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Synthesis and characterization of dithiocarbamate carbon nanotubes for the removal of heavy metal ions from aqueous solutions

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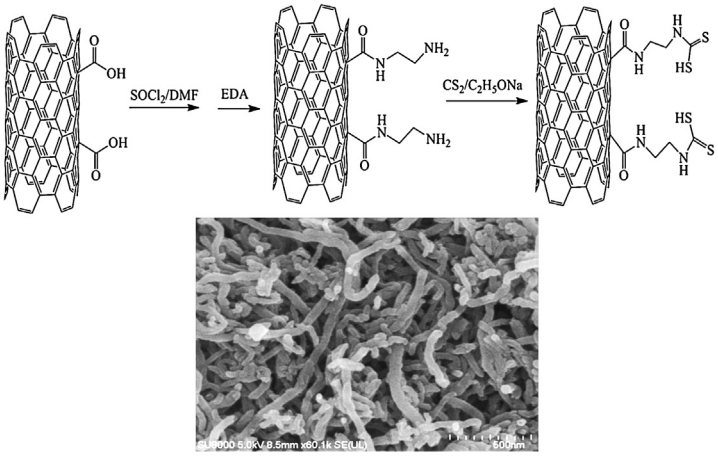
HIGHLIGHTS

- Dithiocarbamate-groups modified MWCNTs were prepared and characterized.
- The adsorption capacities of DTC-MWCNT for Cd(Π), Cu(Π) and Zn(Π) were evaluated.
- The possible adsorption mechanism of DTC-MWCNT for metal ions was proposed.

GRAPHICAL ABSTRACT



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ABSTRACT

A new carbon nanotube (CNT) composite, dithiocarbamate groups functionalized multi-walled CNT (DTC-MWCNT), was prepared by reaction of oxidized MWCNT with ethylenediamine and carbon disulfide. The physical structure and chemical properties of DTC-MWCNT were characterized using Fourier transform infrared (FT-IR) spectroscopy, thermal gravimetric analysis (TGA) and scanning electron microscopy (SEM). The adsorption performance of Cd(II), Cu(II) and Zn(II) onto DTC-MWCNT was evaluated. The adsorption conditions such as pH value, adsorption time and initial concentration were systematically investigated. The adsorption isotherms, adsorption kinetics, adsorption thermodynamics and adsorption mechanism were discussed in detail. The results indicated that the adsorption process matched well with the pseudo-second-order kinetic model and the Langmuir model. The values of ΔG^{q} and ΔH^{θ} calculated from the experiment data indicated that the adsorption process was spontaneous and endothermic in nature. DTC-MWCNT possesses higher maximum adsorption capacities for Cd(II), Cu(II) and Zn(II) of 167.2, 98.1 and 11.2 mg/g, respectively.

1. Introduction

Environmental pollution by toxic metals occurs globally. Heavy metal pollutants mainly come from industries, such as mining, metal processing, rubber, leather, plastic and medicine [1]. The

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most common poisonous heavy metal ions, including lead, mercury, zinc, nickel and copper, are different from other pollutants due to their accumulation in living organisms [2,3]. Both animals and plants would be endangered by the heavy metals polluted water and soil. Heavy metalscan enter human body and causeirreversible damage to bone, liver and brain, and the toxicity is not easy to eliminate [4]. Therefore, the removal of heavy metal ions from water environment benefits both public health and environment. Various separation methods including chemical deposition, ion exchange, membrane filtration, flotation, electrochemical and adsorption [1,5] have been developed to remove heavy metal ions from aqueous solutions. Among the existing separation technologies, the adsorption was recognized as one of the most effective method for removing heavy metal ions due to the significant advantages such as high removal efficiency, simplicity and low cost.

Nowadays, the selective adsorption of heavy metal ions by carbon nanotubes (CNTs) has been of great concern because of the simpler preparation process, higher adsorption ability and shorter adsorption time. CNTs could be used to remove various pollutants such as dyes, phenols, aniline and divalent metal ions from aqueous solutions [6,7] due to the II–II interactions, electrostatic interactions and large specific surface areas [8]. However, the dispersion of CNTs into solvent was poor due to the strong intermolecular van der Waals interactions between tubes, which has largely decreased their adsorption performance [9]. To enhance the dispersion and the adsorption capacity of CNTs,the surface modification to generate functional groups is one of the most common and most effective approaches. Numerous functionalized CNTs have been used to remove heavy metal ions from aqueous solution or wastewaters. For example, functionalized CNTs containing iodo functional groups have been used to remove heavy metal ions from compact fluorescent bulbs and water streams[10]. Amino modified CNTs were used for the adsorption of lead and cadmium ions [11]. CNTs containing various oxygen-containing functional groups (COOH, C=O, OH) were developed to remove various heavy metal ions [12,13]. The sulphur-containing complex agent anchored adsorbents were also used for removal of heavy metal ions [8,14,15].

Based on the theory of hard and soft acids and bases (HSAB), dithiocarbamate, a soft base, could be used as selective adsorption material for removal of heavy metal ions [16]. Dithiocarbamate modified chelating resins showed high adsorption capacity for various heavy metal ions such as Pb(II), Hg(II), Cd(II), Ni(II) and Cu(II) [17–20]. To the best of our knowledge, dithiocarbamate-modified MWCNT (DTC-MWCNT) as adsorbent have never been reported in previous literature for the removal of heavy metal ions.

In this paper, a novel adsorbent, dithiocarbamate groups functionalized multi-walled CNT (DTC-MWCNT) was developed and used to remove Cd(II), Cu(II) and Zn(II) from aqueous solution. The morphology of DTC-MWCNT was characterized by Fourier transform infrared (FT-IR) spectroscopy, thermal gravimetric analysis (TGA) and scanning electron microscopy (SEM). The adsorption performance of Cd(II), Cu(II) and Zn(II) onto DTC-MWCNT was investigated. The adsorption conditions pH value, adsorption time and initial concentration were investigated in detail. The adsorption isotherms, adsorption kinetics, adsorption thermodynamics were discussed. The adsorption mechanism was also proposed.

2. Experimental

2.1. Chemicals

CNTs (purity > 95%) were purchased from Shenzhen Nanotech Port Co., Ltd. The range of diameters is 20–40 nm and the length exceeds 5 μm. Ethylenediamine (EDA) and *N*′*N*-dimethylformamide (DMF) were purchased from Sinopharm Chemical Reagent Co., Ltd. Sodium ethoxide, sulfoxide chloride and carbon disulfide were obtained from Tianjin Kermel Chemical Reagent Co., Ltd. Metal salts including $Cd(NO_3)_2{\cdot}4H_2O$, $Cu(NO_3)_2{\cdot}3H_2O$ and $ZnCl_2$ were used as sources for Cd(II), Cu(II) and Zn(II), respectively. All the chemicals used were of analytical grade and used as received without any further.

2.2. Pretreatment of multi-walled carbon nanotubes

In a 100 mL round bottomed flask was added 500 mg of raw MWCNTs and 50.0 mL of nitric acid, which was dispersed well by sonication for 10 min. Then this mixture was stirred continuously at 120 °C for 24 h to introduce oxygen groups onto the MWCNTs surface. After cooling to room temperature, the mixture was added to 500 mL of deionizer water and filtered through a 0.45 μm PTFE membrane. The oxidized MWCNTs (o-MWCNTs) was washed with deionized water until the pH was neutral. Then, it was dried under vacuum at 70 °C for 24 h. Next step, 300 mg o-MWCNTs were converted to chloride-functionalized MWCNTs by reacting with 50.0 mL of sulfoxide chloride and 1.5 mL of coupling agent (DMF) at 70 °C for 24 h. The residual sulfoxide chloride was removed by distillation. Subsequently, 45.0 mL of EDA were added under magnetic stirring and reacted at 120 °C for 24 h. The obtained product was diluted with 300 mL of deionized water and filtered using a 0.45 μm PTFE membrane, then washed extensively with excess methanol. Thus obtained amine group functionalized MWCNTs (MWCNTs-$CONHCH_2CH_2NH_2$, abbreviated as e-MWCNTs) were dried in a vacuum oven at 70 °C for 24 h.

2.3. Synthesis of dithiocarbamate group functionalized MWCNTs

400 mg of e-MWCNTs in 50.0 mL sodium ethoxide solution was reacted with 5.0 mL CS_2 at 50 °C for 72 h under magnetic stirring. Then, the mixture was separated through a 0.45 μm PTFE membrane. The solid residuals were washed with deionized water, diluted HCl solution, diluted NaOH solution and acetone in sequence. Finally, the obtained DTC-MWCNT was kept in a vacuum oven at 70 °C for 24 h. The procedure for the functionalization of MWCNTs was depicted in Fig. 1.

2.4. Sorption experiment

The effect of pH on the adsorption of the investigated metal ions was studied at 25 °C. For these experiments, a series of 50 mL flasks were used. Each flask was added with 5.0 mg of adsorbent and 20.0 mL of metal ions with concentration of 10 mg/L. The desired pH was adjusted by using aqueous solution of 0.1 mol/L HCl and 0.1 mol/L NaOH. A pH range of 2.0–6.0 was used to avoid the precipitation of metal hydroxides. The flask was shaken in the thermostat shaker for a certain time. After filtration, the residual concentration of each metal ion was determined by atomic absorption to calculate the adsorption capacities of metal ions according to Eq. (1):

$$q_e = \frac{c_o - c_e}{m} \times V \quad (1)$$

where c_o and c_e (mg/L) are the initial and equilibrium concentrations of metal ions in the liquid phase, respectively, q_e is the adsorption capacity of metal ions (mg/g), V is the volume of the solution (L), and m is the mass of the absorbent used in adsorption experiments (mg).

The equilibrium sorption experiments were performed by agitating 5.0 mg of adsorbent with 20.0 mL of solution containing a known amount of each metal ion (varying from 5.0 to 100.0 mg/L) at the optimum pH value for 2 h. The temperature was maintained at 25, 35 and 45 °C, respectively. After equilibration, the adsorbent