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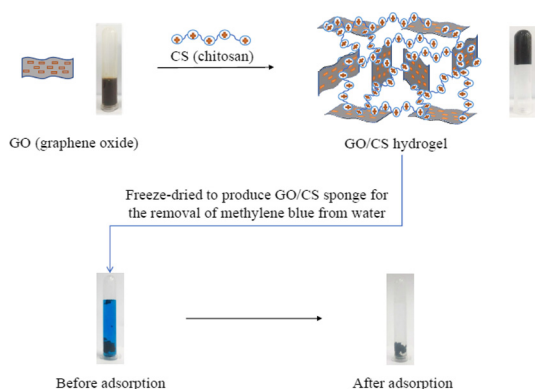
Graphene oxide/chitosan sponge as a novel filtering material for the removal of dye from water



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GRAPHICAL ABSTRACT



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ABSTRACT

Although graphene oxide (GO)-based materials are attractive media for water treatment, their separation from water for reuse remains a challenge. This study investigated the self-assembly of GO sheets in the presence of chitosan (CS), a natural polyaminosaccharide, into sponges. We found that about 93% of added CS could be combined with GO, regardless of the CS concentration. There exists an upper critical gelation limit, below which hydrogel forms and above which precipitation takes place. Results indicate that upon freeze-drying, a stable GO/CS sponge was generated only at a CS content of $\geq 9\%$. Sponges with CS content between 9% and 41% had good filtering performance. The sponges were characterized with XRD, SEM and FTIR measurements and the interaction between GO and CS was analyzed. The GO/CS sponge with CS content of 9% had adsorption capacity of 275.5 mg/g for methylene blue (MB), a model dye molecule. Both electrostatic attraction and hydrophobic interactions are responsible for MB adsorption by GO/CS sponges. The GO/CS sponge could be regenerated for repeated use using 0.5 M NaOH solution as desorption reagent. Our fixed-bed column studies illustrate that the GO/CS sponge performed well as a filtering material for removing MB from water.

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1. Introduction

Graphene, a two-dimensional (2D) carbon nanomaterial with one-atom thickness, was first discovered in 2004 [1]. The unique

structure of graphene suggests its promising potential applications in areas such as electronic devices, solar cells, sensors, nanomaterials, batteries, supercapacitors and hydrogen storage [2]. On a large scale, graphene can be synthesized by exfoliation of naturally occurring graphite in liquid phase to form a graphene oxide (GO) intermediate, followed by reduction [3,4]. Recently, GO has drawn much attention because of its use as an adsorbent for the removal

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of pollutants from water; the intermediate product for graphene production possesses high surface area, abundant oxygen-containing functional groups, and a π -electron system [5–14]. In addition, studies have shown that the performance of GO in the removal of pollutants from water can be improved by functionalization of GO with a number of reagents [15–22].

Nevertheless, for regeneration and reuse, collection of GO-based materials from water with simple methods is needed in practical applications of water treatment. To this end, previous studies have attempted to combine magnetic nanoparticles and GO to obtain magnetic nanocomposites, which allows the collection of the adsorbent from water by providing an external magnetic field [23–28].

Flow-through process using filter media such as granulated adsorbents packed in a fixed-bed column is a simple, widely used adsorption technology for water treatment. Therefore, another attempt was to prepare porous GO sponge as a filtering material for the decontamination of pollutants. Because of their high surface area, high accessible pore volume, as well as high strength and durability at low density, highly ordered three-dimensional (3D) graphene and GO sponges are attractive for a number of practical applications [29,30]. However, investigations of GO-based sponges with high stability in water and strong ability to capture pollutants are still rare.

Chitosan (CS) is a natural polyaminosaccharide that is produced by the deacetylation of chitin, which is the second most abundant polymer in nature, next to cellulose. It may be extracted from crustacean such as prawns and crabs, as well as from fungi and insects [31,32]. CS has good biocompatibility, biodegradability, and multiple functional groups (hydroxyls and amines) and is easily available. Taking advantages of both GO and CS, a number of previous studies have already investigated GO/CS composites for the removal of pollutants from water, as recently reviewed [33]. In them, most of GO/CS composites have been developed with the addition of different cross linkers, and only few studied cross linker-free GO/CS composites [34,35]. It is obvious that, without the addition of cross linkers, the preparation is simple and environmentally friendly. However, to our best knowledge, GO/CS sponge has not been investigated yet as a novel filtering material in flow-through process for the removal of pollutants. In our present study, cross linker-free GO/CS sponges with varying CS content were prepared from the precursor material of GO/CS composites. The influence of CS on the formation and properties of GO/CS sponge was particularly addressed. The performance of the sponges in the decontamination of water containing methylene blue (MB), a typical model dye pollutant in adsorption studies, was also investigated using both batch and column experiments.

2. Materials and methods

2.1. Reagents

Reagent-grade MB ($C_{16}H_{18}N_3S$) was purchased from Amresco Company (USA). Graphite powder and other chemical reagents of analytical grade were all obtained from Sinopharm Chemical Co. (Shanghai, China) and were used as received without further purification.

2.2. Preparation of materials

GO was synthesized using the modified Hummer's method [3]. In brief, 3 g of graphite powder ($\geq 99.85\%$ purity), 2.5 g of $K_2S_2O_8$, 2.5 g of P_2O_5 , and 12 mL of 98% H_2SO_4 were successively added to a flask, and the mixture was then stirred for 4.5 h at 80 °C. The solution was then transferred into 300 mL of distilled water and

filtered. The solid obtained was dried in an oven. Afterward, 120 mL of 98% sulfuric acid and 15 g of K_2MnO_4 were added slowly with stirring, and the mixture was vigorously stirred for 2 h. The mixture was then placed in a 250 mL ice-water bath for 2 h. After quick addition of 500 mL of distilled water, 200 mL of 30% H_2O_2 solution was added. The black solution turned yellow and formed numerous bubbles. The mixture was then filtered and washed with HCl (1:10, v/v) four times. Finally, the solid product was dialyzed for 4 days. The obtained GO suspension at a concentration of 10.71 mg/mL could be evenly dispersed into individual nanosheets by ultrasonic treatment.

To obtain GO/CS hydrogels and sponges, the CS stock solution was first prepared by dissolving 1.407 g of CS in 100 mL of 1% acetic acid solution followed by adjusting the pH to 5.0 with 1 M NaOH solution. A series of 100 mL CS working solutions with different CS concentrations were then obtained by dilution with 1% $CH_3COOH-CH_3COONa$ buffer solution (pH 5.0). To test whether the hydrogel could form, 2 mL of the prepared CS solutions were separately added to 2 mL GO suspensions (10.71 mg/mL) in 10 mL polypropylene tubes. After ultrasonic treatment for 30 min and storage for 12 h, the formation of the hydrogel was examined by the tube inversion method. To obtain GO/CS sponges for batch adsorption studies, 100 mL of the aforementioned CS solutions were mixed with 100 mL of GO dispersion (10.71 mg/mL) for 30 min under ultrasonication and then allowed to stand for 12 h. The composites were washed several times with 1% (v/v) $CH_3COOH-CH_3COONa$ buffer solution (pH 5.0) and deionized water and finally freeze-dried under vacuum. The obtained GO/CS samples were denoted as 3% GO/CS, 7% GO/CS, 9% GO/CS, 12% GO/CS, 20% GO/CS, 26% GO/CS, 34% GO/CS, 41% GO/CS, 47% GO/CS, 51% GO/CS, and 55% GO/CS, according to the mass percentage of CS in the product. For comparison purposes, GO sample without CS was also prepared.

To understand the interaction of CS with GO, experiments for the adsorption isotherms of CS on GO were also undertaken. For this purpose, 8 mL portions of CS solution with varying CS concentrations were transferred to centrifuge tubes containing 20 mg of freeze-dried GO. The mixtures were shaken for 24 h at 180 rpm at 298 ± 1 K. After centrifugation, the concentration of CS in the supernatants was determined by spectrophotometric analysis of the total nitrogen concentration after digestion with potassium persulfate solution at 122 °C [36]. The amount of CS adsorbed was calculated from the CS concentrations before and after adsorption. The experiments were conducted in triplicate. Mean data and standard deviations are reported.

2.3. Characterization of materials

Powder X-ray diffraction (XRD) patterns were recorded by a D8 Advance (Bruker-AXS Company) using Cu $K\alpha$ filtered radiation (30 kV, 15 mA). The scanning electron micrograph (SEM) images were observed by a JEOL JSM-7401F microscope (Japan). Fourier transform infrared (FTIR) spectra were recorded with a FT-IR spectrophotometer (Shimadzu IRPrestige-21) using the KBr method. To measure the cation-exchange capacity of GO, GO was first saturated with 1 M $CH_3COONH_4-NH_4OH$ buffer solution (pH ≤ 7.0) or NH_4Cl-NH_4OH buffer solution (pH > 7.0) with stirring at 298 K for 24 h and then washed repeatedly with ethanol to remove residual ammonium that had not been retained by GO. NH_4^+ ions adsorbed by GO were finally extracted using 1 M NaCl solution and were determined through the salicylic acid spectrophotometry method [36]. The swelling degrees were measured as follows. About 0.1 g of dry GO/CS sponge samples were immersed in deionized water at 298 K for 60 min to reach the swelling equilibrium. The swollen materials were filtered through a 100-mesh sieve to remove unabsorbed water and were weighed again. The swelling ratio was expressed as:

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