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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

MnO₂ 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 MnO₂/carbon fiber (CF) composite as an electrosorptive electrode. The thin MnO₂ film was deposited onto CF by an anodic electrodeposition method. The MnO₂/CF electrodes had ideal pseudocapacitive behavior and high capacitive reversibility. The specific capacitance of the MnO₂/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 Cu²⁺ adsorption capacity of the MnO₂/CF electrode was 172.88 mg/g, which is more than 2 times higher than common MnO₂ adsorbents without an electric field imposed. SEM images showed that MnO₂ 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 MnO₂ may be the source of the outstanding adsorption ability of the MnO₂/CF electrode. The MnO₂/CF electrode could be regenerated quickly by reversing the voltage. The deposition time of 1000 s was optimum for achieving maximum capacitance and Cu²⁺ removal performance. The MnO₂/CF composite electrosorptive electrode is a promising candidate for Cu²⁺ 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 (MnO₂) 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, MnO₂ 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]. MnO₂ 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 MnO₂-based materials as electrochemical supercapacitor electrodes. However, the capacitance of MnO₂ electrodes is ultimately limited by poor electrical conductivity. A way to overcome this drawback is to deposit a thin MnO₂ layer on the surface of carbon materials such as carbon nanofiber [20], carbon cloth [21], carbon nanotubes [22], carbon aerogel [23], and graphene [24].

MnO₂/carbon composite materials have also shown great adsorption ability for the removal of heavy metal ions from waste water [16,25,26]. Therefore, MnO₂ 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 MnO₂/nanoporous carbon and MnO₂/graphene composites and successfully used them as electrodes in electrosorptive desalination. However, no previous study has combined the two properties and used MnO₂/carbon composite materials as electrodes to remove metal ions through the electrosorption process. MnO₂/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 MnO₂ layer on the surface of carbon fiber (CF). The surface morphology, structure and capacitive properties of the prepared MnO₂/CF electrode based on deposited MnO₂ were characterized. We evaluated the electrosorptive performance of the MnO₂/CF electrode on Cu²⁺ removal. The effect of MnO₂ mass loading, cell voltage, and pH on Cu²⁺ removal by the electrosorptive electrode were also examined.

2. Materials and methods

2.1. Preparation of the MnO₂/CF electrode

A commercially available CF (A090, TORAY, Japan) was used as the supporting material for MnO₂. MnO₂ was electrodeposited onto CF by the galvanostatic method with a three-electrode setup, where CF, graphite and Hg/HgCl₂ were used as working electrode, counter electrode and reference electrode, respectively. An aqueous precursor solution with 0.1 mol/L MnSO₄ and 0.01 mol/L H₂SO₄ was used as the electrolyte, and the deposition was performed at a constant current of 0.5 mA/cm². The MnO₂ 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 MnO₂ took place uniformly and firmly on the CF surface, the CF was treated with 5% HNO₃ solution at 80 °C for 30 min before the deposition. Typically, the area of the working electrode was 3 × 2 cm². 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 MnO₂/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 MnO₂/CF electrodes and CF was determined by an X-ray powder diffractometer (X'Pert PRO MPD, PANalytical, Netherland) with copper K α radiation. The XRD patterns of the samples were recorded between 10° and 80° (2 θ) at a scan step size of 0.026°, and a time per step of 58.14 s. Chemical state analysis of the deposited MnO₂ 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 MnO₂/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 Na₂SO₄ 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 MnO₂ loaded, ΔV (V) is the potential window, *I* (A) is the charge–discharge current, and Δt (s) is the charge–discharge time.

2.4. Performance of Cu²⁺ 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 MnO₂/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(NO₃)₂ solutions. The Cu²⁺ removal was performed with a constant voltage of −0.8 V. 2 mL samples were withdrawn at predetermined time intervals to determine the Cu²⁺ 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 MnO₂/CF electrodes prepared at different deposition times, which yielded different MnO₂ mass loadings, was carried out at a constant initial Cu²⁺ concentration of 6 mg/L with the above apparatus. The amount of Cu²⁺ adsorbed on the MnO₂/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 Cu²⁺ adsorbed on the MnO₂/CF electrode at time *t* (min); *C₀* and *C_e* (mg/L) are the initial and equilibrium concentrations of Cu²⁺ in the solution, respectively; *V* (L) is the volume of the solution; *m* (g) is the amount of MnO₂ loaded onto the composite electrode.

Langmuir and Freundlich isotherms [4] were used to validate the experimental data for the electrosorption of Cu²⁺. Kinetic experiments were performed to determine the rate of Cu²⁺ ion removal from the water by the MnO₂/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.

3. Results and discussions

3.1. Morphological and structural characterization

Fig. 2 presents the SEM images of CF and the MnO_2/CF electrode with deposition time of 1000 s. It can be seen that the smooth surface of CF (Fig. 2a) had been uniformly covered by a clustered substance with the size about 200 nm. The EDX results (Fig. 2e and f) show that the surface composition of the electrochemically deposited electrodes was composed of the elements C, O and Mn, which confirmed that the nano-clusters were manganese oxides. As shown in Fig. 2c, each nano-cluster was comprised of irregular sheets to form a petal-like nanostructure. These nano-sized MnO_2 clusters exhibited microporous architectures. The clusters appeared to consist of irregular sheets with thickness of a few nm and width of about 100 nm, which is in accordance with the result of Chen et al. [21]. Such a microstructure ensures outstanding performance in the intercalation/deintercalation of electrolyte cations into electrode materials, and we therefore expect high performance electrosorption.

Fig. 3 shows the XRD patterns for MnO_2/CF electrodes with deposition time of 1000 s and 7200 s, as well as that of CF. For all samples, two diffraction peaks appearing around 26° and 55° are associated with graphitic carbon. Magnifying the XRD patterns (inset of Fig. 3a), a weak peak at around 37° that can be assigned to the diffraction peak of birnessite MnO_2 (JCPDE 18-0802) can be observed for the two MnO_2/CF electrodes. The peak intensity increased with the increase of deposition time, which is a result of the increased amount of MnO_2 deposited onto CF with longer deposition time. Overall, XRD patterns of the MnO_2/CF electrodes indicated an amorphous structure for the manganese oxide in the composite. This also contributes to the large surface area of the MnO_2/CF electrodes. As shown in Fig. 4a, the Mn $2p_{3/2}$ peak is centered at 642.1 eV and Mn $2p_{1/2}$ peak at 653.8 eV, with a spin-energy separation of 11.7 eV, in good agreement with the reported data for Mn $2p_{3/2}$ and Mn $2p_{1/2}$ in MnO_2 . The O 1s spectrum was

deconvoluted into three constituents, corresponding to oxygen in the Mn—O—Mn bond (529 eV) of the tetravalent oxide, Mn—O—H bond (531 eV) of Mn hydroxide, and H—O—H bond (532 eV) of water (Fig. 4b). These results are consistent with the XRD analysis as mentioned above.

3.2. Electrochemical properties

The CV responses of the MnO_2/CF electrodes prepared with various deposition times are shown in Fig. 5, at the specific scan rates of 5 mV/s and 50 mV/s, respectively. All CV curves in Fig. 5a have a relatively symmetrical rectangular shape. When the scan rate changed from 5 mV/s to 50 mV/s (Fig. 5b), the CV shapes remained almost rectangular, with only a few deviations for the samples with large deposition time. The anodic and cathodic regimes are essentially mirror-images of each other. The results indicate that the prepared MnO_2/CF electrodes exhibited ideal pseudocapacitive behavior. The areas enclosed under the CV curves correspond to the energy storage capability of the electrode material. The voltammetric current response increased with the increase of deposition time and was directly proportional to the MnO_2 mass loading on the CF substrates. The results in Fig. 5 suggest that the capacitance of CF was improved by depositing MnO_2 , and high MnO_2 content in the composite electrode contributed to higher charge storage.

The charge/discharge curves of the MnO_2/CF electrodes prepared with different deposition times at a fixed current density of 0.1 A/g are shown in Fig. 6a. The anodic charging segments were generally symmetric to their corresponding cathodic discharging counterparts for all the samples, indicating high reversibility typical of a capacitive material. In addition, the MnO_2/CF electrodes had an increase of discharge time with increasing deposition time. This ideal electrochemical capacity behavior was also confirmed by the results shown in Fig. 6a. The specific capacitances for the MnO_2/CF electrodes were calculated from the charge/discharge curves based on the MnO_2 mass loading. As shown in Fig. 6b, the capacitances increased with the MnO_2 mass loading for deposition

Fig. 2. SEM images of (a) CF and the MnO_2/CF electrode prepared with deposition time of 1000 s at different magnifications: (b) $\times 11$ K, (c) $\times 18$ K, (d) $\times 150$ K; EDX analysis on the marked square area of (e) CF and the (f) MnO_2/CF electrode with deposition time of 1000 s.

Fig. 3. XRD pattern of CF (blank) and MnO₂/CF electrodes with deposition times of 1000 s and 7200 s.

Fig. 4. XPS spectra of (a) Mn 2p core level and (b) O 1s core level for MnO₂/CF electrode with deposition time of 1000 s.

times up to 1000 s. The capacitances decreased for deposition times exceeding 1000 s, which is mainly due to aggregation of the MnO₂ nanosheets and the limited conductivity of the high mass loading samples [21,22]. The maximal capacitance attained in this study was as high as 387 F/g, which is quite competitive with literature values [20]. Thus, the deposition time of 1000 s was optimum for achieving maximum capacitance and acceptable characteristics for application as an electro-sorptive electrode.

3.3. Electro-sorptive performance in Cu²⁺ removal

Fig. 7 displays both the experimental and modeled electro-sorption isotherms of Cu²⁺ on the MnO₂/CF electrode at pH 5. The experimental data were fitted to the well-known Langmuir and Freundlich isotherm models. The weight of deposited MnO₂, which is the active component in the composite electrodes, was used as the mass of adsorbent. The estimated isotherm parameters from these

Fig. 5. Cyclic voltammograms of MnO₂/CF electrodes prepared with different deposition times at scan rates of (a) 5 mV/s and (b) 50 mV/s.

model fits are summarized in Table 1. It was found that the electro-sorption isotherms were consistent with both Langmuir and Freundlich models. At applied potential of -0.8 V, the maximum adsorption capacity of the MnO₂/CF electrode was 172.88 mg/g, which is considerably higher than 56.62 and 24.57 mg/g, the reported electro-sorptive Cu²⁺ uptake capacities of ordered mesoporous carbon [10] and activated carbon electrodes [6], respectively. The maximum adsorption capacity of Cu²⁺ with this composite electrode based on the MnO₂ loading is 2.2 times higher than that [28] of MnO₂ absorbent without an electric field imposed. This should be ascribed to the enhanced adsorption by the polarization potential and the unique microstructure of the nano-MnO₂ generated by the electro-deposition method.

Fig. 8 shows the Cu²⁺ electro-sorption kinetic data fitted with pseudo-first-order equations. The simulated parameters are listed in Table 2. The electro-sorption process could be divided into two steps, a quick step and a slow one. In the first step, the electro-sorption rate was fast, and over 85% of the equilibrium adsorption capacity was achieved within 8 h. In the subsequent step, the adsorption was slow. After 12 h, over 96% of the maximum adsorption had taken place, thus 24 h was an adequate time for equilibration to occur. The deposition time influenced the rate of Cu²⁺ removal by electro-sorption on the MnO₂/CF electrode. The electro-sorption rate of the MnO₂/CF electrode with deposition time of near 1000 s was higher than that with lower (300 s) or greater (5000 s) deposition time. A pseudo-first-order kinetics equation could represent the Cu²⁺ electro-sorption kinetic data well, as evident from the high coefficient of determination (R^2) value.

To examine the regeneration of the MnO₂/CF electrode, an electro-sorption/desorption experiment was conducted at the initial Cu²⁺ concentration of 5.6 mg/L. After 24 h running at -0.8 V, an opposite cell voltage of 0.8 V was applied in order to desorb the Cu²⁺. As shown in Fig. 9, the adsorbed 4.6 mg/L Cu²⁺ was released from the electrode surfaces back to the solution under the effect of

Fig. 6. (a) Galvanostatic charge/discharge curves at the current density of 0.1 A/g; (b) specific capacitances of MnO₂/CF electrodes and MnO₂ mass loading at different deposition times.

Fig. 7. Electro sorption isotherms of Cu²⁺ ions on the MnO₂/CF electrode with Langmuir and Freundlich model correlations. pH = 5. Applied voltage = -0.8 V.

Table 1

Parameters of Langmuir and Freundlich isotherms for Cu²⁺ electro sorption on the MnO₂/CF electrode at pH 5 and -0.8 V applied voltage.

Freundlich			Langmuir		
K_F (mg ^{1-1/n} L ^{1/n} /g)	n	R^2	q_m (mg/g)	b (L/mg)	R^2
104.56	2.13	0.95	172.88	1.73	0.96

reversed voltage, and the Cu²⁺ recovered in the solution only returned to about 82% of the adsorbed Cu²⁺, with the difference corresponding to the equilibrium state of chemisorption. This result implies that Cu²⁺ ions have a strong affinity for MnO₂ [17,28], and also indicates that most Cu²⁺ ions were electroad-

Fig. 8. Effect of contact time on Cu²⁺ electro sorption by MnO₂/CF electrodes and fitting plots using the pseudo-first-order equation for -0.8 V applied voltage and pH 5. (Symbols) experimental data; (—) pseudo-first-order model fitting.

sorbed by forming an electrical double-layer within the MnO₂/CF electrode. The regeneration of the MnO₂/CF electrode can be achieved by applying reversed voltage.

3.4. Parameter optimization for Cu²⁺ removal

The Cu²⁺ electro sorption removal efficiency was studied using MnO₂/CF electrodes prepared under different deposition times. As shown in Fig. 10a, longer deposition time favored Cu²⁺ removal. The Cu²⁺ removal efficiency of CF via electro sorption was significantly enhanced after loading MnO₂ onto the electrodes. The Cu²⁺ removal efficiency of the MnO₂/CF electrode prepared with deposition time of 1000 s was twice as high as that of CF and approximately half that of the MnO₂/CF electrode prepared with deposition time of 3600 s. This result could be explained by the greater mass of MnO₂ loaded on CF with longer deposition time, which could provide the composite electrodes with higher capacitance. The concentration of the released Mn²⁺ from the electrode was measured during the electro sorption process. It was very low (up to 0.3 mg/L) and just accounted for 0.9% of the loaded MnO₂ for the electrode with deposition time of 1000 s. Thus the release of Mn²⁺ had little influence on the electro sorptive ability of the MnO₂/CF electrode.

Fig. 10b shows the Cu²⁺ removal by MnO₂/CF electrodes at five different applied voltages. It was found that the Cu²⁺ removal efficiency increased from 43% to 90% after about 720 min electro sorption, as the voltage shifted from 0 to 1.0 V. As expected, the greater the cell voltage applied, the higher the Cu²⁺ removal efficiency that could be achieved. It is believed that the flow velocity of electrons is promoted and the electrostatic attraction becomes stronger with increasing applied voltage, resulting in an increase in Cu²⁺ removal. It indicated that, for the electro sorption process of 1.0 V, about 50% of removed Cu²⁺ could be attributed to the adsorption onto the electrode material rather than the effect of electric field. The own adsorption to Cu²⁺ due to the electrode microstructure contributed at least half the electro sorptive capacity.

The effect of solution pH on Cu²⁺ removal was investigated with solution pH adjusted to 3, 4, 5 and 6. As shown in Fig. 10c, the Cu²⁺ removal efficiency increased with increasing pH value. This result could be ascribed the competitive advantage of Cu²⁺ compared with H₃O⁺ at high solution pH, where the H₃O⁺ concentration is relatively lower. In addition, generally, the surface potential of MnO₂ loaded on CF is more negative at high solution pH, which could lead to a greater electrostatic attraction between Cu²⁺ and MnO₂.

Table 2
Parameters of pseudo-first-order kinetic model for Cu^{2+} electrosorption on MnO_2/CF electrodes prepared with different deposition times under -0.8 V applied voltage and pH 5.

Pseudo-first-order rate parameters	Deposition time				
	300 s	500 s	1000 s	2000 s	5000 s
q_e (mg/g)	123.83	123.97	145.42	105.81	88.35
K_1 (1/h)	0.15	0.29	0.25	0.28	0.17
R^2	0.95	0.96	0.99	0.98	0.99

Fig. 9. Electrosorption/desorption profiles of MnO_2/CF electrodes at pH 5.

Fig. 10. Effect of (a) deposition time, (b) applied voltage and (c) solution pH on Cu^{2+} removal by the MnO_2/CF electrode. The general experimental conditions of deposition time, applied voltage and solution pH were 1000 s, -0.8 V and pH 5, respectively.

4. Conclusions

A MnO_2/CF electrode has been successfully synthesized by an anodic electrodeposition method for application in electrosorption. MnO_2 nanoflowers with several “petals” were found to be distributed uniformly on the CF surface. The specific capacitance of the MnO_2/CF electrode based on MnO_2 reached a maximum value of 387 F/g at the current density of 0.1 A/g. With 0.8 V applied potential, the maximum Cu^{2+} adsorption capacity of the MnO_2/CF electrode was 172.88 mg/g, which is more than two times higher than common MnO_2 absorbent without an electric field imposed. Enhancement of adsorption by the polarization potential and the unique microstructure of the deposited MnO_2 may equally contribute the outstanding adsorption ability of the MnO_2/CF electrode. A pseudo-first-order kinetics equation could represent the Cu^{2+} electrosorption kinetic data well. The MnO_2/CF electrode could be regenerated quickly by applying a reversed voltage. The deposition time of 1000 s was optimum for achieving maximum capacitance and Cu^{2+} removal performance. The Cu^{2+} removal efficiency by electrosorption with the MnO_2/CF electrode was positively correlated to applied voltage and solution pH. The efficiency of heavy metal removal by the MnO_2/CF electrode needs to be further evaluated in practical wastewater.

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