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Synthesis of water-dispersible graphene-modified magnetic polypyrrole nanocomposite and its ability to efficiently adsorb methylene blue from aqueous solution

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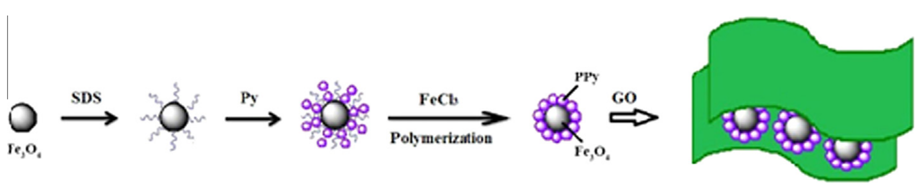
HIGHLIGHTS

- Fe_3O_4@PPy/RGO were fabricated through a facile chemical route for adsorption of dyes.
- The maximum adsorption capacity of Fe_3O_4@PPy/RGO for methylene blue removal is 270.3 mg g^{-1} at 30 °C.
- Sorption kinetic is fast and the data are in good agreement with pseudo-second-order kinetic model.
- The equilibrium adsorption data fitted the Langmuir isotherm well.
- Fe_3O_4@PPy/RGO can be easily separated from the water by external magnetic field.

GRAPHICAL ABSTRACT



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ABSTRACT

A graphene-modified, magnetic polypyrrole nanocomposite (Fe_3O_4@PPy/RGO) was fabricated through a facile chemical route and its application as an adsorbent for the removal of a dye was also demonstrated. The as-prepared Fe_3O_4@PPy/RGO nanocomposite was characterized by Fourier transform infrared (FT-IR) spectroscopy, transmission electron microscopy (TEM), X-ray diffraction (XRD), N_2 adsorption–desorption, and zeta potential analysis techniques. The Fe_3O_4@PPy/RGO nanocomposite showed excellent water dispersibility because of the hydrophilicity of Fe_3O_4 and RGO. Adsorption experiments indicated that Fe_3O_4@PPy/RGO adsorbs methylene blue fast and efficiently, with an adsorption capacity of up to 270.3 mg g^{-1}. The kinetic adsorption data fit the pseudo-second-order model and the isotherm data followed the Langmuir model. Additionally, adsorption of MB on Fe_3O_4@PPy/RGO also can utilize the electrostatic interaction and π–π interaction between Fe_3O_4@PPy/RGO and MB. Moreover, compared to other nanoparticle adsorbents, the as-prepared Fe_3O_4@PPy/RGO is highly flexible and easy to operate and retrieve. Most importantly, it is easy to disperse, which enables its potential application in wastewater treatment.

1. Introduction

The presence of dyes in effluents may cause serious problems for the environment because of the high toxicity of dyes to humans and other living organisms. For this reason, dye wastewater

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treatment draws serious attention [1,2]. Methylene blue (MB) is one of the most commonly used substances for dyeing silk, wood, and cotton. Hence, the development of cost-effective methods for the removal of methylene blue from waste effluents is of considerable environmental importance [3].

In recent years, several treatment methods, including chemical oxidation [4], photocatalytic degradation [5], biodegradation [6], and adsorption [1–3], have been developed to remove dyes from waste effluents. Adsorption is the most widely used of these methods, because it is easy and safe to perform, has a high efficiency, and is comparatively cheap. Various adsorbents, such as activated carbon [7], nanoporous silica [8], clay materials [9], and solid waste [10], have been used to remove dyes from sewage. However, these adsorbents suffer from low adsorption capacities and inconvenient separation procedures, and the adsorbents might cause secondary environmental contamination if they are not fully recovered from the environment. The development of dye adsorbents that have high adsorption capacities and can be easily separated is much anticipated, both in scientific and in technological societies [11].

Polypyrrole-based nanocomposites have been extensively studied in various types of applications. Because of their many excellent properties, such as facile synthetic accessibility, good biocompatibility, high electrical conductivity, and intriguing electronic and redox properties [12], they have also received attention in environmental remediation [13]. For this purpose, polypyrrole (PPy) is normally dispersed into the sample solution for adsorption. This is followed by centrifugation or filtration to separate or retrieve the PPy from the dispersion, which is a little tedious and troublesome. Moreover, pure PPy has a low adsorption capacity [13]. Magnetic adsorbents have been used to simplify the retrieval procedure [14]. For example, PPy can be coated onto Fe_3O_4 to fabricate a magnetic PPy nanocomposite. The magnetic PPy nanocomposite can then be collected and separated from the dispersion simply by using an external magnetic field, without requiring filtration or centrifugation.

However, the poor dispersion of PPy in water and its tendency to agglomerate in an irregular morphology via π–π stacking may result in the self-aggregation of Fe_3O_4@PPy composites, leading to the inefficient use of Fe_3O_4@PPy. Nanocomposites are considered to be one of the most effective materials to overcome the aggregation of PPy and to increase the surface area. Therefore, the PPy polymer was modified to prepare composites/nanocomposites to be used as potential adsorbents for the remediation of toxic dyes from aqueous solutions.

Graphene, a single layer two-dimensional graphite structure, has attracted significant attention owing to its large surface area, exceptional electrical, mechanical, and thermal properties [15,16]. Graphene and its functionalized preparations exhibit exciting adsorption abilities for removing hazardous anions, heavy metals, and cationic dyes from contaminated water [15–18]. Wu et al. [17] prepared rhamnolipid-functionalized graphene oxide (RL-GO) via one-step ultrasonication, showing the adsorption capacities of 529.10 mg g^{-1}. Fe_3O_4/SiO_2-GO nanoparticles were also used for the removal of MB, and the maximum adsorption capacity reached up to 111.1 mg g^{-1} [18]. However, the main shortcomings of graphene are the easy agglomeration during storage, which result in the decline of adsorption capacity in practical application. Coating graphene nanosheets onto anchored nanoparticles through strong π–π stacking interactions and van der Waals forces will increase the specific surface areas of the resultant composites and the graphene sheets themselves. The restacking of graphene sheets is thus prevented, which is beneficial for the adsorption of contaminants [15].

Recently, Wang et al. [19] reported the polypyrrole decorated reduced graphene oxide-Fe_3O_4 magnetic composites (PPy-Fe_3O_4/RGO) as an adsorbent for Cr(VI) removal, suggesting that the ternary magnetic composite could be a potential adsorbent in water treatment. However, there is a major shortcoming of the PPy-Fe_3O_4/RGO adsorbent. The problem is that the strong hydrophobic property of PPy prevents the PPy-Fe_3O_4/RGO well dispersed in water, which is a disadvantage in promoting absorption ability. Furthermore, no relevant studies have been performed on the modification of magnetic PPy-based materials with graphene for the removal of aqueous dyes. Thus, we tend to fabricate a type of Fe_3O_4@PPy/RGO hybrid nanocomposites with excellent adsorption capacity and good water-dispersibility.

In this study, a graphene-modified, magnetic polypyrrole nanocomposite was synthesized via a facile chemical route and it was applied as a potential adsorbent for the removal of methylene blue from aqueous solution. The effects of pH, initial concentration of MB, contact time, and temperature on the adsorption efficiency were investigated. Additionally, the kinetic and thermodynamic parameters of the adsorption process were also evaluated. This study reveals that Fe_3O_4@PPy/RGO is a high-efficiency adsorbent for the removal of MB from aqueous solution.

2. Experimental part

2.1. Materials

Ethylene glycol (EG), iron(III) chloride hexahydrate ($FeCl_3·6H_2O$), sodium acetate, methylene blue, ethanol, trisodium citrate dihydrate, sodium dodecyl sulfate (SDS), and sodium nitrate were purchased from Sinopharm Chemical Reagent Company. Pyrrole was purified by vacuum distillation and stored below 0 °C for further use.

2.2. Synthesis of magnetite particles

Fe_3O_4 microspheres were prepared using a modified solvothermal reaction [20]. Typically, $FeCl_3·6H_2O$ (1.08 g, 4.0 mmol) and trisodium citrate dihydrate (0.20 g, 0.68 mmol) were dissolved in ethylene glycol (20 mL), after which NaAc (1.20 g) was added with stirring. The mixture was stirred vigorously for 30 min and then sealed in a Teflon-lined stainless-steel autoclave (50 mL capacity). The autoclave was heated to 200 °C, maintained at that temperature for 10 h, and then allowed to cool to room temperature. The product was collected and removed from the solution by applying an external magnetic field; it was washed several times with ethanol and deionized water. Finally, a homogeneous aqueous dispersion of Fe_3O_4 was obtained for further use.

2.3. Synthesis of Fe_3O_4@PPy nanocomposite

To prepare core–shell Fe_3O_4@PPy microspheres, 150.0 mL of distilled water was placed in a 250 mL three-necked, round-bottomed flask. The water was deaerated by bubbling highly pure nitrogen through it for 0.5 h. SDS (0.015 g) was then added, and ultrasound was used for about 10 min until it was dissolved [21,22]. Fe_3O_4 (0.075 g) was added and ultrasound was used for about 10 min, followed by vigorous stirring for about 2 h at room temperature. Then, 0.31 mL of pyrrole was added and the mixture was stirred for 1 h. The polymerization was started by adding $FeCl_3$ (0.289 g of $FeCl_3·6H_2O$ was dissolved in 3.1 mL of water and the solution was added dropwise to the flask) and the reaction mixture was subjected to ultrasonic irradiation for about 10 min and then stirred for about 2 h. The product was collected and washed several times with ethanol and water. Finally, a homogeneous aqueous dispersion of Fe_3O_4@PPy was obtained for further use.