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One-step facile synthesis of mesoporous graphene/Fe_3O_4/chitosan nanocomposite and its adsorption capacity for a textile dye

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ABSTRACT

Hierarchical mesoporous graphene@Fe_3O_4@chitosan hybrids were prepared by a one-step facile solvothermal method. SEM and TEM pictures showed that the Fe_3O_4@chitosan nanoparticles were well dispersed on the graphene matrix. The incorporation of Fe_3O_4 in the nanocomposite was confirmed by FT-IR and XRD. The adsorption behavior of the as-prepared composite to methylene blue was conducted, where the effect of the adsorbent dosage, pH, contact time, dye concentration, and recyclability were studied. The composite exhibited rapid adsorption, high capacity, and easy separation and reuse owing to the mesoporous nature of graphene sheets and Fe_3O_4@chitosan nanoparticles, as well as to the magnetic property of Fe_3O_4 nanoparticles. The adsorption capacity could reach 98% within a contact time of 5 min at pH 9 and an initial dye concentration of 25 mg L^{-1}.

1. Introduction

The textile industry normally uses a large amount of water for dying and washing. As a result, effluent from the dying process often has a certain amount of color compounds, which cause the pollution of the receiving water. Moreover, the presence of the synthetic dyes in wastewater may undergo chemical and/or biological reactions, which consume dissolved oxygen and destroy aquatic life [1,2]. Thus, from an environmental point of view, the removal of synthetic dyes is of great concern. So far, various techniques have been developed for the treatment of wastewater containing dyes such as adsorption, filtration, chemical precipitation, photo degradation, biodegradation, coagulation and flotation, membrane process, electrolytic chemical treatment, membrane technology, ozonation [2–5]. Among them, the adsorption has proven to be a versatile and efficient approach to separate a wide range of dye compounds from wastewater because of easy operational procedures and facilitation of recovery of materials [1–3].

Up to date, there are huge interests in the preparation of various macromolecular adsorbents for the removal of dyes from wastewater, such as deoiled soya [4], waste orange peel [5], cotton waste, rice husk [6], betonite clay [7], neem leaf powder, powdered activated sludge [8], perlite [9], bamboo dust, coconut shell, groundnut shell, rice husk and straw, duck weed [10], sewage sludge [11], sawdust carbon [12] and gram husk [13], coal bottom ash [14], bagasse fly ash [15], blast furnace slag [16], red mud [17] and sawdust [18]. These adsorbents are often waste materials with low cost and quite high porosity, which can ensure an adequate surface area for adsorption. However, their adsorption rate and available capacity are quite low because of the intraparticle diffusion in these materials [3]. To solve this problem, a range of effective adsorbents, such as chitosan [19–21], cyclodextrin [22], poly(methacrylic acid) [23], and poly(ethylene terephthalate) [24], have been prepared.

Recently, magnetic nanoparticle (MNP) adsorbents have attracted increasing attention for application in the removal of dyes because of the ease and simplicity in recovering adsorbent from the liquid phase [19–24]. Chen et al. developed a composites of MNP and poly(acrylic acid) (Fe_3O_4/PAA) [1,25]. This magnetic polymer composite consists of both MNP and magnetic microspheres, in which magnetic cores were coated with polymer shells. After treatment process, Fe_3O_4/PAA composites can be rapidly separated from the mixtures by a magnetic field. Very recently, in our previous studies, chemical bonding Fe_3O_4/PAA composites were prepared in supercritical CO_2 and used as absorbents for removing dyes in aqueous solution [26,27]. The as-prepared nanocomposites can be manipulated magnetically easily and exhibit a quite high adsorption capacity and fast adsorption rate. Unfortunately, the intrinsically low surface area and non-porosity of these composites may result in relatively poor absorption of dyes. To address this issue, it is necessary to develop the composite materials with a large surface area, which can improve the performance of absorbents.

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Based on the abovementioned considerations, in this study, a simple, fast and efficient one-step route to synthesize graphene@Fe_3O_4@chitosan composites with uniform-sized and mesoporous Fe_3O_4@chitosan nanoparticles on the graphene sheets was reported. The obtained samples were characterized by Brunauer–Emmett–Teller (BET) surface area measurement, X-ray diffraction (XRD) analysis, scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), and thermogravimetric analysis (TGA). Moreover, the adsorption of methylene blue onto the obtained nanocomposite was investigated in phosphate buffer at 25 °C, where the effect of the adsorbent dosage, pH, contact time, dye concentration, and recyclability were studied.

2. Experimental

2.1. Materials

Chitosan (83% deacetylated, from Nha Trang University), $FeCl_3{\cdot}6H_2O$ (Aldrich), graphite powder (99.995%, Alfa Aesar), ammonium acetate ($\geq$98%, Aldrich), and ethylene glycol (99.8%, Aldrich) were used as received. Other chemicals were of analytical grade and used as received. Graphene oxide (GO) was synthesized from graphite powder using a modified Hummers method [28].

2.2. Synthesis of RGO@Fe_3O_4@chitosan nanocomposites

In a typical reaction, 13.6 mg of GO and 0.68 g of $FeCl_3{\cdot}6H_2O$ was dissolved in 35 mL of EG to form a homogeneous solution. Subsequently, a mixture of NH_4Ac (1.92 g) and chitosan (0.68 g) was added to above suspension and dispersed for 1 h by sonication. Then, the resulting mixture was transferred into a Teflon-lined stainless-steel autoclave (40 mL) and heated to 180 °C and kept at this temperature for 12 h. After cooling down to room temperature, the obtained products were washed with deionized water and ethanol and dried in a vacuum at 65 °C for 12 h. For comparison, the Fe_3O_4@chitosan composite was prepared at the same condition without using GO.

2.3. Characterization

The Fourier transform infrared (FT-IR, Nicolet iS10, Thermo Scientific) spectra were recorded over 500–4000 cm^{-1} at a resolution of 16 cm^{-1} within 32 scans using a diamond ATR attachment. Microscopy images of the nanocomposite were obtained on a Hitachi S-4100 field emission scanning electron microscope (SEM). The TEM images were obtained on a transmission electron microscope (Philips, CM-200) operating at an accelerating voltage of 200 kV. The XRD patterns of the composites were collected on a powder X-ray diffractometer (PANalytical, MPD) with Cu Kα radiation. The thermal stability was investigated using a thermal gravimetric analyzer (TA Instruments, SDT Q600) under a nitrogen flow (35 mL/min). The heating rate was 10 °C/min under a nitrogen atmosphere.

2.4. Adsorption experiment

For adsorption application, the as-prepared products were used to remove methylene blue (MB) from aqueous solution. The effects of solution pH, adsorbent dosage, and initial MB concentration on the adsorption performance of the as-prepared product were examined. All measurements were carried out in triplicate. Typically, certain amount of the composite were added in 10 mL solution of MB, and the pH value of this solution was adjusted using 0.1 M HCl or 0.1 M NaOH solution, and the solution was sealed at 25 °C for certain time. After collecting the composite by a magnet, the MB concentration of the remaining solution was measured using UV–vis spectrometer at 665 nm. The equilibrium adsorption amount of MB, q_e (mg/g), was calculated using the following equation:

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{1}$$

Removal percentage, R (%), was calculated using the following equation:

$$R(\%) = \frac{C_0 - C_e}{C_0} \times 100\% \tag{2}$$

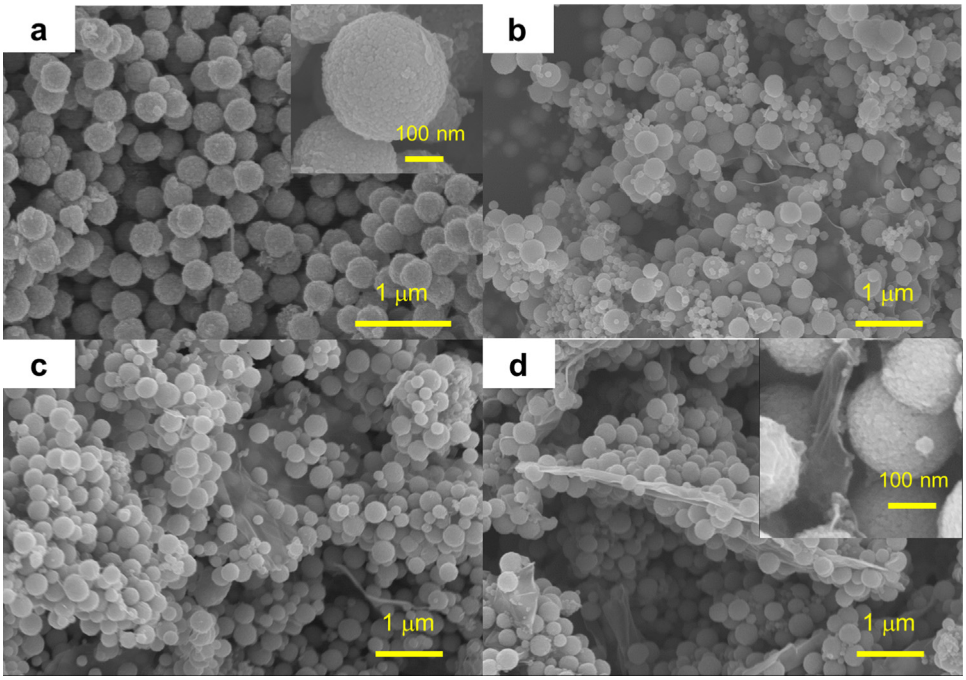

Fig. 1. SEM images of (a) Fe_3O_4@CS, (b) RGO@Fe_3O_4@CS-1, (c) RGO@Fe_3O_4@CS-2, and (d) RGO@Fe_3O_4@CS-3.