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A sandwich-structured graphene-based composite: Preparation, characterization, and its adsorption behaviors for Congo red

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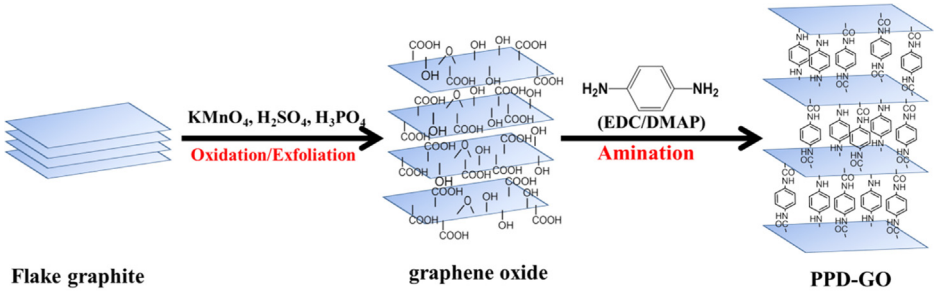
HIGHLIGHTS

- Superior graphene-based adsorbent of PPD-GO was successfully prepared.
- The aqueous adsorption of Congo red by PPD-GO was investigated.
- PPD-GO exhibits excellent adsorption performance.
- The whole adsorption process was investigated systematically.

GRAPHICAL ABSTRACT

Schematic for the preparation of PPD-GO.



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ABSTRACT

In this work, a novel sandwich-structured graphene-based composite (PPD-GO) was prepared. The graphene-based composite was prepared by amination of graphene oxide (GO) with *p*-phenylenediamine (PPD) with the aid of the coupling reagents. And PPD was introduced into the interlayers of graphene nanosheets. The morphology, composition, and grafted functional groups of the composite were investigated by scanning electron microscopy (SEM) and Fourier transform infrared (FT-IR) spectroscopy. And PPD-GO was used as a highly efficient adsorbent for removal of Congo red from used from aqueous solutions. The whole adsorption process was studied in depth and elucidated systematically. A maximum Congo red adsorption capacity of 892.8 mg/g was obtained for PPD-GO composite at an initial temperature of 298 K and pH of 3.0. The second-order kinetic equation could well describe the sorption kinetics. The equilibrium data were perfectly fitted by the Langmuir isotherm. The thermodynamic analysis indicated that the adsorption of Congo red onto the PPD-GO composite was a spontaneous and endothermic process.

1. Introduction

Synthetic dyestuffs are widely applied in various industries such as textile, printing and pharmaceutical industry. However, due to their complex aromatic structures, most dyes are toxic and carcinogenic and can pose great threat to human health [1,2]. Serious

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environmental problems have been caused by the random discharge of synthetic dyestuffs into water bodies. Therefore, it is of considerable environmental importance to develop applicable approaches for the treatment of dye-contaminated wastewater [3,4].

Up to now, various physical or chemical methods such as electrochemical oxidation [5], photocatalytic degradation [6], nanofiltration [7], ion flotation [8], and adsorption [9,10] have been applied in treatment of dye-contaminated wastewater. Among these methods, adsorption is an effective and favorable method for the removal of dyes due to its ease of operation, high removal efficiency, and low cost [11,12]. Generally, the physicochemical properties of the adsorbents have great influence on the efficiency of adsorption properties [13,14]. Therefore, it is necessary to seek suitable adsorbents with high capacity, easy preparation and low cost [15,16].

Recently, much attention has been paid to graphene and its derivatives due to their favorable properties [15,17,18]. Graphene is a fascinating two dimensional carbon materials possessing honeycomb structure. Graphene and its derivatives have aroused tremendous interest in adsorption because of their prominent properties such as large surface area, good electronic properties, and high strength [19,20]. However, graphene sheets exhibit serious agglomeration due to the strong van der Waals interactions. The surface area of the bulk material loses dramatically as the number of layers per stack increases. Therefore, the agglomeration causes a great loss of accessible surface area for the adsorbates [21,22].

To avoid the secondary accumulation and exfoliate the layered structure of graphene, pillaring emerges as one of the most useful techniques. Organic or non-organic spacers would act as interlayer "pillars" for graphene to create enlarged spaces that allow the adsorbates to access [23–26]. P-phenylenediamine (PPD) molecules possess two amine groups on the *para*-position of benzene rings. The amine groups were found to react with the functional group of graphene oxide (GO) sheets in certain conditions [27,28]. Simiutanously, the benzene rings of PPD can occupy the space between the graphene layers and prevents the restacking and aggregation of graphene [29]. Therefore, PPD is expected to be efficient in reducing and functionalization of GO to form a pillared nanostructure.

Nowadays, several strategies have been developed to functionalize GO with PPD. For most of the developed strategies, PPD was usually wrapped on the surfaces of GO, and thus nitrogen-containing groups were introduced on the surfaces of the composite. An enhanced adsorption capacity would be obtained due to the chelation or redox reaction between the nitrogen-containing groups and the adsorbates [30,31]. A new thought was proposed by intercalating PPD between the interlayers of graphene based nanostructures, the interlayer spacing of graphene would be widened due to the benzene rings of PPD occupy the space, creating enlarged contact area that allowed various adsorbates to access. Therefore, the surface area of the sorbents would be enlarged along with the introducing nitrogen-containing groups, gaining greater adsorption capacity.

Based on the above considerations, a novel pillared graphene-based composite, PPD functionalized GO (PPD-GO), was designed and prepared. The reaction between GO and amine groups of PPD was carried out with the aid of the coupling reagents. To evaluate the adsorption performance of PPD-GO, Congo red, one of the anionic azo dyes, was selected as a pollutant model molecule. Furthermore, the factors affecting the adsorption process, including pH, contact time, initial solution concentration, and solution temperature were investigated. The adsorption thermodynamic, adsorption kinetics and adsorption isotherms were analyzed and discussed in detail.

2. Experimental

2.1. Reagents and chemicals

Flake graphite with an average particle size of 100 meshes was purchased from Nanjing XFNano Material Technology (Nanjing, China), potassium permanganate ($KMnO_4$), concentrated sulfuric acid (H_2SO_4, 98%), concentrated phosphoric acid (H_3PO_4, 85%), hydrogen peroxide (30%, v/v), and PPD were provided by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), 1-ethyl-3-(3-dimethylaminoprophy) carbondiimide hydrochloride (EDC), 4-dimethylaminopyridine (DMAP), and sodium hydrosulfite ($Na_2S_2O_4$) were supplied by Sigma–Aldrich (Sigma-Aldrich, St. Louis, MO, USA). Ultrapure water was obtained from a Milli-Q Water Purification System (Millipore, Milford, MA). All materials used in this work were analytical grade and used as received without any further purification.

2.2. Preparation of PPD-GO composites

2.2.1. Preparation of GO

Graphene oxide (GO) was prepared from natural graphite by the modified Marcano method [32]. Firstly, 0.3 g of flake graphite and 1.5 g of $KMnO_4$ were homogenized and placed in a 100 mL round bottomed flask. Then 4.0 mL of concentrated H_3PO_4 and 36.0 mL of concentrated H_2SO_4 were charged into the flask slowly, and the suspension was kept stirring for 12 h at 50 °C. After the reaction, 130 mL of ice water was used to dilute the mixture, and then 30% H_2O_2 solution was added in drops until the bubbles were no longer formed. The mixture was centrifuged and washed several times with HCl (1 M), and subsequently washed with water until the pH of solution was neutral. Finally, the products were freeze-dried at −48 °C under vacuum.

2.2.2. Preparation of PPD-GO composite

The PPD-GO composite was synthesized by amination of GO with PPD and with the help of coupling reagents of EDC and DMAP. In a typical amination process, 50 mg of GO was dissolved in 30 mL of DMF *via* ultrasonication. Then 250 mg of EDC and 120 mg of DMAP were added into the dispersion and sonicated for another 20 min to activate carboxyl groups. Subsequently, 300 mg of PPD was put into the mixture and 25 mg of sodium hydrosulfite was added to avoid the oxidation of PPD. Finally, the reaction was carried out under N_2 protection at 90 °C for 24 h. The products were rinsed using deionized water and acetone for several times, and finally freeze-dried at −48 °C under vacuum. A description was carried out for the possible preparation process by adopting a schematic diagram (Fig. 1).

2.3. Characterization and instruments

The morphologies of samples were characterized by TESCAN MIRA3 LMH/LMU field emission scanning electron microscopes (FE-SEM, accelerating voltage: 20 KV). Fourier-transform infrared (FT-IR) spectra were carried out on a Nicolet avatar 360 FT-IR spectrophotometer. GO or PPD-GO sample was pressed into a pellet using spectroscopic grade potassium bromide (KBr), which were subsequently scanned from 4000 to 400 cm^{-1}.

2.4. Adsorption experiments

Batch adsorption experiments of Congo red on PPD-GO were performed in 50 mL conical glass flasks in a thermostatic shaking water bath at different temperature (298 K, 308 K, and 318 K, respectively). 5 mg of adsorbent was added to a conical glass flask containing 20 mL of congo red solution (100–800 mg/L). The flasks