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High-performance Cu^{2+} adsorption of birnessite using electrochemically controlled redox reactions

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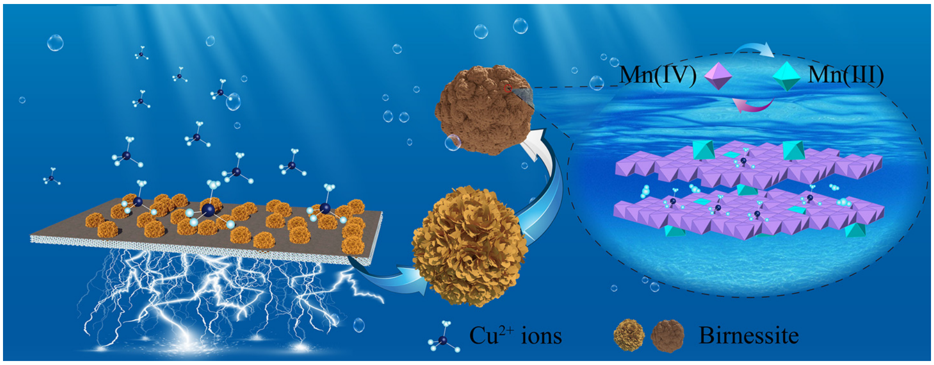
GRAPHICAL ABSTRACT



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ABSTRACT

Manganese oxides are proposed as superior adsorbents for heavy metal ions, and their adsorption capacities can be greatly improved by electrochemical methods. In this work, birnessite was used as electrode material for Cu^{2+} adsorption by multi-cycle electrochemical redox reaction. The effects of solution pH and potential window on Cu^{2+} electrosorption capacity were further investigated. The results showed that the electrosorption capacity for Cu^{2+} reached as high as 372.3 mg g^{-1} by electrochemical redox, which was remarkably larger than the adsorption isotherm capacity (44.3 mg g^{-1}). In addition, birnessite could be reused for many times after electrochemical activation. In the process of electrosorption, the amount of copper electrodeposited on the counter electrode accounted for less than 3.2% of the total removal capacity. The enhancement of Cu^{2+} adsorption capacity could be attributed to the changes in the chemical composition and the dissolution-recrystallization processes of birnessite during the electrochemical redox reactions. The electrosorption capacity increased with increasing pH from 3.0 to 5.0 and potential window width. The present work shows that controllable redox reaction of birnessite is a promising method for the removal of Cu^{2+} from wastewater.

1. Introduction

Heavy metal ions have aroused great public concern because of their characteristics of non-biodegradability, high toxicity and large possibility to accumulate in living organisms [1]. Copper is an essential trace element for health. However, an excess of copper in the body can lead to various diseases. The maximum concentration recommended by the World Health Organization (WHO) for Cu^{2+} in drinking water is

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0.05 mg L^{-1} [2,3]. A great quantity of copper-containing wastewater is discharged from the industrial processes such as mining, plating and metallurgy [3–5]. Therefore, it is crucial to develop effective measures to remove Cu^{2+} from effluent. Various treatment technologies have been utilized to remove Cu^{2+} from aqueous solutions, such as adsorption, chemical precipitation, ion-exchange and membrane filtration [6–9]. Among them, adsorption techniques have received wide attention for its advantages of easy operation and economic feasibility [10–12].

Manganese oxides are promising candidates for the adsorption of heavy metal ions due to their characteristics of environmental friendliness, abundant reserves, and economic viability [13–17]. The surface properties and chemical composition of manganese oxides affect their adsorption performance for heavy metal ions. For example, the adsorption capacities for Cu^{2+} follow the order of birnessite > todorokite ≈ hausmannite > cryptomelane, which is closely related to their surface charges [18]. In addition, the adsorption capacities for heavy metal ions increase with increasing manganese average oxidation state (Mn AOS) in birnessite [19]. More interlayer negative charges and hydroxyl groups of co-doped birnessite result in the higher adsorption capacity for Pb^{2+} [20]. The types of cations in layered manganese oxides affect the adsorption capacity. For example, the Pb^{2+} adsorption capacities of *K*-birnessite and *H*-birnessite were estimated to be 164.3 and 133.2 mg g^{-1}, respectively [14]. Hence, the adsorption capacity of manganese oxides can be enhanced by adjusting the surface properties and chemical composition.

Electrochemical methods can efficiently alter the micromorphology and crystal structure of manganese oxides. During charge–discharge in Cd^{2+} solution, the dissolution–recrystallization processes led to the disappearance of flower-like morphology, and increased the effective adsorption area, resulting in enhanced Cd^{2+} adsorption capacity of birnessite [21]. Birnessite was transformed into Zn-buserite during charge–discharge in Zn^{2+} solution, and was transformed into hausmannite (Mn_3O_4) and hetaerolite ($ZnMn_2O_4$) during constant potential electrolysis in Zn^{2+} and Ni^{2+} solutions, respectively [22,23]. Recently, manganese oxides have been widely used in electrochemical adsorption for Na^{+} and heavy metal ions. But the superior adsorption capacities were traditionally attributed to the electrostatic interaction or chemisorption of oxygenic groups [24–26]. In fact, manganese oxides exhibit excellent electrochemical redox activity when used as electrode materials in batteries and supercapacitors [27]. The redox of manganese oxides during the electrosorption process may contribute much to the adsorption performance. In the process of Na^{+} removal, the electrosorption capacity driven simultaneously by electrostatic interaction and redox process is about 1.6-fold higher than that driven by single electrostatic interaction [28]. Thus, the critical role of redox in the electrosorption of manganese oxides for heavy metal ions has been underestimated.

There are many Mn(IV) vacancies in the MnO_6 octahedral layer of birnessite and heavy metal ions can be adsorbed above or below these vacancy sites [29,30]. Hence, birnessite is a suitable material for the adsorption of heavy metals ions by electrochemical methods. In our previous work, the electrosorption capacities of birnessite for Cd^{2+} and Zn^{2+} reached 900.7 and 530.0 mg g^{-1}, respectively [21,22]. Reproducibility is important to electrosorption materials. Despite the excellent capacities, the electrosorption causes a greater release of Mn^{2+} into the solution and a rapid decay of the adsorption capacities. Therefore, further studies are needed to improve the reusability of birnessite electrodes. In addition, it should be noticed that Cu^{2+} is readily reduced in an electrochemical adsorption procedure owing to its higher standard reduction potential (0.1 V *vs.* SCE). When the applied voltage was controlled at 1.2 V, elemental Cu was formed on the surface of activated carbon electrodes in 50 mg L^{-1} Cu^{2+} solution [31]. The electrochemical reduction process of Cu^{2+} hampers the regeneration of electrode materials and leads to the increased energy consumption. However, little attention has been paid to the optimization of electrosorption conditions for copper removal.

In this work, the Cu^{2+} adsorption capacity was improved by the electrochemical redox of birnessite. The electrochemical adsorption mechanism was analyzed by power X-ray diffractometer (XRD), field emission scanning electron microscopy (FESEM), X-ray absorption fine structure (XAFS) and X-ray photoelectron spectroscopy (XPS). The influence of potential window width and initial pH on the Cu^{2+} electrosorption capacity of birnessite was further investigated.

2. Experimental section

2.1. Sample preparation

Birnessite was prepared from the reduction of a boiling solution of $KMnO_4$ by concentrated hydrochloric acid [32]. The preparation process is described in Supporting Information (S1). The preparation of birnessite electrodes is described in Supporting Information (S2). The birnessite of 10 mg was used in the working electrode. Cu-containing wastewater was prepared by dissolving $CuSO_4{\cdot}5H_2O$ in 0.1 mol L^{-1} Na_2SO_4. The initial concentration of Cu^{2+} was controlled within 200–2600 mg L^{-1}. The initial pH of the wastewater was adjusted to 3.0–5.0 using 0.1 mol L^{-1} H_2SO_4 or NaOH. All reagents used in this experiment were of analytical grade, which were purchased from China National Medicine Group Shanghai Chemical Reagent Company.

2.2. Electrosorption of Cu^{2+}

The electrosorption of birnessite for Cu^{2+} was conducted in a three-electrode cell at room temperature. The birnessite electrode was used as working electrode, and pure carbon fabric and a saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. The volume of wastewater in the electrochemical system was 30 mL. The electrosorption of Cu^{2+} was performed by galvanostatic charge–discharge at a current density of 0.1 A g^{-1} using a battery testing system (CT-3008W-5V5mA-S4, Shenzhen Neware Electronic Ltd., China). The initial concentration of Cu^{2+} was controlled within 200–2600 mg L^{-1} to investigate the electrosorption capacity of the birnessite for Cu^{2+} within the potential window of 0.4–0.9 V (*vs.* SCE), and the initial pH of solution was adjusted to 4.0 to avoid the precipitation of copper hydroxide ($K_{sp} = 2.2 \times 10^{-20}$, at 25 °C). The tests of influencing factors including pH and potential windows on the electrochemical adsorption capacity were carried out with the initial Cu^{2+} concentration of 200 mg L^{-1}. The potential windows were controlled within 0–0.9, 0.2–0.9, 0.4–0.9, and 0.6–0.9 V (*vs.* SCE) to study the effect of potential window on electrosorption capacity with initial pH 4.0. The influence of initial pH on electrosorption capacity was studied within pH 3.0–5.0. Each electrosorption experiment was performed three times and the mean was recorded. The Cu^{2+} electrosorption capacity was calculated according to the change of Cu^{2+} concentration in solutions.

The adsorption isotherms of Cu^{2+} on the synthesized birnessite were conducted. The details of the isothermal adsorption experiment are presented in Supporting Information (S3). The result was compared with that of electrochemical adsorption.

2.3. Analytical methods

The crystal structure of the samples was characterized by XRD (Bruker D8 ADVANCE, Cu Kα, $\lambda = 0.15406$ nm) at a tube voltage of 40 kV and a scanning rate of 1° min^{-1}. FESEM (Hitachi, SU8000) was used for micromorphology analyses and the energy dispersive spectrum (EDS) of the electrodes were measured. The BET specific surface area and pore volume of the sample were measured by N_2 adsorption–desorption isotherms (Micromeritics ASAP 2020). Mn AOS in birnessite was determined by XAFS spectroscopy (collected on the 1W1B beamline at the Beijing Synchrotron Radiation Facility, China)