

Adsorption, concentration, and recovery of aqueous heavy metal ions with the root powder of *Eichhornia crassipes*



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ABSTRACT

We investigated the adsorption of aqueous Cu^{2+} and Cr^{3+} , as model heavy metal ions, by the root powder of *Eichhornia crassipes*, followed by combustion to establish an economical route suitable for large-scale recovery of heavy metal ions from wastewater. In the optimal pH range of 5.0–6.0, the adsorption reached equilibrium after 30 min and could be described by Langmuir isotherms with maximum adsorption capacities of 32.51 mg/g for Cu^{2+} and 33.98 mg/g for Cr^{3+} . A pseudo-second-order kinetic model was applied to describe the adsorption kinetics. We concluded from Fourier transform infrared spectroscopy that functional groups containing $-\text{OH}$ and $-\text{COOH}$ contributed to the adsorption. During adsorption, Ca^{2+} , Mg^{2+} , and K^{+} were discharged from the root powder. Electrostatic interactions also played an important role in the adsorption process. X-ray photoelectron spectroscopy analysis suggested that this long-root adsorbent appeared to chelate Cr^{3+} more strongly than Cu^{2+} , both of which appeared on the surface and in the interior of the adsorbent; both were eluted best with H_2SO_4 . Combusting the saturated adsorbent generated a product with high concentrations of metal ions: 23% w/w Cu^{2+} and 30% w/w Cr^{3+} , values equal or higher than the regular contents of mine ore (20–25% w/w). Thus, this process created a product that was favorable for subsequent processing.

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1. Introduction

Recovering heavy metal ions from industrial or urban effluents, particularly those toxic to human beings, animals, and plants, is an important issue for both environmental safety and resource sustainability. A number of methods to remove heavy metal ions, such as precipitation, coagulation, solvent extraction, electrolysis, membrane separation, ion exchange, and adsorption (Bai and Abraham, 2003; Bailey et al., 1999; Ucin et al., 2002) have been developed and tested. These methods are not efficient for treating dilute solutions, and recovering valuable heavy metals is an important but unfulfilled objective. Increasing efforts have been made in recent years to find biodegradable adsorbents, such as plants (Dhir and Srivastava, 2011; Zuo et al., 2012), fungi (Bingol et al., 2004), lignin (Sciban et al., 2011), alginate (Singh et al., 2012), algae (Areco et al., 2012; Aravindhan et al., 2004; Bulgariu and Bulgariu, 2012; Cabatingan et al., 2001; Lee and Chang, 2011), and other biomaterials (Sharma and Bhattacharyya, 2005; Schneegurt et al., 2001) that can recover metal ions. These biodegradable adsorbents are advantageous over chemically synthesized adsorbents

because a saturated biodegradable adsorbent can be combusted to remove the majority of the adsorbent, concentrating the heavy metal species into a feedstock for subsequent processing. Because of this advantage, the adsorption/desorption mechanism and the microstructure of these adsorbents should be investigated more thoroughly.

Long-root *Eichhornia crassipes*, termed because of its morphological characteristics, is being tested for the on-site treatment of Dianchi Lake in China because of its extraordinary uptake of aqueous nitrogen and phosphorus and its ability to adsorb other hazardous compounds such as arsenic contaminants (Lin et al., 2012). It is also expected that recovery and concentration of the adsorbed metal ions from the saturated plant adsorbent can be done conveniently. This method could provide an ecologically friendly way to deal with eutrophic wastewater while recovering valuable heavy metals. Thus, this study aims to examine the adsorption behavior toward heavy metal ions, the mechanism of adsorption, and the adsorbent microstructure of long-root *E. crassipes* and subsequent recovery of the metal ions by combustion.

In this work, we prepared the root powder of long-root *E. crassipes* as the adsorbent, and we chose Cu^{2+} and Cr^{3+} as representative heavy metal ions. We began the experimental study by examining the adsorption of Cu^{2+} and Cr^{3+} as a function of pH and salt concentration, followed by a study of adsorption kinetics and isotherms.

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Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) were used to explore the interactions between the metal ions and the adsorbent. The adsorption of Cu^{2+} and Cr^{3+} was accompanied by the discharge of Ca^{2+} , Mg^{2+} , and K^{+} from the adsorbent, indicating an ion-exchange mechanism. A scanning electron microscopy (SEM) with a back-scattered electron detector (BSE) was used to determine the adsorption sites. We combusted the root powder of long-root *E. crassipes* saturated with adsorbed metal ions to confirm the effectiveness of the process in removing biomass while concentrating metal ions.

2. Materials and methods

2.1. Materials

The chemical reagents used in this work were of analytically pure grade. The heavy metal solutions were prepared by dissolving appropriate amounts of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ in deionized water. NaOH and HCl solutions were used to adjust the pH of the heavy metal solutions. Standard metal solutions with concentrations of 1000 mg/L purchased from the National Institute of Metrology (Beijing, China) were used to calibrate our flame atomic absorption spectroscope. All glassware was soaked in 10% HCl and washed with deionized water at least three times before use. The particle size of the adsorbent prepared from the root powder of long-root *E. crassipes* was 300–600 μm in diameter. The elemental contents of C, H, O, and N were 47.23%, 4.72%, 44.4%, and 1.98%, respectively.

2.2. Adsorption experiment

One gram of the adsorbent was added to a 100 mL aliquot containing the Cu^{2+} or Cr^{3+} solution at an appropriate pH and concentration in a 300 mL flask. The initial concentration of the metal was 100 mg/L. The flask was then placed in a BOD incubator shaker (Sky-111B, SuKun, China) at 30 °C with a rotation speed of 175 rpm. The supernatants were sampled at given time intervals. After filtering through a 0.45 μm membrane, we determined the concentrations of Cu^{2+} and Cr^{3+} using flame atomic absorption spectroscopy (FAAS; Z-5000, Hitachi, Japan). The wavelengths of heavy metal were 324.8 nm for Cu^{2+} and 357.9 nm for Cr^{3+} with operational currents of 5.0 mA and 7.5 mA, respectively. We interpreted the extent of adsorption according to the initial and final concentrations of the solution. The removal ratio (R) was then calculated using Eq. (1).

$$R = \frac{C_i - C_{eq}}{C_i} \times 100\% \quad (1)$$

Where C_i and C_{eq} are the initial and equilibrium concentrations of the solution, respectively. We performed adsorptions of Cu^{2+} and Cr^{3+} ions at different pH values from 1.0 to 7.0. We studied the effect of salt on the adsorption behavior at a pH of 5.0 with a NaCl concentration of 0–300 mmol/L. Each experiment was carried out in triplicate with deviation less than 5%.

2.3. Desorption experiment

The desorption of metal ions was carried out using 100 mL of elution buffer containing 0.2 M HCl, 0.2 M HNO_3 , 0.2 M H_2SO_4 , 0.2 M thiourea, 0.2 M HCl, and 0.2 M EDTA. During each run, the above solution was mixed with the adsorbent saturated with metal ions in a 300 mL flask. The flask was then placed in the BOD incubator shaker at 30 °C with a rotation speed of 175 rpm for 2 h. The solutions were filtered through a 0.45 μm membrane and the concentrations of metal ions were measured by FAAS as mentioned

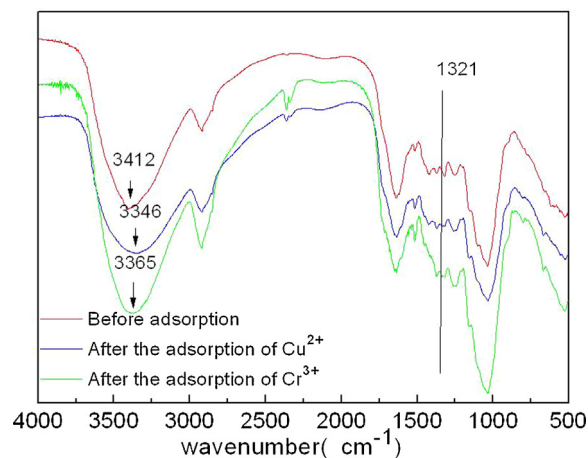


Fig. 1. FTIR spectra of the root powders before and after adsorption.

above, based on which the recovery yield was obtained. Each experiment was triplicate with deviation less than 5%.

2.4. Assays

We used FTIR (Nicoletis10, Thermo Scientific, USA), XPS (PHI-5300, Perkin-Elmer, USA), and SEM-BSE (JSM-6460LV Japan) to identify the major functional groups of the adsorbent and the sites responsible for the adsorption. We first added the root-powder adsorbents to the 300 mg/L metal solutions at a pH of 5.0. After the samples reached adsorption equilibrium, they were analyzed by FTIR, XPS, and SEM-BSE.

The concentrations of Ca^{2+} , Mg^{2+} , and K^{+} in solution were measured by FAAS before and after adsorption; one adsorbent washed with deionized water served as the control. For these experiments, 1 g of root powder was added into 100 mL of the metal solution (500 mg/L) at a pH of 5.0. The pH value of the solution was determined using a pH meter (SevenEasy, Mettler, Switzerland). The net release of cations (mM/g of adsorbent) was confirmed using a solution without metal ions as the control. After combustion, we used X-ray diffraction (XRD; D8-Advance, Bruker, Germany) and X-ray fluorescence (XRF; XRF-1800, Shimadzu, Japan) to determine the compositions of the residual materials.

3. Results and discussion

3.1. Characterization of the adsorption of Cu^{2+} and Cr^{3+}

FTIR and XPS, which have been extensively used to characterize adsorption of metal compounds (Altenor et al., 2009; Hartono et al., 2009; Wang et al., 2013), were used in this study to study the adsorbent. As shown in Fig. 1 and Table 1, after adsorption the $-\text{OH}$ peak shifted from 3412 cm^{-1} to around 3350 cm^{-1} . This shift could be caused by the formation of a complex between metal ions and the $-\text{OH}$ groups of the adsorbent. The peak at 1321 cm^{-1}

Table 1
List of peak shifts.

Peak	Associated functional group	Shift
Before adsorption 3412	After adsorption 3350	$-\text{OH}$ 62 ± 8
1321	disappeared	$-\text{COOH}$ –

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