Synergistic effect of co-existence of hematite (α-Fe$_2$O$_3$) and magnetite (Fe$_3$O$_4$) nanoparticles on graphene sheet for dye adsorption

B. Saiphaneendra[a], Tejas Saxena[a], Satyapaul A. Singh[b], Giridhar Madras[b], Chandan Srivastava[a,*]

[a] Department of Materials Engineering, Indian Institute of Science, Bangalore 560012, India
[b] Department of Chemical Engineering, Indian Institute of Science, Bangalore 560012, India

ABSTRACT

Graphene oxide (GO) functionalized with hematite (α-Fe$_2$O$_3$) and magnetite (Fe$_3$O$_4$) nanoparticles (rGO-Fe$_2$O$_3$–Fe$_3$O$_4$) was prepared using a facile one-step co-precipitation technique. It shows superior performance towards methylene blue (MB) adsorption for water purification, compared to GO functionalized with hematite (rGO-Fe$_2$O$_3$) or magnetite (rGO-Fe$_3$O$_4$) nanoparticles. It also shows better performance compared to a composite mixture of rGO-Fe$_2$O$_3$ and rGO-Fe$_3$O$_4$ (rGO-M). It has been postulated that the co-existence of hematite and magnetite nanoparticles on graphene sheet causes the synergistic effect towards MB adsorption. The adsorption behaviour of GO, reduced graphene oxide (rGO), rGO-Fe$_2$O$_3$, rGO-Fe$_3$O$_4$, rGO-Fe$_2$O$_3$–Fe$_3$O$_4$ and rGO-M was studied. These materials were characterized using XRD, XPS, Raman spectroscopy, TGA, TEM, VSM and BET surface area analyzer. The phases present in the as-synthesized adsorbents were identified by XRD, Raman and XPS techniques. TGA studies confirmed the strong bonding between iron oxide particles and graphene sheet. TEM characterization was used for nanoparticles morphology and size distribution studies. Kinetics of MB adsorption was well described by the pseudo second order model. Langmuir adsorption isotherm better fits the equilibrium adsorption behaviour of rGO-Fe$_2$O$_3$–Fe$_3$O$_4$ as compared to Freundlich isotherm and the maximum adsorption capacity was determined to be 72.8 ± 2.7 mg/g. Regeneration and reusability studies performed on rGO-Fe$_2$O$_3$–Fe$_3$O$_4$ revealed that it retains more than 65% of the original adsorption capacity even after 3 cycles thus making it a potential candidate for water treatment.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Dyes such as methylene blue (MB) and malachite green are common pollutants present in waste water. They are known to be toxic, carcinogenic and thus their presence in water is harmful to both aquatic and human life [1,2]. Thus it is important to treat the waste water and many techniques such as biodegradation [3], photocatalytic degradation [4], adsorption [5] and chemical oxidation [6] are available. Adsorption is the most widely used technique owing to its simplicity in operation, low cost and less time consumption [7].

Activated carbon [8] has been one of the conventional choices for adsorbents. However, its small particle size hinders its separation from aqueous systems and high regeneration temperatures hinder its use [9]. Recently, there has been intense search for

alternatives for adsorbents that can remedy these problems and offer better adsorption performance. Graphene oxide (GO) [7], graphene [10], carbon nanotubes [11–13], kaolinite [14] are some materials that have emerged as potential alternatives. A comparative study of adsorption characteristics of activated carbon, GO and carbon nanotubes for MB removal from water have indicated that GO had the highest adsorption capacity when normalized with the surface area [7,10,15].

Graphene is 2–dimensional single atomic layer thick graphite with all the carbon atoms in sp^2 hybridization. Its attractive properties include high surface area, good electrical/thermal conductivity and excellent mechanical properties [16]. There are several reports on graphene for sensors [17], supercapacitors [18] and solar cells [19] applications owing to these remarkable properties. GO is a single layer form of the oxidation product of graphite and contains carboxyl, hydroxyl and epoxy groups attached to graphene sheet and thus can readily disperse in water upon sonication [20]. Chemical reduction of GO [21] involves removing the oxygen containing groups attached to graphene

sheet and is an economical way to produce graphene in large quantities. Both GO and reduced GO (rGO) have the potential for removing organic dyes from waste water due to their huge surface area, ability of $\pi-\pi$ interactions [22] with dyes resulting in high adsorption capacity. However, GO and graphene also face a similar problem as activated carbon that it is difficult to remove them from water after adsorption because of their good dispersion in water.

However, functionalizing GO/rGO with magnetic nanoparticles can enable the easy separation from water after adsorption [23]. Few studies with magnetic iron oxide functionalized carbon nanotubes for the removal of arsenic, xylene, toluene and ethyl benzene [13,24]. Various nanoparticles that GO can be functionalized with are Fe_2O_3 [25], Fe_3O_4 [26], TiO_2 [27], Ni [28] and ZnO [29]. Among them, magnetite (Fe_3O_4) nanoparticle functionalized GO has wide range of applications in catalysis [30], MRI contrasting agent [31], energy storage [32] and dye adsorption [33] because of the excellent properties of Fe_3O_4 nanoparticles such as low toxicity, good biocompatibility and ferromagnetism. Hematite (α-Fe_2O_3) finds applications like wave absorption [34] and waste water treatment [35]. These attributes render graphene supported iron oxide based nanocomposites as good candidates for organic dye adsorption.

The objective of this study was to investigate the possible synergy of co-existence of hematite (α-Fe_2O_3) and magnetite (Fe_3O_4) nanoparticles on graphene sheet towards dye removal from water. The adsorption kinetics studies of MB were carried out on six adsorbents namely, GO, rGO, rGO-Fe_2O_3, rGO-Fe_3O_4, rGO-Fe_2O_3–Fe_3O_4 and rGO-M. The adsorbents were characterized using XRD, XPS, Raman spectroscopy, TGA, TEM, VSM and BET surface area analyzer. The adsorption isotherms and regeneration studies were conducted for rGO $-$ Fe_2O_3–Fe_3O_4.

2. Experimental

2.1. Chemicals and materials

Graphite powder (universal grade, 200 mesh, 99.9995% pure) that had been used for synthesizing GO was purchased from Alfa Aesar company, MA. Methylamine solution (CH_5N), ~40 wt.% LR was purchased from S D Fine Chem. Ltd., Mumbai. Iron precursors, anhydrous $FeCl_3$ (pure) and $FeCl_2 \cdot 4H_2O$ (98% pure) were procured from Sisco Research Laboratories Pvt. Ltd., Mumbai and Alfa Aesar company, UK respectively. Methylene Blue (MB), Rhodamine B base (RB) and Pyronine Y (PY) dyes were purchased from Merck Specialties Pvt. Ltd., Mumbai, Sigma $-$ Aldrich Company and Rolex Chemical Industries, Mumbai respectively. All other cationic dyes (Azur II (AII), Auramine (M.S.) (AO), Safranine O (SO) and Acriflaven (AF)) used in this study were purchased from S D Fine Chem. Ltd., Mumbai. Deionized water (DI water) was used for all the experiments.

2.2. Synthesis of adsorbents

2.2.1. GO and rGO
GO was synthesized by oxidizing the graphite powder using Hummers method [36]. Thus prepared GO was reduced using chemical reduction method under alkali conditions, wherein methylamine was used as both reducing and stabilizing agent. In a typical procedure, 200 mg of as-synthesized GO was dispersed in 40 mL of water by ultrasonication and it was further diluted to 200 mL. The pH of the diluted dispersion was adjusted to 11 by drop wise addition of methylamine under constant stirring. The stirring was allowed to continue for 1 h before heating the dispersion to 95 °C and held for 1 h in a sealed round-bottom flask. The solution was then cooled to room temperature as it remained a stable dispersion. It was subsequently centrifuged several times

and dried in oven under vacuum at 50 °C for 12 h to obtain a black powder of rGO.

2.2.2. RGO-Fe₂O₃, rGO-Fe₃O₄ and rGO-Fe₂O₃–Fe₃O₄
The composite adsorbents were prepared using a facile co-precipitation technique with $FeCl_3$ and $FeCl_2 \cdot 4H_2O$ as iron precursors. First, a dispersion of GO (200 mg in 40 mL) was prepared and aqueous solutions containing certain amounts of iron precursors were added to it under constant stirring. After 30 min of stirring, methylamine was added drop wise to the dispersion till the pH reached 11. The stirring was allowed to continue for a further 30 min at a predetermined reaction temperature to precipitate iron oxide nanoparticles, wherein the reaction temperatures were different for different composites to ensure proper phase formations. The solution was then allowed to cool to room temperature and the precipitate formed was separated using a magnet and finally dried in oven under vacuum at 50 °C for 12 h. The amounts of precursors added in above synthesis protocol were as follows: 0.407 g of $FeCl_3$ was loaded for preparing rGO-Fe_2O_3, whereas 0.280 g of $FeCl_3$ and 0.172 g of $FeCl_2 \cdot 4H_2O$ were added for the synthesis of rGO-Fe_3O_4 and rGO-Fe_2O_3–Fe_3O_4. The different reaction temperatures maintained were 30 °C for the synthesis of rGO-Fe_3O_4 whereas 80 °C for the synthesis of rGO-Fe_2O_3 and rGO-Fe_2O_3–Fe_3O_4.

2.2.3. Physical mixture of rGO-Fe₂O₃ and rGO-Fe₃O₄ (rGO-M)
An additional composite was prepared by physically mixing rGO-Fe_2O_3 and rGO-Fe_3O_4 powders in the same weight ratio as the hematite and magnetite phases present in rGO-Fe_2O_3–Fe_3O_4.

2.3. Characterization

X-ray diffraction (XRD) peak profiles of the as-synthesized adsorbents were obtained from X'Pert PRO, PANalytical using Cu Kα (λ = 1.5406 Å) radiation. XRD patterns were recorded from 5° to 70° with a scan rate of 0.5°/min. X-ray photoelectron spectroscopy (XPS) profiles were collected from AXIS ULTRA instrument with Al Kα as radiation source. Raman spectra were obtained using microscope setup (HORIBA JOBIN YVON, Lab RAM HR) consisting of Diode-pumped solid-state laser operating at 532 nm with a charge coupled detector. Thermogravimetric analysis (TGA) studies were carried out using Netzsch STA 409 PC thermogravimetry analyzer in air atmosphere at a heating rate of 10 °C/min. A 300 kV field emission FEI Tecnai F-30 transmission electron microscope (TEM) was used for morphology, size distribution and diffraction related studies on magnetic nanoparticles attached to the graphene sheet. Magnetic hysteresis loops of the composite adsorbents were generated using Lakeshore vibrating sample magnetometer (VSM). Brunauer–Emmett–Teller (BET) surface area measurements and pore size and volume analysis were carried out using a Micrometric ASAP 2020 system. Phase fraction analysis of rGO-Fe_2O_3–Fe_3O_4 was performed using Rietveld method using FULL-PROF package [37].

2.4. Adsorption experiments

Batch adsorption studies were performed on a shaker operating at 100 rpm and 37 °C. Dye solutions of concentrations ranging from 20 to 500 mg/L were taken in a beaker and the adsorbent was added to it at a loading of 1 g/L. The solution was sonicated for 1 min and kept in the shaker. Dye solution samples of approximately 2 mL were collected at specific intervals up to 3 h. From the collected samples, composite adsorbents were separated using a magnet and others (GO and rGO) were separated using a centrifuge. The concentrations of the supernatant dye solutions thus collected were determined using UV–vis spectrophotometer