Journal of Solid State Chemistry 261 (2018) 53–61

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

Competitive adsorption of Pb(II), Cu(II), and Zn(II) ions onto hydroxyapatite-biochar nanocomposite in aqueous solutions

Yu-Ying Wang[a,b], Yu-Xue Liu[a,b], Hao-Hao Lu[a,b], Rui-Qin Yang[c,d], Sheng-Mao Yang[a,b,*]

[a] *Institute of Environment, Resource, Soil, and Fertilizer, Zhejiang Academy of Agricultural Sciences, Hangzhou 310021, PR China*
[b] *Engineering Research Center of Biochar of Zhejiang Province, Hangzhou 310021, PR China*
[c] *Zhejiang Provincial Collaborative Innovation Center of Agricultural Biological Resources Biochemical Manufacturing, Zhejiang University of Science and Technology, Hangzhou 310023, PR China*
[d] *Zhejiang Provincial Key Lab for Chem & Bio Processing Technology of Farm Product, Zhejiang University of Science and Technology, Hangzhou 310023, PR China*

ARTICLE INFO

Keywords:
Biochar
Hydroxyapatite
Nanocomposite
Competitive adsorption
Heavy metal

ABSTRACT

A hydroxyapatite-biochar nanocomposite (HAP-BC) was successfully fabricated and its physicochemical properties characterized. The analyses showed that HAP nanoparticles were successfully loaded on the biochar surface. The adsorption of Pb(II), Cu(II), and Zn(II) by HAP-BC was systematically studied in single and ternary metal systems. The results demonstrated that pH affects the adsorption of heavy metals onto HAP-BC. Regarding the adsorption kinetics, the pseudo-second-order model showed the best fit for all three heavy metal ions on HAP-BC. In both single and ternary metal ion systems, the adsorption isotherm of Pb(II) by HAP-BC followed Langmuir model, while those of Cu(II) and Zn(II) fitted well with Freundlich model. The maximum adsorption capacity for each tested metal by HAP-BC was higher than that of pristine rice straw biochar (especially for Pb(II)) or those of other reported adsorbents. Therefore, HAP-BC could explore as a new material for future application in heavy metal removal.

1. Introduction

Recently, heavy metals in water have become a worldwide problem, because most of them are toxic to organisms and accumulate in biota. In particular, Cd, Cu, Pb, and Zn cause cancers and damage the immune system [1–3]. Unlike other inorganic and organic pollutants, heavy metals are non-degradable and therefore persistent. Moreover, multiple heavy metals often coexist in contaminated water [4,5] due to a common geological source or co-disposal in the wastewater [6]. For instance, Zn and Pb are simultaneously discharged into the environment during the mining and milling of copper [7]. The coexistence of heavy metal pollutants in wastewater and contaminated soil means that their competitive sorption as well as their mobilities in the presence of each other should be studied [8]. Several methodes (adsorption, ion exchange, chemical precipitation, etc.) have been applied to remove these heavy metals from the environment [9–11]. While many of them have drawbacks (e.g., excessive time required, high costs, low efficiency, and high energy consumption), the adsorption process for aqueous effluents has become very attractive from the economic point of view [12,13]. Activated carbon, silica gels, iron oxide, carbonaceous nanofibers, zeolite, and attapulgite are among the conventional absorbent materials [13,14]. However, they have some disadvantages including tendencies for oxidation and aggregation, limited adsorption capacity, high cost, and low selectivity [15]. Therefore, developing multi-functional adsorbents is considered critical for treating heavy metal pollution.

Nowadays, biochar (biomass-derived black carbon) has attracted attention as a new adsorbent. It is carbon-rich and pyrolyzed in a closed container under anaerobic condition [16]. Because of its especial properties (e.g., high surface area and cation exchange capacity), biochar can be used for soil improvement, fertility enhancement, and carbon sequestration, etc. [17,18]. Moreover, biochar based on agricultural and forestry by-products could potentially replace activated carbons as an economical adsorbent for contaminants. However, the as-prepared biochars usually have a relatively low adsorption capacity for heavy metals [19]. Several methods have thus been developed to modify biochars. In particular, surface modifications such as loading nanoparticles to prepare biochar nanocomposites can remarkably improve the removal ability for various water pollutants [20–22].

Hydroxyapatite [HAP, $Ca_{10}(PO_4)_6(OH)_2$] is found naturally in human bones and teeth. It is usually applied as hard tissue implants and carriers of genes, enzymes, and proteins [23,24]. Hydroxyapatite is

---

[*] Corresponding author at: Institute of Environment, Resource, Soil, and Fertilizer, Zhejiang Academy of Agricultural Sciences, Hangzhou 310021, PR China.
E-mail address: yangshengmao@263.net (S.-M. Yang).

https://doi.org/10.1016/j.jssc.2018.02.010
Received 20 December 2017; Received in revised form 9 February 2018; Accepted 12 February 2018

also particularly well-suited for immobilizing metallic cations on several sites of P-OH groups on its surface. Being environmentally friendly, HAP-based adsorbents can be safely used in natural water [25]. However, because of the high surface energy caused by van der Waals forces, HAP nanoparticles tend to form aggregates in aqueous solutions., dramatically decreasing their surface area and removal performance. Therefore, compositing hydroxyapatite with biochar may produce desirable adsorption properties that cannot be achieved by either component alone.

The objective of this work was to fabricate hydroxyapatite-biochar nanocomposite wtih the advantages of both biochar and hydroxyapatite nanoparticles for removing Pb(II), Cu(II), and Zn(II). The hydroxyapatite-biochar (HAP-BC) nanocomposite was carefully characterized. The adsorption behaviors of single and ternary metal solutions on HAP-BC nanocomposite were also investigated. The unmodified biochar derived from rice straw was used as a comparison. The influences of pH, contact time, initial ion concentration, ionic strength, and other coexisting ions on the performance were studied. Langmuir and Freundlich adsorption isotherm models, and different kinetic equations were applied to calculate the isotherm parameters and study the adsorption kinetics, respectively. In addition, the mechanisms for heavy metal removal by modified and unmodified biochars were explained.

2. Materials and methods

2.1. Materials

The chemicals used in the experiments, including NaCl, KCl, $MgCl_2 \cdot 6H_2O$, $CaCl_2$, $(NH_4)_2HPO_4$, HCl, NaOH, $Cu(NO_3)_2 \cdot 3H_2O$, $Pb(NO_3)_2$, and $Zn(NO_3)_2 \cdot 6H_2O$, being commercially available and of analytical grade, were purchased from Sinopharm Chemical Reagent Co., Ltd. Deionized water was used in all experiments.

2.2. Preparation of biochar

The biochar prepared in this study was derived from rice straw through a typical slow pyrolysis process [26]. The rice straw came from the Yangdu experimental baseof Zhejiang Academy of Agricultural Sciences. Firstly, rice straw was put in a programmable tube furnace (Hangzhou Lan Tian Instrument Co., LTD) and pyrolyzed under anaerobic conditions at 500 °C for 3 h with the heating rate of 25 °C min^{-1}. Then, the sample was cooled to room temperature naturally to obtain the pristine biochar (BC). The HAP-BC nanocomposite was prepared as follows. $CaCl_2$ (1.11 g, 0.1 M) was first dissolved in 100 mL of deionized water with vigorous stirring, to which 1 g of the prepared BC was added to form a suspension solution A. $(NH_4)_2HPO_4$ (0.792 g, 0.06 M) was then dissolved in 100 mL of deionized water with vigorous stirring to form solution B. The solutions A and B were both adjusted to pH = 10.0 using 0.1 M HCl or NaOH. Finally, solution B was added into A gradually. After 24 h of incubation, the precipitate was isolated by centrifugation and washed three times with anhydrous ethanol, and then dried overnight to obtain the HAP-BC nanocomposite.

2.3. Biochar characterization

SEM analysis was performed on a JSM-6700F field emission scanning electron microscope (FESEM). The biochar samples were coated with a thin film of gold to increase the conductivity. Elemental composition analysis of the biochars was conducted by Energy-dispersive X-ray spectroscopy (EDX). The XRD patterns were measured with a Bruker D8 Advance X-ray diffractometer. IR spectra of the biochars were obtained on a Nicolet iS10 FT-IR spectrometer in the range from 4000–400 cm^{-1}. The specific surface area was measured by a Nova 2000e surface area analyzer (Quantachrome, USA). The zeta potential was obtained using a particle analyzer (Nano ZS90).

2.4. Sorption experiments

The standard stock solutions of Pb(II), Cu(II), and Zn(II) ions (each of 1000 mg L^{-1}) were prepared with $Pb(NO_3)_2$, $Cu(NO_3)_2 \cdot 3H_2O$, and $Zn(NO_3)_2 \cdot 6H_2O$, respectively. The adsorption experiments were conducted by mixing biochar (50 mg) with the heavy metal solution (50 mL) at 25 °C. The influence of pH on the adsorption ability of biochars was examined for pH = 2–6. The pH of the solution was controlled by HCl and/or NaOH. To measure the sorption kinetics, the adsorption on biochars was examined at different time intervals (10, 30, 60, 180, 300, 480, 720, and 1440 min). Different initial concentrations of the heavy metals (25, 50, 100, 200, 300, 500, 800, and 1000 mg L^{-1}) were applied to obtain the sorption isotherms. In addition, the influence of ionic strength on the competitive adsorption was also studied, by adjusting the ionic strengths of the solution to 0, 0.001, 0.005, 0.01, 0.05, 0.1 and 0.5 M using NaCl. The effects of four common coexisting cations, Na(I), K(I), Ca(II), and Mg(II), were also studied by adding 0.01 M of NaCl, KCl, $CaCl_2$, or $MgCl_2 \cdot 6H_2O$ to 50 mg L^{-1} heavy metal solutions, respectively.

At the end of each experiment, the mixture was filtered and the concentration of residual heavy metal ions in the filtrate was determined by inductively coupled plasma–atomic emission spectroscopy (ICP-AES, Prodigy). All adsorption studies were repeated in triplicate, and the averaged values were given. The adsorption efficiency (q_e) and uptake percentage (U%) were calculated as follows:

$$q_e = \frac{(C_0 - C_e)V}{W}$$

$$U\% = \frac{(C_0 - C_e)100\%}{C_0}$$

where C_0 and C_e ($mg \cdot L^{-1}$) are the initial and equilibrium concentrations of the heavy metal, respectively, V (mL) is the total volume of the solution, and W (mg) is the weight of the biochar.

2.5. Regeneration of the sorbent

First, 0.05 g of HAP-BC was added to 50.0 mL of 50 mg L^{-1} mixed heavy metal solutions, buffered at optimum pH, and stirred for 24 h. After reaching adsorption equilibrium in the ternary metal system, the metal-loaded HAP-BC was removed and placed in 50 mL of 0.2 M HCl and shaken in an oscillator for 30 min. Afterwards, HAP-BC was collected by centrifugation, washed, and dried for the next cycle. This process was repeated for five cycles.

3. Results and discussion

3.1. Biochar characterization findings

The XRD patterns of BC and HAP-BC were shown in Fig. 1a. The peaks for BC at 28° and 41° confirmed the presence of sylvite (KCl), while those at 29.5° and 31° were attributed to $CaMg(CO_3)_2$/dolomite [27]. The XRD pattern of HAP-BC was significantly different: all the diffraction peaks can be indexed as hydroxyapatite with the lattice parameters a = 9.423 Å, c = 6.883 Å, and space group $P6_3/m$ (JCPDS 89–6440), indicating that HAP was loaded on the surface of biochar. The average crystalline size calculated by Scherrer's formula was 3.85 nm. The FT-IR spectra of the two samples are shown in Fig. 1b. In the spectrum for BC, the broad band centered at 3445 cm^{-1} (between 3000 and 3500 cm^{-1}) can be assigned to –OH stretching vibrations of water [28]. The peak at 1093 cm^{-1} was assigned to C–O stretching of the $–OCH_3$ group, and that at 1434 cm^{-1} was assigned to $–CH_2–$ groups [29]. The band at 1601 cm^{-1} represented C=O stretching vibrations, whereas those at 2357 cm^{-1} could be assigned to the O=C=O stretching vibrations [29]. These organic functional groups may be attributed to the lignin structure in rice straw. The vibration peaks of