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Adsorbent for hydroquinone removal based on graphene oxide functionalized with magnetic cyclodextrin–chitosan

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ABSTRACT

Magnetic cyclodextrin–chitosan/graphene oxide (CCGO) with high surface area was synthesized via a simple chemical bonding method. The characteristics results of FTIR, SEM, TEM and XRD showed that CCGO was prepared. The large saturation magnetization (22.35 emu/g) of the synthesized nanoparticles allows fast separation of the CCGO from liquid suspension. These composites could efficiently remove hydroquinone from simulated wastewater with a facile subsequent solid–liquid separation because of their large area, abundant hydroxyl and amino groups with handy operation, and hydrophobicity. The hydroquinone removal process was found to obey the Freundlich adsorption model and its kinetics followed pseudo-second-order rate equation. The hydroquinone removal mechanism of CCGO might be attributed to the electrostatic adsorption of hydroquinone in the form of negatively charged hydroquinone by positively charged chitosan, accompanying hydroquinone absorbed by cavities of the cyclodextrin, and forming hydrogen bonds between hydroquinone and the hydroxyl groups on the surface of CCGO. The used CCGO could be recovered with ethanol. This study provides a promising nanostructured adsorbent with easy separation property for heavy metal ions removal.

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1. Introduction

Hydroquinone is widely used in pesticides, medicine, rubber, medicine, and the fine chemicals are considered to be hazardous and toxic to some organisms and can cause vomiting, tinnitus, nausea, and abdominal pain to human [1]. Thus, it is necessary to remove them from contaminated waters. In recent years, interest has been focused on the removal of hydroquinone from aqueous solution, and a variety of techniques are available to purify water contaminated such as an electrochemical technique, extraction method [2] and acid catalytic oxidation [3]. However, these methods have been used with limited success because of several disadvantages, such as high costing and inefficiency. Among these methods, adsorption is the most widely used method because of the ease of operation and comparable low cost of application. Thus, there is a strongly desire to find a high-performance, low-cost, and easily regenerated adsorbent to remove hydroquinone from wastewater.

The excellent absorbent materials must have high specific surface area, chemical stability, and a lot of adsorption sites [4]. The absorbents which contain these features above show good adsorptive property. Graphene, a single layer of sp^2 bonded carbon atoms in a two-dimensional hexagonal lattice, has attracted considerable attention as a potential biomaterial due to its physico-chemical properties, such as a large surface area, high dispersibility and hydrophilicity [5,6]. However, graphene is easy to aggregate, which will lead to great reduction in the surface area and the adsorption. Therefore, chemical modification of graphene is imperative. Graphene oxides (GO) contain many oxygen-containing functional groups on the surfaces [4], and the functional groups make GO to be water soluble and easily chemical modification. But the graphene oxides could not be separated easily from aqueous solution by filtration or centrifugation. The application of magnetic adsorbent technology to solve environmental problems has received considerable attention in recent years [7–11].

The magnetic β-cyclodextrin–chitosan nanoparticles have attracted tremendous attentions due to their many excellent properties arising from either the components themselves or functionalization and synergy [12], such as (a) the magnetic biosorbents are easy to be separated and recovered; (b) the hydrophobicity of β-cyclodextrin improved the adsorption capacity. The magnetic β-cyclodextrin–chitosan can be as an effective biosorbent in hydroquinone from effluents.

In this study, the magnetic β-cyclodextrin–chitosan/graphene oxide (CCGO) materials were prepared and investigated. The aim of this study was to explore and prepare CCGO with higher adsorption capacity and excellent separation properties. It was used to remove hydroquinone from simulated wastewater. The

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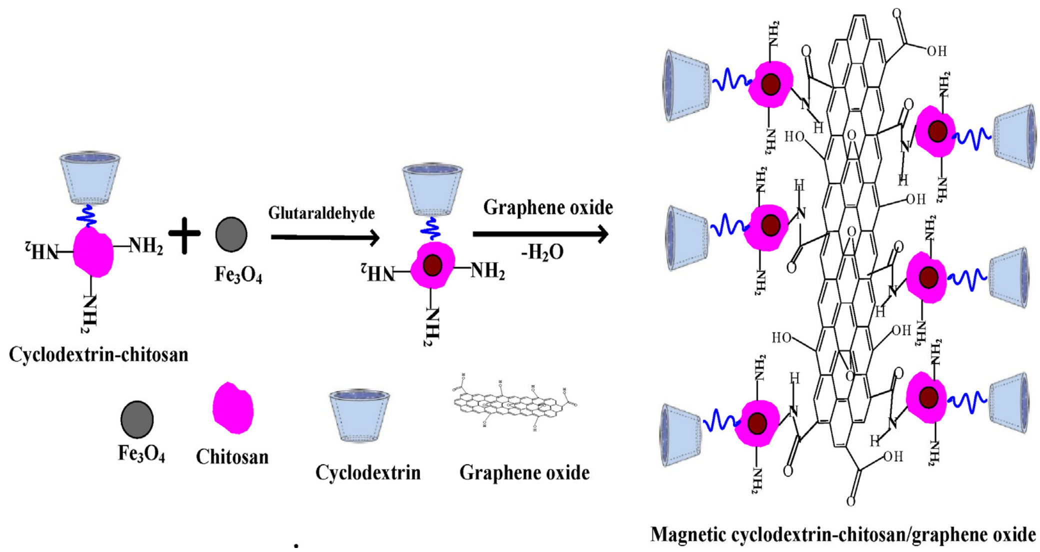

Scheme 1. Schematic depiction of the formation of CCGO.

adsorption kinetics and the possible hydroquinone removal mechanism of CCGO as well as the recovery of used CCGO were investigated in detail. The results demonstrated that the CCGO has good adsorption performance for hydroquinone. This new type of magnetic adsorbent, featuring good adaptability, low cost, easy and rapid extraction/regeneration, and handy operation, may be useful for further research and practical applications of the novel magnetic biosorbent in phenols wastewater treatment.

2. Experimental

2.1. Materials

Ferric chloride hexahydrate ($FeCl_3{\cdot}6H_2O$, 98%) and ferrous chloride tetrahydrate ($FeCl_2{\cdot}4H_2O$, 99.0%) were purchased from Shanghai Sangon. Chitosan with 80 mesh and average-molecular weight of 6.36×10^5 was purchased from Qingdao Baicheng Biochemical Corp. Glutaradehyde, 1-ethyl-3-(3-dimethyl-aminoprophy) carbondiimide hydrochloride (EDC), N-hydroxyl succinimide (NHS), and β-cyclodextrin were Aldrich products. All other reagents used in this study were analytical grade.

2.2. Preparation of CCGO

Magnetic β-cyclodextrin–chitosan was prepared according to our previous method [13]. GO was prepared from purified natural graphite by the modified Hummers method [14]. A GO dispersion was prepared by sonicating GO for 2 h in ultrapure water. A solution of 0.1 M EDC and 0.1 M NHS was added to the GO dispersion with continuous stirring for 2 h in order to activate the carboxyl groups of GO [15]. The pH of the resulting solution was maintained at 7.0 using dilute sodium hydroxide. Magnetic β-cyclodextrin–chitosan (0.1 g), the activated GO solution and 5 mL glutaraldehyde were added in a flask and dispersed in distilled water by ultrasonic dispersion for 10 min. After ultrasonic dispersion, the mixed solutions were stirred at 65 °C for 2 h. The precipitate was washed with 2% (w/v) NaOH and distilled water in turn until pH was about 7 [16]. Then, the obtained product was collected by the aid of an adscititious magnet and dried in a vacuum oven at 50 °C. The obtained product was CCGO. The application of CCGO for removal of hydroquinone with the help of an external magnetic field. The preparation of CCGO is shown in Scheme 1.

2.3. Methods

All batch adsorption experiments were performed on a model KYC-1102C thermostat shaker (Ningbo, China) with a shaking speed of 180 rpm. Simulated wastewater with different hydroquinone concentrations (20.0, 50.0, 80.0, 100.0, 130.0, 150.0 mg L^{-1}) were prepared by dilution of the stock hydroquinone standard solution with DI water. CCGO (0.10 g) were added to 100 mL of the above hydroquinone solution under mechanical agitation. For all adsorption tests, the initial pH values of the hydroquinone solutions were adjusted with 0.1 mol L^{-1} HCl solution or 0.1 mol L^{-1} NaOH solution. After the adsorption processes, CCGO was conveniently separated by magnetic separation and the supernatant was immediately analyzed by atomic absorption spectrometry (WFX-1F2, China). To study the influence of initial pH on the removal of hydroquinone, the initial pH values of the solutions were adjusted to 2, 3, 4, 5, 6, and 7. The concentration of CCGO was 1.0 g L^{-1}. The initial hydroquinone concentration was 80.0 mg L^{-1}. For the regeneration, the hydroquinone-adsorbed CCGO were immerged in 5 mL of NaOH solution (0.1 mol L^{-1}) for 5 h and then washed six times with DI water to remove adsorbed alkali. The adsorption amount and adsorption rate are calculated based on the difference in the hydroquinone concentration in the aqueous solution before and after adsorption, according to the following equation:

$$Q = (C_0 - C_e)\frac{V}{W}, \quad E = \frac{C_0 - C_e}{C_0} \times 100\% \tag{1}$$

where, C_0 and C_e are the initial and equilibrium concentrations of hydroquinone in milligrams per liter, respectively, V is the volume of hydroquinone solution, in liters, and W is the weight of the CCGO used, in grams.

2.4. Characterization methods

FT-IR spectra were measured on a PerkinElmer 580B IR spectrophotometer using the KBr pellet technique. Morphological structures of samples were examined by scanning electron microscopy (SEM) with a Hitachi SX-650 machine (Tokyo, Japan) and transmission electron microscopy (TEM) with model JEM 2010 machine (Tokyo, Japan). A HH-15 vibrating sample magnetometer (Nanjing, China) was used to measure magnetization curve of samples. Wide angle X-ray diffraction (WAXRD) patterns were recorded

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