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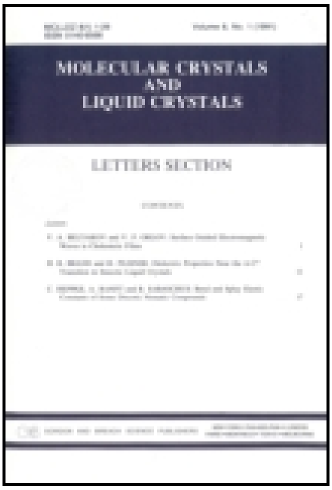

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A Facile Route towards the Synthesis of Fe_3O_4/Graphene Oxide Nanocomposites for Environmental Applications

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A Facile Route towards the Synthesis of Fe_3O_4/Graphene Oxide Nanocomposites for Environmental Applications

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A simple approach for preparing Fe_3O_4/graphene oxide (GO) nanocomposites through electrostatic self-assembly and their utilization in dye removal from aqueous media were investigated. Fe_3O_4 magnetic nanoparticles were synthesized by adding 1:2 ratio of Fe^{+2}/Fe^{+3} to an aqueous solution, maintained in an inert atmosphere at a high pH. With the highly hydrophilic graphene oxide sheets and positively charged surface of the Fe_3O_4 nanoparticles, the nanocomposites were synthesized through electrostatic interaction in aqueous solutions. The nanocomposites were characterized by TEM, XRD, FT-IR, and UV-Vis. The adsorption properties of the Fe_3O_4/GO nanocomposites toward Congo Red as an anionic dye and Methylene Blue as a cationic dye in aqueous solutions were investigated.

Keywords Graphene oxide; Fe_3O_4 magnetic nanoparticle; electrostatic self-assembly; adsorption; dyes

1. Introduction

Graphene, a class of carbon-based nanomaterials, has attracted tremendous attention for possible applications in various fields [1–4]. The common approach for the preparation of graphene oxide (GO) is graphite exfoliation by using strong oxidizing agents, such as strong acid. The GO have characteristic structures and electronic properties make them interact strongly with organic dye molecules, via non-covalent bonding, such as hydrogen bonding, π–π stacking, electrostatic forces, van der Waals forces, and hydrophobic interactions. Therefore GO is a promising material for adsorbent of organic dyes in water treatment

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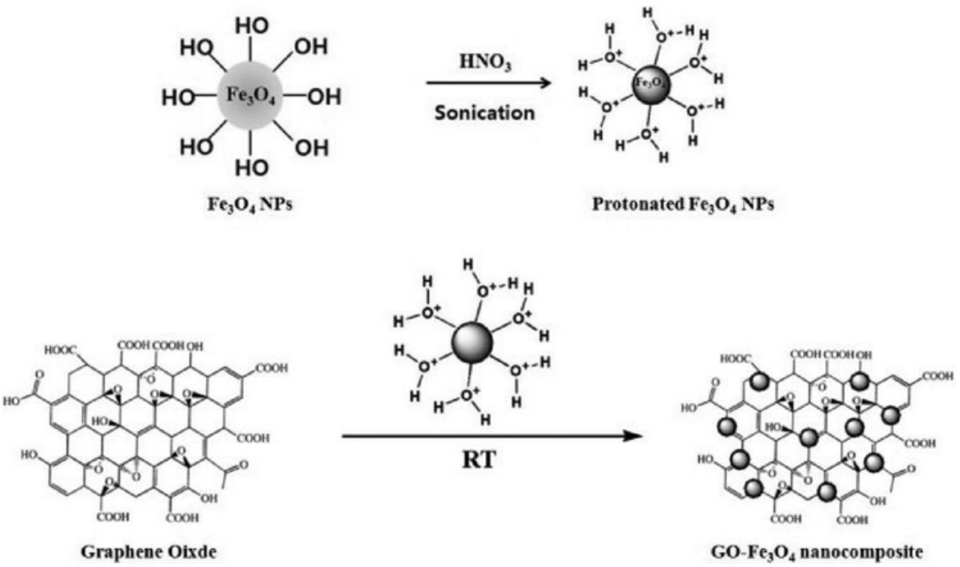

Scheme 1. Preparation of Fe_3O_4/GO nanocomposites.

[5–9]. In spite of many unique property of adsorption, GO was difficult to re-collect from aqueous media [10].

Recently, graphene hybrid materials have aroused extensive interests because of their excellent performance as well as extensive applications [11–17]. Among these nanocomposites, Fe_3O_4/GO system has unique characterization of superparamagnetism, which was supported to re-collect GO adsorbent. The preparation methods for Fe_3O_4/graphene composites, such as chemical precipitation, solvothermal reaction, and covalent bonding, are generally multistep, hard to control and they also require some rigorous conditions.

In this regard, we report a simple strategy for preparing Fe_3O_4/GO nanocomposites through electrostatic self-assembly. GO sheets are highly negatively charged when dispersed in an aqueous solution as a result of the ionization of the carboxylic acid and phenolic hydroxyl groups on the GO sheets. The nanocomposites could be formed through electrostatic interaction after adding Fe_3O_4 which has a positively charged surface. The resulting product of Fe_3O_4/GO nanocomposites were characterized by TEM, FT-IR and XRD. The dye adsorption of Fe_3O_4/GO nanocomposites for Congo Red (CR) anionic dye and Methylene Blue (MB) cationic dye in aqueous solutions were investigated by UV-Vis analysis.

2. Experimental

2.1. Reagents and Materials

Graphite powder, $FeCl_3.6H_2O$ ($\geq$98%), $FeCl_2.4H_2O$ (99%) were purchased from Sigma-Aldrich. Congo Red (80%), Methylene Blue ($\geq$82%) dyes were purchased from Alfa Aesar. The chemicals were used without any further treatment and purification.

2.2. Preparation of GO

The GO was prepared by the improved method using graphite flakes [18]. The mixture of concentrated H_2SO_4/H_3PO_4 (360:40 mL) was added to graphite flakes (3.0 g) and $KMnO_4$ (18.0 g). The mixture was then heated to 50°C and stirred for 12 h. The reaction mixture was cooled using an ice bath to room temperature followed by adding 3 mL H_2O_2 (30%). The obtained product was centrifuged and washed with water until pH 7. The collected solid was dried under vacuum for 12 h at 40°C.

2.3. Preparation of Fe_3O_4 NPs

$FeCl_3.6H_2O$ (3.00 g) and $FeCl_2.4H_2O$ (1.10 g) were dissolved in 150 mL of ultrapure water and heated to 50°C with vigorous magnetic stirring until a clear yellow solution obtained then pH of the solution was adjusted to 11∼12 by adding 28% ammonia solution drop wise. The reaction was maintained for 30 min under N_2 atmosphere. After completion the reaction, a black color precipitate was obtained, which was separated by magnet. The separated black precipitate was washed several times with ultrapure water and dried under vacuum for12 h at 40°C.

2.4. Synthesis of Fe_3O_4/GO Nanocomposites

The GO (10 mg) was added in ultrapure water (50 mL) and sonicated for 1 h to disperse GO in water uniformly. To make another solution, Fe_3O_4 NPs (10 mg) was added to 1 M HNO_3 (10 mL) with sonication to increase the concentration of H^+ ion around the Fe_3O_4 NPs, which made them protonated [12]. After 30 minutes, acid-treated Fe_3O_4 NPs was removed by using magnet. Afterwards, acid-treated Fe_3O_4 NPs was added to 50 mL of GO solution and stirred vigorous for 3 h. Fe_3O_4/GO nanocomposites were separated using magnet, washed with ultrapure water several times and dried under vacuum for 12 h at 40°C. The same procedure was applied for the synthesis of Fe_3O_4/GO nanocomposites having different ratio of GO and Fe_3O_4.

2.5. Experimental Procedure for Dye Adsorption

The Fe_3O_4/GO nanocomposites was added to 30 mL of water and sonicated for 1 h. 20 mL of CR and MB solutions were added to the Fe_3O_4/GO solution (30 mL). The concentrations of dyes were taken 40 mg/L for CR and 20 mg/L for MB, respectively. After 30 min, the Fe_3O_4/GO nanocomposites were removed by magnetic and the remaining concentration of the corresponding dye was determined with UV-Vis spectroscopy.

3. Result and Discussion

3.1. Characterization of Fe_3O_4/GO Nanocomposites

The TEM image of Fe_3O_4/GO nanocomposites clearly shows the presence of Fe_3O_4 NPs on the sheets of GO as shown in Fig. 1. It is found that the Fe_3O_4 NPs were held on the GO sheets by the ionic interaction between electron cloud of GO and protonated Fe_3O_4 NPs. Fig. 1C and Fig. 1D images exhibit different Fe_3O_4 NPs loading at Fe_3O_4/GO nanocomposites and the nanocomposites of higher Fe_3O_4/GO ratio are decorated with more Fe_3O_4 NPs on GO sheets than the lower ratio.

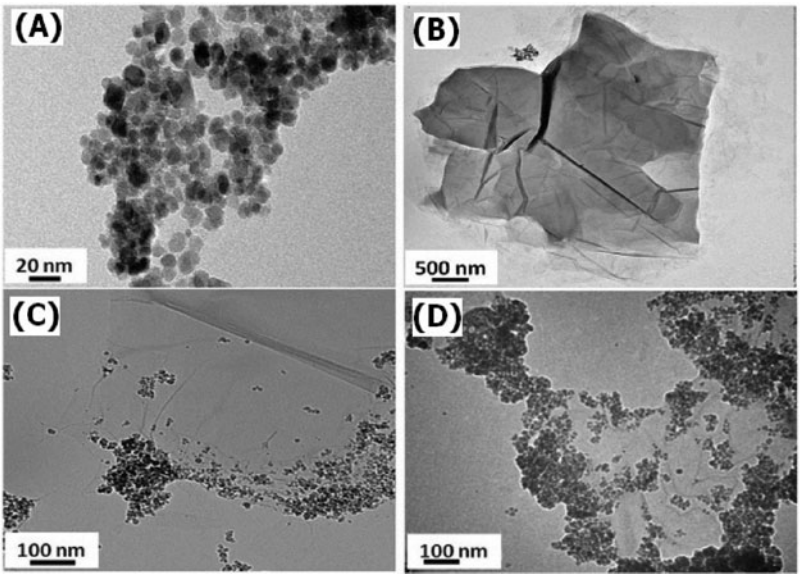

Figure 1. TEM images of (A) Fe_3O_4 NPs, (B) GO and (C), (D) Fe_3O_4/GO nanocomposites with GO: Fe_3O_4 ratio of 1: 1 and 1: 2 (wt%), respectively.

XRD measurements also support the confirmation of Fe_3O_4 NPs on the GO sheets as shown in Fig. 2C. All the characteristic peaks of NPs and GO are identified in the spectrum of Fe_3O_4/GO nanocomposites. The XRD spectra also show cubic spinel crystal structure of Fe_3O_4 NPs, which is well documented in the literature [19].

The FT-IR spectra of GO (Fig. 3B) shows the O—H stretching adsorption peak at 3391 cm^{-1} and the carboxyl and carbonyl stretching peaks at 1725 cm^{-1} and 1380 cm^{-1}; the peak at 1635 cm^{-1} was attributed to C=C stretching vibration of aromatic; the peak at 1224 cm^{-1} and 1050 cm^{-1} was attributed to C—O stretching vibration of epoxy and alkoxy groups. These peaks demonstrate the existence of carboxyl acid, hydroxide, epoxy

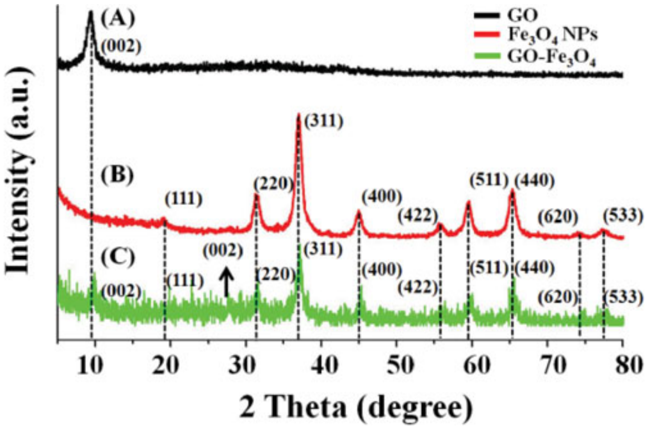

Figure 2. X-ray diffraction patterns of (A) GO, (B) Fe_3O_4 NPs, and (C) Fe_3O_4/GO nanocomposites.

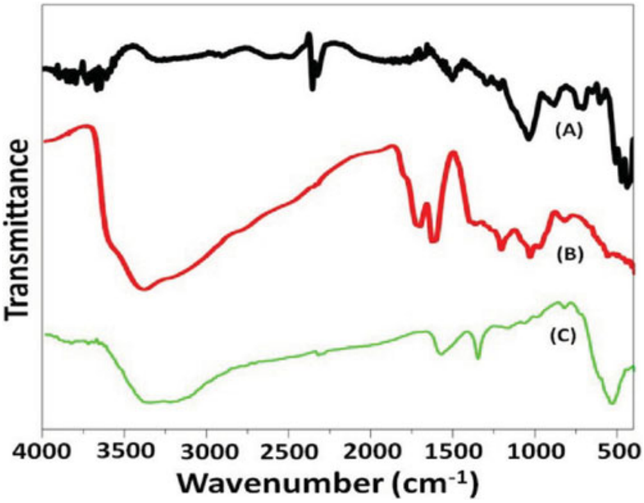

Figure 3. FT-IR spectra of (A) graphite, (B) GO and (C) Fe_3O_4/GO nanocomposites.

groups and carbonyl groups on GO sheets. In Fig. 3C, the FT-IR spectra of Fe_3O_4/GO nanocomposites exhibits the different stretching to GO. The new peak at 586 cm^{-1} was attributed to Fe–O stretching, which also proved the presence of Fe_3O_4 NPs on GO sheet. In addition, the peaks at 1725 cm^{-1} and 1224 cm^{-1} are very week. This result was attributed to the positive surface charge on the Fe_3O_4 NPs. The acid modified Fe_3O_4 NPs has positive surface charge due to the protonation of —OH groups present on the Fe_3O_4 NPs and sonicated GO has a negatively charged surface, which is apparently a result of ionization of the carboxylic acid and phenolic hydroxyl groups that are known to exist on the GO sheets by the sonication. The electrostatic interaction between the positively charged surface of Fe_3O_4 NPs and the negatively charge surface of GO cause the Fe_3O_4 NPs held on the GO surface. The place of majority decoration of Fe_3O_4 NPs was edge on GO sheets due to carboxylic acid and carbonyl groups. From the result, it can be considered that Fe_3O_4/GO nanocomposites form by the facile route of electrostatic interaction.

3.2. The Dye Adsorption Studies

MB was used as a cationic dye and CR as an anionic dye for the adsorption from aqueous solutions (Fig. 4). Figs. 5 and 6 show the UV-Vis absorbance result of MB and CR dyes in aqueous medium respectively using Fe_3O_4/GO nanocomposites of different ratios (1:1 and 1:2 wt%).

10 mg/L of MB was taken as a standard solution, and UV absorbance was found 92.65% at 668 nm wavelength (Fig. 5). The adsorption result of MB with Fe_3O_4/GO nanocomposites (1:1 and 1:2 ratio) were recorded 2.52% and 5.26% with corresponding concentration of 0.2725 mg/L and 0.5680 mg/L, respectively. These results reveal the contribution of the negatively charged surface of GO. The amount of GO in Fe_3O_4/GO nanocomposites affects the catalyst activity towards dye absorption capacity. It indicates that the nanocomposites having more available area of the negative surface on GO sheets facilate better adsorption capacity of the cationic dye.

In Fig. 6, the blank is 20 mg/L of CR standard solution and absorbance is 99.89% at 498 nm wavelength. The adsorption result of CR by Fe_3O_4/GO nanocomposites (1:1 and

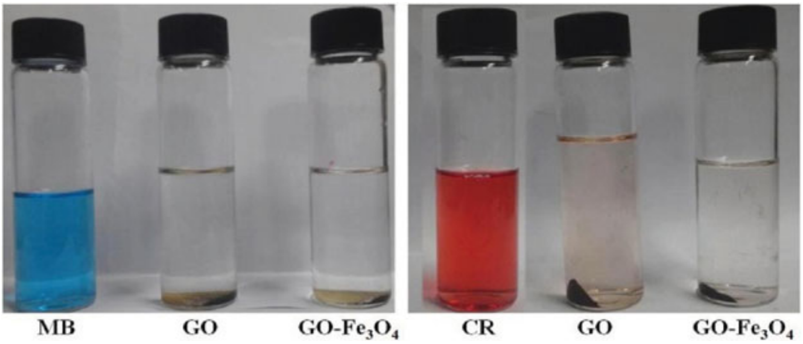

Figure 4. Photographs of aqueous solutions after dye adsorption with GO and Fe_3O_4/GO nanocomposites.

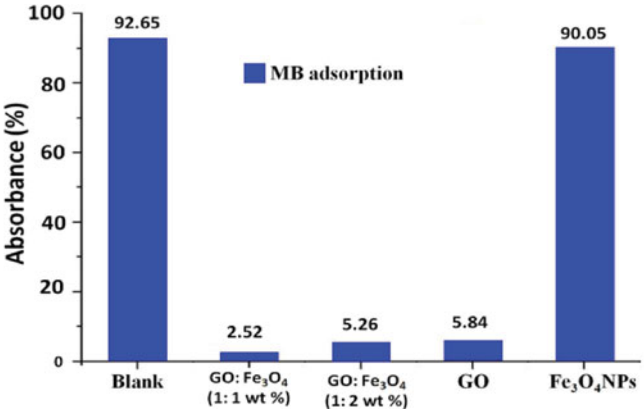

Figure 5. Dye adsorption measurement of GO, Fe_3O_4 NPs and Fe_3O_4/GO nanocomposites in MB solutions.

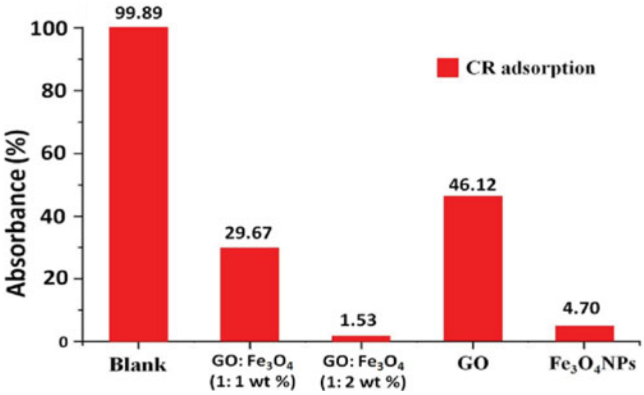

Figure 6. Dye adsorption measurement of GO, Fe_3O_4 and Fe_3O_4/GO in CR solutions.

1:2 ratio) shows the absorbance of 29.67% and 1.53% with corresponding concentration of 5.9415 mg/L and 0.3085 mg/L, respectively. The reason for these results is possibly the positively charged surface of Fe_3O_4 NPs. The presence of Fe_3O_4 NPs in the nanocomposite makes it more suitable for anionic dye absorption. Additional experimentes were performed for dye adsorption using GO, Fe_3O_4 NPs. GO (10 mg) was added to water (20 mL) and the mixture sonicated for 30 min. Then 20 mL of MB was added into the GO solution. In another experiment, Fe_3O_4 NPs (20 mg) were put into water (20 mL) and the mixture was sonicated for 30 min. Afterwards, 20 mL of CR was introduced in the mixture. The concentration of dyes was checked by UV-Vis analysis after 30 min. It is clear to see that GO and Fe_3O_4 NPs have the superior adsorption capacity of the cationic and anionic dyes, respectively as shown in Figs. 5 and 6. It is also found that GO is very good for adsorption of the cationic dye but moderate for the anionic dye. On the other hand, Fe_3O_4 NPs have an excellent adsorption capacity of the anionic dye but much low for the cationic dye. Consequently, Fe_3O_4/GO nanocomposites are recollectable by magnet as well as capable of absorbing anionic and cationic dyes. The Fe_3O_4/GO nanocomposites may be useful to remove dyes from waste water.

4. Conclusions

Fe_3O_4/GO nanocomposites were prepared by a simple electrostatic self-assembly method using acid-treated Fe_3O_4 NPs, and their formation was confirmed by FT-IR, TEM, and XRD analysis. The adsorption study was performed with cationic and anionic dyes using Fe_3O_4/GO nanocomposites of different ratios. It was found that GO had good adsorption capacity of the cationic dye, MB due to the negative surface charge on GO sheets and Fe_3O_4 NPs showed excellent adsorption capacity of the anionic dye, CR due to the positively charged surface. By combination of the properties, Fe_3O_4/GO nanocomposites could remove both dyes effectively from water.

Acknowledgments

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