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Low concentration Re(VII) recovery from acidic solution by Cu-biochar composite prepared from bamboo (*Acidosasa longiligula*) shoot shell

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ABSTRACT

In this work, new Cu-coated biochar composites for the adsorption of Re(VII) through complexation mechanism was synthesized successfully. The sensitivity of Cu-coated biochars to solution pH decreased greatly and the adsorption capacity was increased by 3–12 times compared with pristine biochar at pH 3–6. The environmental effect factors and mechanisms of Re(VII) adsorption onto Cu-coated biochar composites (Cu-BC) were investigated. The Re(VII) adsorption nicely fits the Redlich-Peterson isotherm model, and the recovery of Re(VII) from acidic solution by Cu-coated biochar composites follows pseudo-second-order kinetics. Besides, the thermodynamic parameters depicted the spontaneous endothermic nature for the adsorption of low concentration Re (VII). These results demonstrate that easily synthetic Cu-coated biochar composites have promising potential for the recovery of low concentration Re(VII) in acidic solution.

1. Introduction

Rhenium (Re) is a scattered metal element with an average concentration of less than 1 $ng{\cdot}g^{-1}$ in the earth's crust. However, there are wide applications of rhenium and its alloys in aerospace, petrochemical, national defense, etc. The major uses of rhenium are in superalloys used in high-temperature turbine engine components and in petroleum-reforming catalysts, representing an estimated 70% and 20%, respectively, of end uses (Polyak, 2017). The demand for rhenium is rising due to its widespread utilization. The recovery of rhenium is thus of great economic significance because of its high use value. More importantly, it can also greatly lower the potential threat of rhenium to environment. In nature, Re occurs usually among molybdenite ores, and is predominantly extracted as a by-product of molybdenum production. Several conventional extraction methods, such as precipitation, ion-exchange and solvent extraction, have been applied for separation of rhenium during the past decades (Abisheva et al., 2011; Anderson et al., 2013; Dong et al., 2013). However, these methods are only suitable for the recovery of high concentration rhenium (100–250 $mg{\cdot}L^{-1}$) in acidic solutions and most of them associated with high operating cost and/or secondary pollution problems. Whereas when pyrometallurgical processing copper concentrate, trace amounts of rhenium pass into acidic solutions in the form of perrhenate (Abisheva et al., 2011; Lou et al., 2013). The Re-containing acidic solutions have variable acidity (pH value from 1 to 6) and low rhenium concentration (10–30 $mg{\cdot}L^{-1}$). For example, initial concentrations of rhenium of copper smelting acidic wastewater, collected from a copper smelter which is located in Hubei province, PRC, is about 20 $mg{\cdot}L^{-1}$. The copper smelter discharges about 300,000 tons of copper smelting acidic wastewater each year. So, there is about 6000 kg rhenium in the wastewater. Due to its scarcity, rhenium demands a high price. The annual average price of rhenium metal pellets was $2700 per kilogram in 2015 (Polyak, 2015). Therefore, it is very important to develop effective technologies to recover rhenium from Re-containing low concentration acidic solutions.

Many researches have suggested that adsorption is one of the most efficient and attractive methods for recovering metal ions from aqueous solutions and it is characterized by sustainable, environmental friendly, easy process control and low cost requirements (Fomina and Gadd, 2014; Tan et al., 2015). Bamboo *(Acidosasa longiligula)* shoot shell, a by-product of the bamboo shoot processing industry, is an abundant and renewable agricultural residue in Fujian province of China. However, it is usually eliminated by either burning or discarding in the fields, causing severe environmental contamination. Our previous work indicated that bamboo (*Acidosasa longiligula*) shoot shell derived biochar is effective in adsorbing Re(VII) from acidic solutions (Hu et al., 2015a). However, biochars are sensitive to the pH value changes of aqueous

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solutions because of strong electrostatic interaction between ReO_4^- and protonated biochar, which is the main mechanism of adsorption. Therefore, it is necessary to reduce the sensitivity of biochar to solution pH value. Some studies have shown that the sensitivity of the adsorbent to the solution pH can be effectively reduced by forming a complex between the adsorbent and the adsorbate (Hu et al., 2017; Jiang et al., 2014; Jing et al., 2012). And some previous works also shown that various complexes can be formed by the reaction of copper and perrhenate (Cao et al., 2011; Mikhailova et al., 2006; Varfolomeev et al., 1994). Thus, Cu-coated biochar composites were prepared to reduce the sensitivity of biochar to solution pH value for the recovery of low concentration Re(VII) from acidic solutions.

The objective of this study was to develop a composite adsorbent with cupric acetate monohydrate impregnated on *Acidosasa longiligula* shoot shell biochar (ASBC) for effective recovery of low concentration Re(VII) from acidic solutions by complexation mechanism. The effectiveness of Cu-coated biochars was evaluated using batch experiments with a comparison to pristine biochar. The specific aims of this work were as follows: (1) prepare and characterize the Cu-coated biochar composites; (2) assess the adsorption ability of the Cu-coated biochar composites to low concentration Re(VII); (3) determine the effects of environmental factors (e.g. initial solution pH, adsorbent concentration, temperature, etc.) on the adsorption of the Re(VII) onto the Cu-coated biochar composites; and (4) investigate the mechanism of Re(VII) adsorption onto Cu-coated biochar composites.

2. Methods

2.1. Material

All chemicals and reagents used in this work were of analytical grade and solutions were prepared using deionized (DI) water (18.2 MΩ). Cupric acetate monohydrate ($Cu(CH_3COO)_2{\cdot}H_2O$) and potassium perrhenate ($KReO_4$) were purchased from Tianjin Hengxing and Tianjin Damao chemical reagent Co. Ltd, respectively. BSS (bamboo (Acidosasa longiligula) shoot shell) were collected from a local market in Fuzhou, Fujian to be used as the feedstock biomass.

2.2. Preparation of Cu-biochar composites

2.2.1. Protocol 1: preparation of biochar

The BSS was firstly washed several times with distilled water and air dried. The dried biomass was crushed and ground to 180–250 μm in particle size. Then BSS particles were placed in a ceramic crucible covered with a lid and heated in a muffle furnace. A slow pyrolysis condition was employed at a 10 °C·min^{-1} heating rate. Feedstock was held at 500 °C for 1 h. The resulting sample was cooled to room temperature inside the furnace and then washed with distilled water to neutral. Then the sample was dried at 80 °C for 24 h. The product was designated as *Acidosasa longiligula* shoot shell biochar (ASBC or Pristine biochar).

2.2.2. Protocol 2: copper coating process

The copper coating process was conducted by immersing ASBC in a 0.2 M cupric acetate monohydrate (CAM) with a ASBC:CAM ratio of 1:20 (g·mL^{-1}) without precipitation at room temperature for 12 h. After filtration, the Cu-impregnated biochar was dried at 80 °C for 24 h. Then the Cu-impregnated biochar was put into a quartz plate and heated to 350 and 500 °C for 4 h in a horizontal tube furnace under nitrogen flow. After cooled down, the resultant samples were repeatedly washed by deionized (DI) water until neutral pH was reached and the filtrate was free from copper, then they were dried at 80 °C for 24 h. The final product was designated as copper-impregnated biochar (Cu-ASBC) and Cu-ASBC pyrolyzed at 350 °C and 500 °C were respectively denoted Cu350 and Cu500. The stability of the copper ions on biochar was tested via dissolution tests with pH variation of 1–6. Negligible amounts of copper in the solution suggested strong stability of copper fixation on the biochar surface.

2.3. Cu-biochar composites characterization

Pore characteristics of the biochars including surface area, pore volume and pore diameter were determined with a Micromeritics Autosorb surface area analyzer (ASAP 2020, Micromeritics, USA). Surface morphology of the biochars was determined using scanning electron microscopy (SEM, HIROX SH-4000M, China) equipped with an energy dispersive X-ray spectroscopy (EDX, Bruker Corporation, USA) for analyzing surface elements. The functional groups on the biochars were characterized using attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR, Nicolet iS50, ThermoFisher, USA) with a resolution of 4 cm^{-1}, accumulating 16 scans per spectra. In addition, a computer-controlled X-ray diffractometer (XRD, X'Pert PRO, PANalytical, Holland) equipped with a stepping motor and graphite crystal monochromator was used to investigate the crystalline Cu minerals on the Cu-biochars. X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Thermo Scientific, USA) was conducted to obtain the surface elemental compositions of the Cu-biochars.

The point of zero charge (pH_{pzc}) of the biochars was measured using the following method. To a series of 20 mL glass vials, 10 mL 0.01 mol·L^{-1} of NaCl aqueous solution was transferred in each vial. The pH_i values of the solution were roughly adjusted from 2 to 12 by adding either 0.1 mol·L^{-1} HCl or 0.1 mol·L^{-1} NaOH. The pH_i values of the solutions were then accurately noted. 0.1 g of adsorbent was added to each vial, which were securely capped immediately. The suspensions were then shaken in an orbital shaker and allowed to equilibrate for 48 h. The pH values of the supernatant liquid were noted. The difference between the final pH (pH_f) and initial pH_i values ($\Delta pH = pH_f - pH_i$) was plotted against the pH_i. The point of intersection of the resulting curve at which ΔpH 0 gave the pH_{pzc}.

In addition, the ash content of the biochars was determined by heating the biochars in a muffle furnace at 750 °C for 6 h and the pH value of the biochars was measured in deionized water at the ratio of 1:20 (g·mL^{-1}) after being shaken for 24 h at 120 rpm (SHA-B, China).

2.4. Adsorption kinetics and isotherms

Re(VII) stock solution (1 g·L^{-1}) was prepared using analytical reagent $KReO_4$ and diluted to the required concentrations (20–100 mg·L^{-1}). The pH of all the tested Re(VII) solutions was pre-adjusted to 1.0 ± 0.05 by using HCl or NaOH prior to testing.

Adsorption kinetics of Re(VII) onto Cu-biochars were investigated by adding 0.03 g of each adsorbent to 20 mL glass vials equipped with Teflon-lined screw caps containing 10 mL 20 mg·L^{-1} Re(VII) solution at 25, 30 and 35 °C respectively. The vessels were shaken at 130 rpm in a mechanical shaker. At different time intervals (0.5, 1, 3, 5, 8, 10 and 12 h), vials were withdrawn and the mixtures were subsequently filtered through 0.45 μm pore size membrane filters. Re(VII) concentrations in the filtrates were determined by using UV–visible spectrophotometry (UV1810, Shanghai Youke, China). The amounts of Re(VII) adsorbed onto the adsorbents were calculated based as the differences between initial and final measured concentrations.

Adsorption isotherms of Re(VII) onto Cu-biochars were determined by adding 0.03 g of each adsorbent to 20 mL glass vials equipped with Teflon-lined screw caps containing 10 mL 20 mg·L^{-1} Re(VII) solution at 25, 30 and 35 °C respectively. Re(VII) concentration in the glass vials is ranging from 20 to 100 mg·L^{-1}. The vessels were shaken in the mechanical shaker for 8 h, and the samples were then withdrawn and subsequently filtered to determine Re(VII) concentrations in the filtrate by the same method as previously to study the kinetics of adsorption.

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