried at 80 °C for 24 h, and sintered at 550 °C for 6 h to achieve the HAP with cotton morphology.

2.3. Materials characterization

The component and the particle structure of both the original HAP and immobilization products were characterized carefully. The powder X-ray diffraction (XRD) pattern was obtained by a Rigaku, Japan, TTRIII X-ray diffractometer with Cu Kα radiation at 40 KV and 250 mA. The surface morphology of both the original HAP and immobilization products were studied with FEI QUANTA200 scanning electron microscope (SEM). Transmission electron microscopy (TEM) images were obtained by JEM-2100 TEM operated at 100 KV. An energy-dispersive X-ray (EDX) analyzer attached to the TEM was used to determine the elemental composition of the original HAP and immobilization products. The surfer area and N_2 adsorption–desorption isotherm of the original HAP and immobilization products were measured by Brunauer–Emmett–Teller (BET) micromerities surface area and porosity Tri StarII.

2.4. Adsorption experiments

2.4.1. pH study

The optimum pH for adsorption was determined by mixing 20 mg of the adsorbent HAP and 20 ml 2000 mg/L Pb^{2+} solutions of different initial pH values in separated conical flask. The mixtures was shaken at a speed of 200 rpm for 1 h at 35 °C. After adsorption, the concentration of Pb^{2+} was measured. The pH of the solution was measured using pH meter (DENVER instrument UB-7). Except for the experiment of pH effect, the pH of the original solution was controlled at 2.5.

2.4.2. Adsorption kinetic study

Adsorption kinetic experiments were carried out by batch adsorption method at 35 °C on a shaker at 200 rpm. A series of samples were prepared by mixing $Pb(NO_3)_2$ solution (20 ml, 2000 mg/L Pb^{2+}) with 0.02 g HAP in a 50 ml conical flask, samples were withdrawn at desired time intervals. The exact concentration of Pb^{2+} was determined by Atomic Adsorption Spectrometer (AAS) (NITACHI Z-2000).

2.4.3. Adsorption isotherm study

Adsorption isotherm studies were conducted by mixing 0.02 g HAP with 20 ml $Pb(NO_3)_2$ solution in a 50 ml conical flask. For the series of measurements, the initial concentration of Pb^{2+} solution was varied in the range of 500–6000 mg/L. To achieve saturated adsorption, the sample solution was shaken at 200 rpm and 308 K for 2 h.The concentrations of the Pb^{2+} were analyzed.

2.4.4. Adsorption thermodynamic study

Solution of 20 ml 2500 mg/L $Pb(NO_3)_2$ was mixed with 0.02 g HAP at different temperature of 278, 288, 298, 308, 318, and 328 K in a temperature-controlled mechanical shaker (SUKUN SKY-200B) to determine the thermodynamic parameters of the thermodynamic parameters of standard free energy change (ΔG^0), standard enthalpy change (ΔH^0), and standard entropy change (ΔS^0).

At the end of the adsorption, all the suspensions were filtered with cellulose acetate membrane filters with pore diameter of 0.45 μm, and the filtrates were analyzed for total Pb^{2+}.

The adsorption capacity was calculated according to the following equation:

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

Where q_e (mg/g) is the amount of lead ions adsorbed onto the unit amount of the adsorbent, C_0 (mg/L) is the initial lead ion concentration, C_e (mg/L) is the final or equilibrium lead ion concentration, V (L) is the volume of the solution, and m (g) is the adsorbent weight in dry form.

The removal efficiency of lead ions was calculated by the difference of lead ion concentration in aqueous solution using the equation expressed as follows:

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

Where C_0 (mg/L) and C_e (mg/L) are the initial and final (equilibrium) lead ion concentration, respectively.

All the experiments were performed twice and the average values were recorded.

3. Result and discussion

3.1. Study on immobilization lead by batch mode experiments

The removal of lead from the aqueous solution was highly dependent on the solution pH. The experiments of different pH values were carried out and the results were shown in Fig. 1. The initial Pb^{2+} concentration was 2000 mg/L and the amount of HAP was 1 g/L. From the experimental data, we can find that pH 2.5 is the optimum pH value for Pb^{2+} removal in this study. However, the percentage of Pb^{2+} removed by the HAP was decreased intensively