



# Synthesis of magnetic polyaniline/graphene oxide composites and their application in the efficient removal of Cu(II) from aqueous solutions



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## ABSTRACT

The magnetic polyaniline/graphene oxide (MPANI/GO) composites were synthesized by using aniline in the presence of GO. The sorption of Cu(II) on the MPANI/GO composites were studied as a function of pH, contact time, ionic strength, foreign cation and anion ions, and the results showed that Cu(II) sorption was strongly dependent on pH, and independent of ionic strength. The sorption of Cu(II) was mainly dominated by outer-sphere surface complexation at low pH, and by inner-sphere surface complexation at high pH. The thermodynamic parameters calculated from temperature-dependent sorption isotherms indicated that the sorption process was endothermic and spontaneous. The MPANI/GO composites were effective materials for the removal of Cu(II) from large volumes of aqueous solutions and could be separated by using magnetic separation method in the practical applications.

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## 1. Introduction

With the rapid development of economy and industry, large amounts of wastewater containing different kinds of heavy metal ions and organic pollutants are generated and it is inevitably to be flowed into the nature water, and thereby results in water contamination and creates a serious threat to environmental pollution and people's living condition [1]. The copper in wastewater in the form of cupric ions is generally from some industries such as paint, metallurgy, fertilizer, mining, battery manufacturing, and wood manufacturing industries [2]. The Cu(II) ions can not be degraded compared to organic pollutants and it will persist in the natural environment as long as possible [3]. Although the Cu(II) ions at low concentration is not dangerous to human health, the excessive Cu(II) intaken through food chain will cause headaches, nausea and even death. According to United States Environmental Protection Agency (USEPA) provisions, the maximum content of copper in the water is 1.3 mg/L [4]. Thereby, the concentration of Cu(II) in wastewater should be reduced as low as possible before it is discharged into the environment. So far, a variety of methods such as ion exchange [5], chemical precipitation [6], membrane separation [7], sorption [8,9], and electrolytic techniques [10] have been applied to eliminate Cu(II) ions from

aqueous solutions. However, the sorption technique is widely used due to its simple operation, low cost and high efficiency [11,12]. The sorption of Cu(II) on different kinds of clay minerals and man-made nanomaterials has been studied extensively, and the results showed that the sorption capacity of clay minerals is not high enough whereas the nanomaterials are difficult to be separated from aqueous solutions because of their small particle sizes. Thereby, it is necessary to synthesize materials with high sorption capacity and easy separation from aqueous solution.

Graphene oxides (GOs), produced through the chemical treatment of natural graphite through oxidation, contain a large amount of oxygen-containing functional groups such as carboxyl and carbonyl groups, which are located in the plate edge of the GO nanosheets [13–16]. These oxygen-containing functional groups and the high specific surface area (theoretical values of  $\sim 2620 \text{ m}^2/\text{g}$ ) make the GOs as suitable materials for the efficient removal of heavy metal ions from aqueous solutions [17–21]. However the capacity of adsorbent is limited by the kind and the number of available functional groups used for binding metal ions. The available functional groups on GOs are very limited, which may lead to be difficult for the efficient removal of metal ions. Thereby, it is necessary to introduce new functional groups to improve the sorption capacity of GOs. Modified GOs have been obtained by introducing new materials such as sulfanilic acid [4], polypyrrole [22], EDTA [23], allylamine hydrochloride [24] and  $\beta$ -CD [25] through a GO backbone.

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Polyaniline (PANI) behaves good performance in the removal of heavy metal ions from the aqueous solutions [26–29] because it contains amino imide groups and can serve as a good sorption point. The PANI-based composites are widely used to remove heavy metal ions such as Cd(II) [27], Pb(II) [30], Hg(II) [31], etc. The PANI/GO composites are suitable materials in the removal of heavy metal ions [32]. However, it is an issue that the efficient removal of the adsorbent from the aqueous solutions. Due to the high separation efficiency, the magnetic materials have been widely applied in environmental pollution management [33]. Many researchers have paid attention to the magnetic GOs as adsorbents for the removal of heavy metal ions [34–37] and dyes [38–40]. Thus the magnetic PANI/GO composites can be easily separated and recovered quickly and have great value for water purification.

In this work, we synthesized MPANI/GO composites and characterized the macroscopic and microscopic properties of MPANI/GO composites by using SEM, FTIR and XRD. The synthesized composites were applied as adsorbent to remove Cu (II) ions from aqueous solutions under different experimental conditions. The experimental results were discussed in detail and the thermodynamic parameters were calculated from temperature-dependent isotherms, and the interaction mechanism was discussed.

## 2. Experimental

### 2.1. Materials and reagents

Graphite powder (99.95% purity) and aniline were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). The potassium permanganate (KMnO<sub>4</sub>), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 30%), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), phosphate (H<sub>3</sub>PO<sub>4</sub>) and (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> were obtained from Yantai Chemical Reagent Co., Ltd. (China). FeCl<sub>3</sub>·6H<sub>2</sub>O and sodium acetate were purchased from Tianjin Bodi Chemical Co., Ltd. (China). CuSO<sub>4</sub>·5H<sub>2</sub>O was obtained from Laiyang Chemical Reagent Co., Ltd. (China). All materials were used directly in the experiments without any further purification.

### 2.2. Preparation of polyaniline/graphene oxide (PANI/GO) composites

GOs were synthesized by a modified Hummers method [41,42]. Graphene oxide powder (25 mg) was dissolved in 50 ml of H<sub>2</sub>SO<sub>4</sub> (1 mol/L), using ultrasonic bath for 1 h to form stable suspension. Then 200 μl aniline was added into 50 ml of 0.5 mg/mL GO suspension and ultrasonic degradation for 30 min. 0.2281 g (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> was added into the mixture and ultrasonic degradation at 20 °C for 2 h. The product was washed with distilled water until the supernatant was colorless.

### 2.3. Synthesis of magnetic polyaniline/graphene oxide (MPANI/GO) composites

0.5 g FeCl<sub>3</sub>·6H<sub>2</sub>O was added into 10 ml ethylene glycol, followed by the addition of 1.5 g sodium acetate, 5 ml ethanediamine and 0.5 g PANI/GO composites. The suspension was continued stirring for 30 min, then the mixture was sealed in an airtight steel container. The mixture was heated in muffle furnace at 200 °C for 8 h and allowed to cool to room temperature. The product was washed 5 times with distilled water and dried at 35 °C under high vacuum.

### 2.4. Characterization

The GOs, PANI/GO and MPANI/GO composites were characterized by Fourier transformed infrared spectroscopy (FTIR), powder X-ray diffraction (XRD), scanning electron microscopy (SEM),

Magnetization curves, zeta potentials in detail. The FTIR spectrum measurement was performed by using Perkin-Elmer Spectrum 100 spectrometer at room temperature. Spectra were obtained in the 4000–500 cm<sup>-1</sup> wavenumber with 4 cm<sup>-1</sup> resolution. The XRD patterns were measured in the 2θ range of 0.0°–60.0° by an Advance D8 diffractometer with Cu Kα radiation, 40 kV, 2° min<sup>-1</sup>. The SEM image was performed on a JEOL JSM-6700, Tokyo, Japan. For magnetization measurement, a vibrating sample magnetometer (VSM) (Model 1600, DMS) was used at room temperature. The zeta potentials of MPANI composites were measured on a Malvern ZEN2600 Zetasizer.

### 2.5. Batch adsorption experiments

The stock solution (1 g/L) of Cu(II) was prepared by dissolving CuSO<sub>4</sub>·5H<sub>2</sub>O in distilled water and diluted to the required initial concentration with distilled water. All sorption experiments were performed in a water bath oscillator with continuous stirring fixed at 180 rpm. The solution pH was adjusted by the addition of 0.1 mol/L HCl or NaOH. Factors that affect the experiments were investigated, such as pH (2.0–11.0), contact time (0–35 min), cations and anions on the sorption of Cu(II). After the sorption tests, the mixture was separated by a permanent magnet. The concentration of Cu(II) was analyzed by ultraviolet spectrophotometer (DAOJIN, UV2550) at 544 nm. Sorption isotherms were carried out by varying the concentration of Cu(II) from 20 to 160 mg/L. And experiments at different conditions at 298.15, 318.15, and 338.15 K were performed for 12 h in a water bath oscillator. The sorption capacity (*q<sub>e</sub>*, mg/g) of Cu(II) on the adsorbent was obtained from the following equation:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where *m* (g) is the mass of the adsorbent in solution, *C*<sub>0</sub> (mg/L) and *C*<sub>*e*</sub> (mg/L) are the initial and equilibrium concentrations of Cu(II), *V* is the volume of solution (L).

### 2.6. Experimental data analysis

For kinetics study, the kinetic data were simulated by using the pseudo-first-order [43] and the pseudo-second-order [44], which are expressed as follows:

$$\frac{1}{q_t} = \frac{k_1}{q_e t} + \frac{1}{q_e} \quad (2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

where *k*<sub>1</sub> (min) and *k*<sub>2</sub> (g/mg min) are the pseudo-first-order sorption rate constant and the pseudo-second-order sorption rate constant, *q<sub>t</sub>* (mg/g) is the sorption of Cu(II) at time *t*, *q<sub>e</sub>* (mg/g) is the sorption of Cu(II) at equilibrium time.

Intra-particle diffusion model [45] was also applied to analyze the experimental data. The intra-particle diffusion can be expressed as follow:

$$q_t = k_p t^{1/2} + C \quad (4)$$

where *C* is a constant related to the thickness of the boundary and *k<sub>p</sub>* (mg/g min<sup>1/2</sup>) is intra-particle diffusion coefficient.

In order to investigate the sorption isotherms, Langmuir and Freundlich models are applied to simulate the sorption data. The Langmuir model is described by the following equation:

$$q_e = \frac{Lq_{\max}C_e}{1 + LC_e} \quad (5)$$

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