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Synthesis of graphene oxide/magnesium oxide nanocomposites with high-rate adsorption of methylene blue

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ABSTRACT

A series of graphene oxide/magnesium oxide nanocomposites (GO/MgO NCs) were and applied for the removal of Methylene Blue (MB) from aqueous solutions. The prepared NCs were characterized using scanning electron microscopy, transmission electron microscopy, X-ray diffraction, Fourier transform infrared spectrum, X-ray photoelectron spectroscopy, and thermogravimetric analysis. The results showed that MgO particles was successfully decorated on GO. The impacts of different experimental variables on the removal of MB including GO/MgO NCs dosage, pH, contact time, and initial MB concentration were investigated. The experimental analysis of adsorption isotherms indicated that adsorption data was best fit with the Langmuir isotherm model. Among the three different synthesized weight ratios of GO/MgO (5:1, 1:1, and 1:5), 5:1 ratio showed the maximum adsorption capacity as 833 mg/g, which is higher than any previously reported GO-based composites. The synthesized GO/MgO NC is also observed to have higher adsorption capacity for MB removal, in comparison with pure GO and MgO. The kinetic adsorption data was best described by pseudo-second-order kinetic model. The pH of point of zero charge (pH_{pzc}) of GO/MgO NCs was determined to be 9.7, 10.5, and 10.5 for ratios 5:1, 1:1, and 1:5, respectively. The results revealed that electrostatic attraction can be the dominant mechanism of adsorption between GO/MgO NCs and MB for pH above pH_{pzc}; whereas for pH below pH_{pzc}, other adsorption mechanisms such as hydrogen bonding and π–π interaction may attribute to adsorption. The high adsorption capacity of GO/MgO composites, thus makes it a promising adsorbent for water and wastewater treatment.

1. Introduction

Wastewaters generated from industrial activity contain a variety of potentially toxic and environmentally harmful compounds. These compounds present an increasingly serious threat to human and environmental health [1]. Organic dyes are aromatic compounds that are commonly used in various fields of industry, such as textile, pulp and paper, printing, food, plastic, and tanneries [2]. These dyes can easily be transported within the aqueous environment because of their high solubility in water, and as a result may pose many serious ecological, environmental, and health hazards [3]. Various conventional methods have been proposed for the removal of dyes from wastewater including physical, chemical, and biological technologies [4–7]. Among the various pollutant-removal technologies, adsorption is the most commonly used due to its low cost, simple operation and design requirements, low residual product generation, and its lack of interaction with toxic substances [1,8]. Recently nanomaterials as -new adsorbents, have been investigated for the removal of various pollutants from water and wastewater, such as dyes, heavy metals, antibiotics, microbial pollutants, arsenic, pharmaceutical and phenolic compounds [9–11]. Nanomaterials provide enhanced removal efficiencies compared to more traditional adsorbents due to their unique chemical and physical characteristics.

Recently, new carbonaceous adsorbents have received the most attention due to their high adsorption capacity. Graphene is one of the most interesting advanced carbon-based nanomaterials with a two dimensional honeycomb sp^2 carbon lattice, large theoretical surface area (2630 m^2/g), good chemical stability, high transparency, giant electron mobility, high thermal conductivity and remarkable elasticity [12–16]. Therefore, graphene is considered a favorable material for various applications such as sensors, transistors, catalysis, and environmental pollution treatment [17–20]. Graphene Oxide (GO) is an oxidized derivative of graphene which contains epoxide, hydroxyl, and carboxyl groups [21]. These functional groups lead to the negative charge, hydrophilicity and easy dispersion of GO in aqueous solutions [22]. These properties make GO a great candidate for the removal of different pollutants by adsorption. Due to its high surface area and functionalities, GO can be used as an excellent platform to grow various nanoparticles. In addition, GO helps prevent agglomeration on nanoparticles.

Magnesium oxide (MgO) is an alkaline earth metal oxide with a destructive sorbent, high surface reactivity, high adsorption capacity, and

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ease of production [2,23]. Recently, MgO nanoparticles (MgO NPs) have been used for the removal of dyes, catechol, phenol, fluoride, and formaldehyde from wastewater [2,3,24–26]. Thus, considering the synergistic advantage and decoration of MgO NPs over GO platform, GO/MgO nanocomposites (NCs) can be considered as a potential adsorbent for removal of pollutants.

In this paper, for the first time to the best of our knowledge, we synthesized graphene oxide/magnesium oxide nanocomposite adsorbents and demonstrated its application for the successful removal of MB dye from aqueous solutions. We investigated the impact of different experimental conditions on the removal of MB by GO/MgO NCs, and discussed the mechanism of MB interaction with the adsorbent.

2. Materials and methods

2.1. Materials

Graphite powder (<20 μm, MW: 12.01) is purchased from Sigma-Aldrich. Magnesium Chloride Hexahydrate ($MgCl_2 \cdot 6H_2O$), Sulfuric Acid (H_2SO_4), Hydrochloric Acid (HCl), Hydrogen Peroxide 30% (H_2O_2), Potassium Permanganate ($KMnO_4$), Sodium Nitrate ($NaNO_3$), Sodium Hydroxide Solution (NaOH) and Methylene Blue ($C_{16}H_{18}ClN_3S$) were obtained from Fisher Scientific. All chemicals used in the experiments were analytical grade.

2.2. Preparation of GO

The GO is prepared according to the modified Hummers method [27]. Briefly, 2 g of graphite powder was mixed with 50 mL sulfuric acid (98 wt.%) and 2 g sodium nitrate in a 500 mL flask in an ice bath at 0 °C. While vigorously stirring, 6 g of potassium permanganate was gradually added to the flask, and stirring was maintained for 2 h whereafter 100 mL of DI water was added to the solution. The solution temperature was rapidly increased to 98 °C and maintained for 30 min. Then 100 mL deionized water was added and the temperature was increased rapidly to 98 °C and kept for 30 min. 300 mL DI water was then added to the flask. Following that, 20 mL hydrogen peroxide (30 wt.%) solution was added, causing the color of the mixture turn to yellow. The mixture was filtered and washed with hydrochloric acid (5%) solution and DI water several times to eliminate any residuals. Ultimately, GO was synthesized by sonication of the dispersion for 60 min and drying at 60 °C.

2.3. Preparation of MgO NPs

MgO nanoparticles were synthesized by Sol-gel Method. This method has been successfully used for MgO nanoparticle synthesis and has been proved to be efficient with respect to its simplicity, cost effectiveness and providing unique surface adsorption characteristics [28]. In this study, 100 g of magnesium chloride hexahydrate was dissolved in 500 mL of DI water in a 1 L flask, and 50 mL of sodium hydroxide solution (1 N). The solution was stirred for 4 h to generate the magnesium hydroxide. The solution was then centrifuged (5000 rpm - 7 min) to separate the $Mg(OH)_2$ gel from the suspension. $Mg(OH)_2$ gel was washed a few times with DI water and dried at 100 °C for 24 h. Finally, MgO nanoparticles were synthesized by calcination in 550 °C for 2 h.

2.4. Preparation of GO/MgO NCs

Three different ratios of GO/MgO NCs (5:1, 1:1, and 1:5) were synthesized by impregnation. Briefly, 0.3 g of GO was added in a baker with 300 mL DI water and sonicated for 60 min. Different amounts of Mg oxide nanoparticles (NPs) (i.e., 0.06 g, 0.3 g, and 1.5 g) were added to the dispersion baker. After 30 min of sonication, suspension was collected by centrifuging and dried at 60 °C.

2.5. Preparation of methylene blue (MB) solution

MB has a molecular weight of 319.85 g/mol. It is water-soluble, which is blue in color (λ max 664 nm). A standard solution (1000 mg/L) was prepared by dissolving accurately weighed amount of MB in a known volume of DI water. The experimental solutions were prepared by diluting the standard solution of MB with DI water to give the appropriate concentration of the desired solutions.

2.6. Characterization

A series of GO/MgO NCs in different ratios (5:1, 1:1, and 1:5) were prepared by sonication method. The surface morphology of the GO, MgO, and GO/MgO was characterized by scanning electron microscopy (SEM) images by Hitachi S-4800 ultra-high-resolution and transmission electron microscopy (TEM) with an ultrahigh-resolution microscope and an accelerated voltage of 300 kV, a point-to-point resolution of 0.18 nm and a lattice resolution of 0.10 nm. Powder X-ray diffraction (XRD) patterns were obtained by Rigaku Ultima III X-ray diffraction system. The system is configured with a vertical Theta: Theta wide angle goniometer, high intensity Cu x-ray tube (1.54 Å wavelength), and a scintillation counter detector. The scans were carried on in 2θ with range of 5° to 80° and 1 s count time per step. Fourier Transform Infrared (FTIR) spectroscopy was used for analysis of chemical bonds from 4000 to 400 cm^{-1} wave number range by using Perkin Elmer Frontier spectrometer at room temperature. X-ray photoelectron spectroscopy (XPS) was performed with PHI 5000™ to determine elements contained in prepared powders and their chemical states. Thermogravimetric analysis (TGA) of GO/MgO NCs was performed with a TA Instrument TGA-SDT 2960 using 10°/min heating rate under 100 mL/min nitrogen gas flow. Chemical stability of GO/MgO NCs was investigated in various pH (i.e., pH = 1, pH = 3, and pH = 7) values. For this purpose 0.1 g/L of NCs in different ratios (5:1, 1:1, and 1:5) were dispersed in water solution while stirring with a magnetic stirrer in 125 mL flasks at room temperature. After 2 h, the solution was filtered by 0.2 μm NYL syringe filter. Then, concentration of Mg ions was measured by colorimetric methods as described previously [29].

2.7. Dye adsorption experiments

The initial and final concentrations of MB solutions were determined by measuring absorbance changes at their respective absorption maxima and sampling at regular intervals, using UV–Visible spectrophotometer (Thermo Scientific, Evolution 201) at the MB maximum adsorption wavelength (664 nm). All dye adsorption experiments were carried out in 125 mL flasks with constant stirring. 100 mL of the 20 mg/L MB solutions were mixed with an appropriate amount of -adsorbent and stirred for defined contact times in an ambient condition. The dye removal efficiency (%) at time t is calculated by the following equation:

$$\text{removal}\ (\%) = \frac{C_0 - C_t}{C_0} \times 100$$

where C_0 and C_t are initial and at time t concentrations of MB (mg/L), respectively. The influences of experimental parameters, dosage of powder (0.1–1 g/L), contact time (5–60 min), and initial dye concentration (5–100 mg/L) on the removal of MB were studied in batch mode of operation. All adsorption experiments were run in duplicates and the mean values were reported. The pH of each solution was adjusted by adding diluted HNO_3 or NaOH and measured with an Orion 5 Star Series Meter.

2.8. Isothermal study

The adsorption isotherms are used for evaluation of equilibrium data. It is necessary to fit the equilibrium absorption data with different