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Preparation of dumbbell manganese dioxide/gelatin composites and their application in the removal of lead and cadmium ions

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ABSTRACT

The nano-sized sorbents restrict their practical application in flow-through system due to excessive pressure. In this study, dumbbell MnO_2/gelatin composites were synthesized based on the protein-assisted synthesis technology. Then they were immobilized on the amino-modified polymethyl methacrylate (PMMA) plate. SEM, TEM, XRD, XPS and FT-IR were employed to study the surface properties and the adsorption mechanism of MnO_2/gelatin composites. Adsorption experiments for Pb(II) and Cd(II) ions were performed to study the adsorption isotherms, kinetics, and thermodynamics as well as the influencing factors. The maximum adsorption capacities of Pb(II) and Cd(II) ions were 318.7 mg g^{-1} and 105.1 mg g^{-1} respectively. The adsorption process met the pseudo-second-order kinetic model. Subsequently, MnO_2/gelatin composites modified plates were used to remove the heavy metal ions in surface water and wastewater samples. The removal efficiencies of Pb(II) ion was changed from 83% (wastewater) to 100% (surface water), when the initial concentration was 10 mg L^{-1}. This device exhibited great application prospect in the removal of heavy metals taking advantage of its high removal efficiency, excellent stability and reusability and ease of operation.

1. Introduction

Water pollution caused by the environmental release of heavy metals has raised public concern in the world. The toxic effects of heavy metals have been investigated extensively and the allowable concentration limits were set by different governments [1]. How to effectively decrease heavy metals pollution is an important but still challenging task for environmental science. Different technologies were proposed for efficient removal of heavy metals nowadays, including adsorption, membrane filtration, chemical precipitation, ion exchange and electrochemical technologies [2–5]. In these strategies, adsorption has advantages of flexibility in its designing and operation, high efficiency, simple running program and a low maintenance cost resulted from regeneration processes [6,7]. Thus, various sorbents are all considered in the literature for the highly effective removal of heavy metals.

Removal efficiency of conventional sorbents always depends on their surface area or active sites, especially for the nano-sized materials [8]. Manganese oxide (MnO_2) can provide an efficient scavenging pathway for many heavy metals [9,10]. Thus, it is considered as one of the most important sorbents due to its large surface area, strong adsorptive and oxidizing abilities, and good stability under acidic conditions [11,12]. However, bare MnO_2 nano particles are inclined to agglomerate, which may greatly affect its adsorption capacity [13,14]. It is also difficult to recover nano-sized MnO_2 sorbents from real water systems, which will lead to the secondary pollution [12]. Moreover, the toxicity of nano-materials should not be ignored [15,16]. The column system provides a way to solve this problem, but nano-sized sorbents restrict their practical application in fluid-bed or flow-through systems due to slow solid-liquid separation or excessive pressure drop [17]. Although magnetic-MnO_2 composites can be easily separated by using a magnetic technique [18], the separation efficiency has become a noticeable problem, especially in the treatment of large-volume samples.

Currently, one solution to the above problem is to prepare MnO_2 on the surface of supported materials to increase the size of sorbents without decreasing removal efficiency. MnO_2 particles could be directly

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coated on the carbon nanomaterials, in which carbon is applied as a sacrificial reductant to convert aqueous permanganate to insoluble MnO_2 particles [11,19]. Carbon/MnO_2 composites with high adsorption efficiency can be used to remove pollutants from water samples. But the size improvement was not significant and the column pressure is still a challenge. Furthermore, the mechanical stability of fixed column is weak, due to the carbon corrosion in the preparation of composites.

Taking these problems into consideration, surface immobilization of nano-materials on the pipes or plates becomes a suitable method to improve their practical applicability. However, MnO_2 nanomaterials do not have any functional groups and the common core-shell modification leads to the loss of excellent performance of MnO_2. Gelatin is a traditional water-soluble biopolymer with the advantages of nontoxicity, biodegradability and low cost. It can act as not only a sorbent to remove metal ions [20,21], but also a template to assist the preparation of functional materials, due to different types of active groups and particular amino acid chains [22,23]. Most importantly, the rich amino groups in gelatin macromolecules can be oxidized to nitrite and then applied as a reductant in the preparation of functional materials. Zhang et al. prepared the gold-gelatin composites using gelatin as a reducing and stabilizing agent [24]. As the synthesis mechanism of MnO_2 is also a redox reaction between reductant and $KMnO_4$, gelatin can be used as a template, reductant and stabilizing agent to assist the preparation of MnO_2. Introduction of function groups from gelatin not only further increases the adsorption capacity of sorbents, but it is also beneficial for the surface immobilization of nano-materials on the pipes or plates. Up to now, there is no report about the protein-assisted synthesis of MnO_2/gelatin composites.

Considering such advantageous properties, dumbbell MnO_2/gelatin composites were synthesized, based on the protein-assisted synthesis technology. The characterization of composites, adsorption mechanism and kinetics procedure were studied. Based on the carboxyl groups, the composites could be immobilized on the surface of amino-modified polymethyl methacrylate (PMMA) plate. Then, this device was applied for the removal of the heavy metals in water samples and the removal mechanism was discussed in this study.

2. Experimental

2.1. Chemicals and reagents

Gelatin from porcine skin, potassium permanganate ($KMnO_4$), manganese sulfate ($MnSO_4$), 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC), N-Hydroxysuccinimide (NHS), Trismabase, catechol and polyethyleneimine (PEI) were purchased from the Sigma Company (St. Louis, MO, USA). Sulfuric acid, hydrochloric acid, sodium phosphate, calcium chloride, magnesium sulphate, ferrous chloride, and ethanol were obtained from the Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). PMMA plates were provided by Shangou PMMA processing company (Guangzhou, China). Standard solutions of lead and cadmium ions (1 mg mL^{-1}) were purchased from the Aladdin Company (Shanghai, China) and then dissolved with ultrapure water. Ultrapure water was obtained from a Milli-R04 purification system (Millipore, Germany).

2.2. Synthesis of dumbbell MnO_2/gelatin composites

Gelatin solution (30 mg mL^{-1}) was prepared by swelling gelatin powder in an aqueous solution and dissolving at 55 °C. Then, 158 mg of $KMnO_4$ and 94 mg of $MnSO_4$ were added into 60 mL of gelatin solution, respectively. The mixture was treated in an ultrasound bath for 20 min and then transferred into a Teflon-lined stainless steel autoclave (100 mL total volume). The resulting solution was heated at 160 °C for 12 h. After cooling down to room temperature, the composites were obtained by centrifugal filtration (10000 rpm) and washed with water and ethanol several times, respectively. Finally, dumbbell MnO_2/gelatin composites were dried under vacuum at 60 °C.

2.3. Characterizations of the materials

The structure and morphology of products were characterized using scanning electron microscopy (SEM, Sirion200, FEI, Holland) and transmission electron microscopy (TEM, Tecnai G220, FEI, Holland). The Fourier transform infrared (FT-IR) spectrums of materials were recorded using a Bruker VERTEX70 spectrometer (Germany) with KBr pellet technique. The crystal forms of dumbbell MnO_2/gelatin composites were analyzed by an X-ray diffractometer (PANalytical BV Company, x'Pert PRO).The sorbents were characterized by X-ray photoelectron spectroscopy (XPS, Kratos AXIS Ultra Dld, Japan). Thermogravimetric analysis (TGA) was performed using a Diamond TG/DTA instruments (PerkinElmer, USA).

2.4. Batch adsorption study

The removal efficiencies of dumbbell MnO_2/gelatin composites for heavy metals were studied by batch mode experiment. In all experiments, 10 mg of the sorbents were added into a 20 mL of solution with initial concentrations of heavy metals from 5 mg L^{-1} to 1000 mg L^{-1}. The mixture was stirred for 120 min at fixed temperature. The two phases were separated by centrifugation, and the target ions in supernatant were determined using a flame atomic absorption spectrometer (FAAS, Unicam model AA-929). The adsorption mechanisms were studied using Freundlich and Langmuir isotherms. Kinetic studies were the same as the adsorption experiments, except for the different time intervals. Mixed solutions containing 0.1 mmol L^{-1} of Pb(II) or Cd(II) ions and 1 mmol L^{-1} of a variety of possible competitive ions were used to evaluate the competitive adsorption behavior. For regeneration, the composites were eluted by 10 mL of HCl solution (0.01 mol L^{-1}) and then washed with water. Regenerated dumbbell MnO_2/gelatin composites were used for adsorption in successive cycles.

2.5. Removal of heavy metals based on the MnO_2/gelatin modified PMMA plate

PMMA plates are often used to construct a device to remove pollutants, due to its biocompatibility, nontoxicity and cost effectiveness. Amino groups were modified on a cross-shaped plate based on the system of catechol and polyethyleneimine (PEI). Then MnO_2/gelatin composites were immobilized on the plate by coupling the amino groups of PEI and the carboxylic groups of gelatin. Briefly, PMMA plate (9 cm × 2.5 cm) was immersed into a 0.2 M of sulfuric acid solution to improve its hydrophilicity. Then, 1 mL of Tris-HCl solution (pH = 8.5, 10 mM) containing catechol (400 mg) and PEI (100 mg) was incubated at room temperature for 24 h. After that, the plate was uniformly smeared with the resulting solution and dried in a vacuum at 90 °C for 5 h to form a transparent thin film. The experimental conditions were optimized in this study to ensure the fastness and stability of membrane, and the number of amino groups. Finally, 200 mg MnO_2/gelatin composites were mixed with 5 mL of PBS buffer (pH = 6.8) containing 0.5 mM of EDC and 0.5 mM of NHS. The amino-modified PMMA plate was inserted into the mixture solution and incubated at room temperature for 24 h with continuous shaking (120 rpm). After washing for three times with water, the final cross-shaped plate was inserted in a centrifugation tube, and then shaken by an up-and-down shaker at room temperature to remove heavy metals from the spiked real water samples. Surface water samples were collected from the Yangtze River and wastewater samples were collected from a local chemical plant in Wuhan city, China. At the different time intervals, the heavy metals in the solution were detected based on a FAAS method. After several cycles of use, the spent adsorbents were immersed into 0.1 M of KOH solution at 80 °C for 3 h to dissociate the gelatin. Then the MnO_2 and the