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## Preparation of a manganese dioxide/carbon fiber electrode for electrosorptive removal of copper ions from water



Chengzhi Hu, Fangyuan Liu, Huachun Lan, Huijuan Liu\*, Jiuhui Qu

Key Laboratory of Drinking Water Science and Technology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

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## ABSTRACT

MnO<sub>2</sub> is an effective adsorbent for many metal ions and a promising electrode material for electrochemical supercapacitors. In this paper, we successfully combined the two functions through preparing a MnO<sub>2</sub>/carbon fiber (CF) composite as an electrosorptive electrode. The thin MnO<sub>2</sub> film was deposited onto CF by an anodic electrodeposition method. The MnO<sub>2</sub>/CF electrodes had ideal pseudocapacitive behavior and high capacitive reversibility. The specific capacitance of the MnO<sub>2</sub>/CF electrode reached a maximum value of 387 F/g, which is quite competitive compared with literature values. At 0.8 V applied potential, the maximum Cu<sup>2+</sup> adsorption capacity of the MnO<sub>2</sub>/CF electrode was 172.88 mg/g, which is more than 2 times higher than common MnO<sub>2</sub> adsorbents without an electric field imposed. SEM images showed that MnO<sub>2</sub> nanoflowers with several “petals” were uniformly distributed on the CF surface. Enhancement of adsorption by the polarization potential and the unique microstructure of the deposited MnO<sub>2</sub> may be the source of the outstanding adsorption ability of the MnO<sub>2</sub>/CF electrode. The MnO<sub>2</sub>/CF electrode could be regenerated quickly by reversing the voltage. The deposition time of 1000 s was optimum for achieving maximum capacitance and Cu<sup>2+</sup> removal performance. The MnO<sub>2</sub>/CF composite electrosorptive electrode is a promising candidate for Cu<sup>2+</sup> removal from aqueous solution.

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### 1. Introduction

Electrosorption is a separation technology combining adsorption and electrochemical methods, used to remove ionic contaminants such as salt ions [1,2], heavy metal ions [3–6], anions [7], and organics [8,9] from water, and has received extensive attention and support due to its advantages of both waste minimization and reduced processing costs. It has been generally defined as potential-induced adsorption on the surface of charged electrodes. During the electrosorption process, ionic contaminants in the aqueous solution will move towards the oppositely charged electrode under the imposed electric field, and withdraw back to the solution if the electric field is removed or reversed. The working principle of electrosorption is similar to that of an electrochemical capacitor. It has been believed that the physical properties and structure of the electrode materials dominate their electrosorptive performance [10,11]. Various forms of carbon are the most widely

used electrode materials for electrosorption technology [5,10,12] and electrochemical capacitors [13,14].

Manganese dioxide (MnO<sub>2</sub>) is a one of the most important scavengers of trace metals in the environment, and has been extensively studied as an effective adsorbent to remove heavy metals from water [15–17]. Apart from its excellent heavy metal uptake capacity, MnO<sub>2</sub> is a promising electrode material for electrochemical supercapacitors because of its high specific capacitance, good cycle stability, low cost, eco-friendly nature and abundant availability [18,19]. MnO<sub>2</sub> possesses a large theoretical capacitance value (1370 F/g), which significantly exceeds those of carbon-based materials, resulting in great interest in the development of MnO<sub>2</sub>-based materials as electrochemical supercapacitor electrodes. However, the capacitance of MnO<sub>2</sub> electrodes is ultimately limited by poor electrical conductivity. A way to overcome this drawback is to deposit a thin MnO<sub>2</sub> layer on the surface of carbon materials such as carbon nanofiber [20], carbon cloth [21], carbon nanotubes [22], carbon aerogel [23], and graphene [24].

MnO<sub>2</sub>/carbon composite materials have also shown great adsorption ability for the removal of heavy metal ions from waste water [16,25,26]. Therefore, MnO<sub>2</sub> is not only an effective adsor-

\* Corresponding author. Fax: +86 10 62849160.

E-mail address: hjliu@rcees.ac.cn (H. Liu).

bent for many metal ions but also a promising electrode material for electrochemical supercapacitors. Recently, some researchers [11,27] synthesized MnO<sub>2</sub>/nanoporous carbon and MnO<sub>2</sub>/graphene composites and successfully used them as electrodes in electro-sorptive desalination. However, no previous study has combined the two properties and used MnO<sub>2</sub>/carbon composite materials as electrodes to remove metal ions through the electrosorption process. MnO<sub>2</sub>/carbon composite materials show great potential as electrodes for the electrosorptive removal of heavy metal ions from water.

In the present study, a simple and cost-effective electroplating approach was used to directly deposit a thin MnO<sub>2</sub> layer on the surface of carbon fiber (CF). The surface morphology, structure and capacitive properties of the prepared MnO<sub>2</sub>/CF electrode based on deposited MnO<sub>2</sub> were characterized. We evaluated the electrosorptive performance of the MnO<sub>2</sub>/CF electrode on Cu<sup>2+</sup> removal. The effect of MnO<sub>2</sub> mass loading, cell voltage, and pH on Cu<sup>2+</sup> removal by the electrosorptive electrode were also examined.

## 2. Materials and methods

### 2.1. Preparation of the MnO<sub>2</sub>/CF electrode

A commercially available CF (A090, TORAY, Japan) was used as the supporting material for MnO<sub>2</sub>. MnO<sub>2</sub> was electrodeposited onto CF by the galvanostatic method with a three-electrode setup, where CF, graphite and Hg/HgCl<sub>2</sub> were used as working electrode, counter electrode and reference electrode, respectively. An aqueous precursor solution with 0.1 mol/L MnSO<sub>4</sub> and 0.01 mol/L H<sub>2</sub>SO<sub>4</sub> was used as the electrolyte, and the deposition was performed at a constant current of 0.5 mA/cm<sup>2</sup>. The MnO<sub>2</sub> mass loading was controlled by varying the deposition time from 0 to 7200 s, and was evaluated by calculating the weight difference of the working electrodes. To ensure that the deposition of MnO<sub>2</sub> took place uniformly and firmly on the CF surface, the CF was treated with 5% HNO<sub>3</sub> solution at 80 °C for 30 min before the deposition. Typically, the area of the working electrode was 3 × 2 cm<sup>2</sup>. After the deposition, the working electrodes were washed with distilled water and then dried at 105 °C for 5 h.

### 2.2. Materials characterization

The surface morphology of the MnO<sub>2</sub>/CF electrodes was examined using an ultra-high resolution field emission scanning electron microscopy (FE-SEM, SU 8020, Hitachi, Japan). The crystal structure of the MnO<sub>2</sub>/CF electrodes and CF was determined by an X-ray powder diffractometer (X'Pert PRO MPD, PANalytical, Netherland) with copper K $\alpha$  radiation. The XRD patterns of the samples were recorded between 10° and 80° (2 $\theta$ ) at a scan step size of 0.026°, and a time per step of 58.14 s. Chemical state analysis of the deposited MnO<sub>2</sub> was carried out by X-ray photoelectron spectroscopy (XPS) using an ESCALAB 250 X-ray photoelectron spectrometer. All XPS spectra were corrected using the C 1s line at 284.6 eV, to investigate the components of the as-prepared samples and the valence of Mn.

### 2.3. Electrochemical evaluation

Electrochemical characteristics of the MnO<sub>2</sub>/CF electrodes prepared at different deposition periods were evaluated by using cyclic voltammetry (CV) and galvanostatic charge/discharge methods with a CHI660C electrochemical workstation (ChenHua, China) at ambient temperature. All electrochemical measurements were carried out in 1 M Na<sub>2</sub>SO<sub>4</sub> aqueous electrolyte solutions. CV was performed at scanning rates of 5 mV/s and 50 mV/s with a poten-

tial window from 0 to 1.0 V. Galvanostatic charge/discharge tests were measured at a current density of 0.1 A/g. The specific capacitance (C, F/g) was calculated according to the following equation (Eq. (1)) [11,21]:

$$C = \frac{I\Delta t}{m\Delta V} \quad (1)$$

where  $m$  (g) is the mass of MnO<sub>2</sub> loaded,  $\Delta V$  (V) is the potential window,  $I$  (A) is the charge–discharge current, and  $\Delta t$  (s) is the charge–discharge time.

### 2.4. Performance of Cu<sup>2+</sup> removal by electrosorption

A schematic diagram of the static state electrosorption system is shown in Fig. 1. The experimental apparatus included an electrosorption tank, a pH meter, and a DC power supply. The working electrode was two MnO<sub>2</sub>/CF electrodes as cathodes, and three pieces of CF sheet were used as anodes for the opposite electrode. The distance between each anode/cathode pair was 5 mm. In each experiment, the total solution volume was 200 mL. All experiments were performed with Cu(NO<sub>3</sub>)<sub>2</sub> solutions. The Cu<sup>2+</sup> removal was performed with a constant voltage of –0.8 V. 2 mL samples were withdrawn at predetermined time intervals to determine the Cu<sup>2+</sup> concentration using an ICP-OES instrument (P700 series, Agilent, USA). The solution pH was continuously monitored with a pH meter (UB-7, Denver, USA) and adjusted using NaOH or HCl solution.

Electrosorptive experiments with MnO<sub>2</sub>/CF electrodes prepared at different deposition times, which yielded different MnO<sub>2</sub> mass loadings, was carried out at a constant initial Cu<sup>2+</sup> concentration of 6 mg/L with the above apparatus. The amount of Cu<sup>2+</sup> adsorbed on the MnO<sub>2</sub>/CF electrodes at electro-adsorption equilibrium was calculated according to Eq. (2):

$$q_t = \frac{(C_0 - C_e)V}{m} \quad (2)$$

where  $q_t$  (mg/g) is the amount of Cu<sup>2+</sup> adsorbed on the MnO<sub>2</sub>/CF electrode at time  $t$  (min);  $C_0$  and  $C_e$  (mg/L) are the initial and equilibrium concentrations of Cu<sup>2+</sup> in the solution, respectively;  $V$  (L) is the volume of the solution;  $m$  (g) is the amount of MnO<sub>2</sub> loaded onto the composite electrode.

Langmuir and Freundlich isotherms [4] were used to validate the experimental data for the electrosorption of Cu<sup>2+</sup>. Kinetic experiments were performed to determine the rate of Cu<sup>2+</sup> ion removal from the water by the MnO<sub>2</sub>/CF electrodes. A pseudo-first order (Lagergren's equation) kinetic model was employed to fit the experimental data [10].

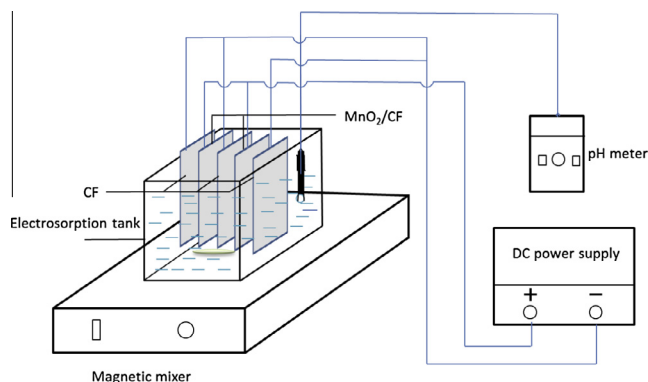


Fig. 1. Schematic diagram of static adsorption/electrosorption apparatus.

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