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Sono-assisted preparation of magnetic ferroferric oxide/graphene oxide nanoparticles and application on dye removal ☆

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ABSTRACT

A simple ultrasound-assisted co-precipitation method was developed to prepare ferroferric oxide/graphene oxide magnetic nanoparticles (Fe_3O_4/GO MNPs). The hysteresis loop of Fe_3O_4/GO MNPs demonstrated that the sample was typical of superparamagnetic material. The samples were characterized by transmission electron microscope, and it is found that the particles are of small size. The Fe_3O_4/GO MNPs were further used as an adsorbent to remove Rhodamine B. The effects of initial pH of the solution, the dosage of adsorbent, temperature, contact time and the presence of interfering dyes on adsorption performance were investigated as well. The adsorption equilibrium and kinetics data were fitted well with the Freundlich isotherm and the pseudo-second-order kinetic model respectively. The adsorption process followed intra-particle diffusion model with more than one process affecting the adsorption of Rhodamine B. And the adsorption process was endothermic in nature. Furthermore, the magnetic composite with a high adsorption capacity of Rhodamine B could be effectively and simply separated using an external magnetic field. And the used particles could be regenerated and recycled easily. The magnetic composite could find potential applications for the removal of dye pollutants.

1. Introduction

Dyes are widely used with the development of textile, paper, tanning and printing industries. It was reported that over 1.47×10^6 tons of organic dyes were produced in China in 2010 [1,2]. Dyes usually have complex aromatic molecular structures which make them more stable and difficult to be biodegraded. Moreover, many dyes are toxic and carcinogenic. Therefore, it's an urgent and serious global problem for efficient treatment of these discharged dyes. Many conventional methods, such as coagulation and flocculation [3], chemical oxidation [4], membrane separation [5] and adsorption [6] have been developed to remove dyes from wastewater. Among these methods, adsorption technology is the most extensively used one because of its easy handling, cost-effectiveness and high efficiency [7].

Nanoparticles have extremely small size, high surface-area-to-volume ratio and good mass transfer efficiency and provide a faster rate for the adsorption of substrates from aqueous solutions [8]. However, they are difficult to be separated and recycled. Thus, it is necessary to develop a method for the separation of nano-scale particles that does not generate secondary waste [9].

Magnetic separation has attracted increasing interest because the magnetic particle can be effectively and simply separated and recovered by the external magnetic field. Moreover, the power and efficiency of magnetic separation procedure are especially attractive for large-scale operations. And magnetic separation is also the basis of various automatic procedure [10]. Due to the ferro- or ferrimagnetic properties, iron oxide nanoparticles such as magnetic materials have been widely used in many fields such as separation of biochemical products [11], targeted drug delivery [12], catalysis [13] and enzyme immobilization [14]. The iron oxide nanoparticles can be modified with functional groups or inorganic compounds to obtain magnetic adsorbents, which require the affinity to target pollutants for applications in the environment.

Since the pioneering study of graphene as a new member of carbon nanostructures by Novoselov *et al.* [15], graphene, two-dimensional graphitic carbon nanomaterial, has attracted increasing interest due to its excellent mobility of charge carrier, a large specific surface area and good electrical and thermal conduction [16]. It also has a great promise for potential applications in many fields such as sensors, nanomaterials, electronic devices, solar cells, supercapacitors and hydrogen storage. Graphene oxide sheets, a derivation of graphene, contain a range of reactive oxygen functional groups on the sheet surface, which could render the sheet a good candidate for supporting metal or metal oxide particles

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[17]. For example, Yao *et al.* have prepared Fe_3O_4@graphene composites *via* a two-step of chemical deposition and reduction method. And they also investigate the adsorption of methylene blue and Congo red on Fe_3O_4@graphene composites. The maximum adsorption capacity reached 45.27 and 33.66 $mg \cdot g^{-1}$, respectively [18]. Nevertheless, a simple method to prepare a magnetic adsorbent with excellent adsorption capacity for the dye removal is needed to be developed.

In this work, magnetic Fe_3O_4 nanoparticles were successfully deposited on graphene oxide (GO) sheets through co-precipitation with the assistance of ultrasound irradiation for the first time. And then, the as-prepared Fe_3O_4/GO magnetic nanoparticles (MNPs) were used as adsorbent materials. The adsorption performance of the nanocomposite toward a cationic dye Rhodamine B (RhB) in aqueous solution was investigated. The parameters including initial solution pH, adsorbent dosage, temperature and contact time were systematically studied. Furthermore, the adsorption kinetics and isotherms for RhB onto the Fe_3O_4/GO MNPs were also investigated. This new adsorbent could be easily recovered with a magnetic separation, which could remove dyes from polluted water effectively. The used adsorbent could be regenerated by hydrogen peroxide and reused.

2. Experimental

2.1. Reagents and apparatus

Nature flake graphite (99%) was obtained from Qingdao Lihaofeng Graphite Co. Ltd. (China). All other chemical reagents were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China) and were of analytical reagent grade. Double distilled water was used throughout experiments.

2.2. Synthesis of the adsorbent

Oxidized graphite was obtained according to the method of Hummers and Offeman [19]. Fe_3O_4/GO MNPs were synthesized by *in situ* precipitation method as described below. Graphite oxide was added to distilled water (40 ml) and ultrasonically exfoliated in a bath sonicator for 1 h to obtain a light-brown solution, namely GO dispersion. $FeSO_4 \cdot 7H_2O$ (3.0×10^{-4} mol) and $FeCl_3 \cdot 6H_2O$ (4.5×10^{-4} mol) were dissolved in 10 ml of distilled water and added to the GO dispersion. The mixed solutions were added dropwise into 10 ml of 12.0 $mol \cdot L^{-1}$ ammonia at 60 °C and reacted for 1 h under ultrasound irradiation in an ultrasound cleaning bath operating at 25 kHz with a power of 140 W (KQ-200KDE, Kunshan Ultrasound Instrument Co. Ltd.). Finally, the product was washed with ethanol and distilled water until neutral and then dried to obtain Fe_3O_4/GO MNPs as adsorbent.

2.3. Characterization of the adsorbent

X-ray diffraction (XRD) patterns of samples were recorded on a Bruker Advance D8 X-ray powder diffractometer with a Cu K_α radiation source generated at 40 kV and 40 mA. The morphology of as-synthesized products was evaluated by transmission electron microscope (TEM, FEI Tecnai G2 20). The magnetic properties were analyzed on an ADE 4HF vibrating sample magnetometer at 300 K. The Brunauer–Emmett–Teller (BET) specific surface area was determined using a BELSORP-mini apparatus. The UV–visible absorption spectra of dye were recorded on an EVOLUTION 201 spectrophotometer (thermo scientific).

2.4. Batch adsorption experiments

0.05 g of Fe_3O_4/GO MNPs and 50 ml of RhB solution of known initial concentration were added to Teflon bottles and then shaken (200 $r \cdot min^{-1}$) on a thermostatic shaker at 313 K for 270 min in order to reach equilibrium. The initial pH of the solutions was adjusted to the desired value using dilute HCl or NaOH solution. The suspensions were then separated by a magnet to analyze dye concentration. The adsorption capacity of adsorbent toward RhB was calculated using the following formula:

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

where q_e ($mg \cdot g^{-1}$) is the amount of the RhB adsorbed on per unit mass of adsorbent at equilibrium; C_0, C_e ($mg \cdot L^{-1}$) are the initial and equilibrium concentrations of RhB in solution respectively; V (L) is the volume of the solution and W (g) is the mass of adsorbent used in the experiments.

2.5. Regeneration experiments

0.5 g of the adsorbent after RhB reaching adsorption equilibrium and 200 ml of H_2O_2 solution with concentration of 0.08 $mol \cdot L^{-1}$ were added to Teflon bottles and then shaken (200 $r \cdot min^{-1}$) on a thermostatic shaker at 313 K for 360 min. The pH of the solution was adjusted to 4.0 throughout the reaction. The adsorbent was collected by a magnet and reused for adsorption again.

3. Results and Discussion

3.1. Structure of the adsorbent

The XRD pattern of adsorbent shows the characteristic peaks of Fe_3O_4 crystalline particles at 18.2°, 30.3°, 35.6°, 43.4°, 53.8°, 57.4° and 62.8°, which are ascribed to the (111), (220), (311), (400), (422), (511) and (440) planes of Fe_3O_4, respectively, as shown in Fig. 1, Curve 1. The broad small diffraction peak around 24° corresponds to C(002) reflection of graphite oxide derived from the short-range order in stacked graphene oxide sheets [20]. A diffraction peak at 11.0° belongs to (001) crystal of GO (Fig. 1, Curve 2). For the Fe_3O_4/GO MNPs, this diffraction peak disappears indicating that the stacking of GO sheets in the composite was almost disordered [21].

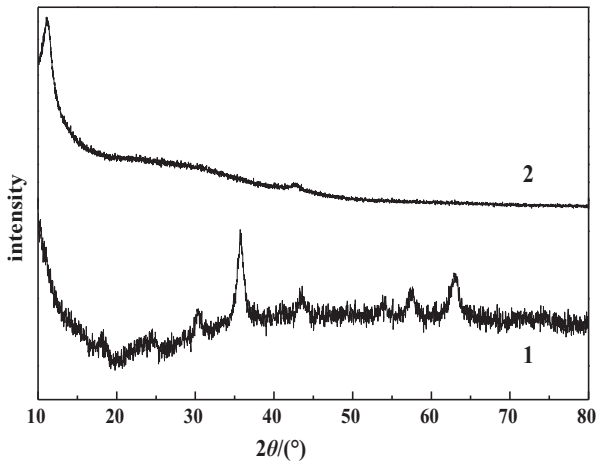

Fig. 1. XRD patterns of Fe_3O_4/GO MNPs (1) and GO (2).

The TEM image is used to observe the morphology of the adsorbent. As shown in Fig. 2, it is evident that graphene sheets are uniformly decorated by Fe_3O_4 nanoparticles with the ultrasound-assisted co-precipitation method, little of which aggregate to form larger particles. When the precursor solution is exposed to the ultrasound irradiation, ultrasound may locally produce extremely high temperatures (>5000 K) and pressures (>20 MPa) during acoustic cavitation