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Preparation of Graphene Oxide-XFe_2O_4 (X = Co, Mn, Ni) Nanocomposites and their Application in Adsorption Organic Dye from Aqueous Solution

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ABSTRACT
The present study compared the properties of XFe_2O_4/GO formed from the magnetic metal sites including Co, Mn and Ni using the polymerized complex method. The profile from scanning electron microscopy (SEM) images revealed an uniform core-shell surface morphology with an average diameter of about 42 nm-54 nm. The Fourier transform infrared spectroscopy (FT-IR) spectra showed a typical functional group of metal-oxygen bonding at from 502 cm^{-1} (Mn-O), 518 cm^{-1} (Co-O) and 580 cm^{-1} (Ni-O). Meanwhile, the magnetizations of XFe2O4/GO were measured using the vibrating sample magnetometer (VSM) technique as a following order: $MnFe_2O_4$/GO (1.57 emu/g) < $NiFe_2O_4$/GO (2.38 emu/g) < $CoFe_2O_4$/GO (4.49 emu/g). With high removal efficiencies (53%- 100%) of methyl blue (MB), Congo red (CR) and methyl red (MR), the materials are suitable for adsorption applications.

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Introduction

Adsorption onto ferrite nanomaterials has paid much attention to many scientists over the past years because they generally possess the crucial properties such as high specific surface area, defect and porous structure, which are attributable to be essential for capturing the cationic and anionic adsorb ate by π-π interactions [1]. Moreover, the ferrets can be easily recovered to promote the recyclability and desorption by using the external magnetic field after adsorption [2]. However, ferrite particles only acquire a limited number of functional groups and this disadvantage can decrease the potential application in term of adsorption. To improve the adsorbability, a small amount of graphene oxide is often modified to attach the nitrogen- and oxygen-containing functional groups into ferrite structure [3].

Graphene, a form of natural graphite, is composed of the two-dimensional carbon layers, which carbon atoms are sp^2-hybridized in a hexagonal crystal structure [4]. Graphene oxide (GO) can be produced from graphite flakes by using modified Hummers method [5]. This method was treated by a mixture of strong oxidants such as potassium permanganate ($KMnO_4$) and sulfuric acid (H_2SO_4) via several steps to exfoliate sp^3 bondings and insert the oxygen bridges on the carbon layers. GO nanomaterials have been widely used for the diverse applications in biomedical such as mass spectrometry, cancer treatment, gene and drug delivery, stem cell differentiation and cell growth control [3]. However, an emergent drawback of GO is the high dispersibility in water combined with low density. Thus, modification of ferrite nanoparticles plays the crucial role in adsorption.

The present research reported the preparation of a series of XFe_2O_4 nanoparticles via the simple polymerized complex route. Then, the graphene oxide was doped into the structure of ferrites. The properties of synthesized XFe_2O_4/GO were characterized using several physical techniques such as SEM, XRD, FT-IR, and VSM. The XFe_2O_4/GO was also used as an efficient adsorbent to eliminate MB, CR, and MR dyes from aqueous solution in this study.

Experimental

Chemicals and instruments

All chemicals for this study were commercially purchased from Merck and used as received without any further purification unless otherwise noted. All samples were pretreated by heating at 105 o C for 1 h. The X–ray powder diffraction (XRD) of XFe_2O_4/GO composites were implemented on D8 Advance Bruker powder diffractometer with a Cu–Kα excitation source and scan rate of 0.02 °/s from 0 ° to 90 °. The scanning electron microscope (SEM) was recorded by instrument S4800, Japan and used an accelerating voltage source of 10 kV with magnification of 7000. The FT–IR spectra were recorded by using the Nicolet 6700 spectrophotometer instrument. Absorption spectra were obtained using an UV-Vis spectrophotometer.

Preparation of graphene oxide

Graphene oxide was synthesized from the natural graphite powder exfoliated using the common oxidants [6]. Firstly, graphite (3.0 g) was mixed with 150 mL H_2SO_4 98% in a 500 mL flask followed by stirring in an ice bath. Then, 10.5 g $KMnO_4$ was slowly added into the solution within 20 min and stirred for another 20 min in the same bath. After stirring for 24h, 250 mL of deionized water, and then 5 mL H_2O_2 30 % were dropwise into the mixture until obtained a golden yellow solution. Finally, the products were filtered and washed with HCl 3% (1 L) for 3 times and deionized water (1 L). The GO product was suspended in distilled water and dialyzed against deionized water overnight to remove metal ions and acids.

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Preparation of XFe_2O_4 by polymerized complex method

Transition metal-based magnetic nanoparticles were prepared by the polymerized complex method[7]. Citric acid (93 g) and ethylene glycol (40 mL) were dissolved in the beaker 500 mL containing 100 mL of deionized water at 80 ^oC. After adding 0.36 g $CoCl_2.6H_2O$ (or 0.303 g for $MnCl_2.6H_2O$ or 0.36 g for $NiCl_2.6H_2O$) and 0.5 g $FeCl_3.H_2O$, the mixture was stirred for several hours at 130 ^oC to obtain a polymeric resin precursor. The powder precursor was then heated in a furnace in an air atmosphere at 1000 ^oC for 2h.

Preparation of XFe_2O_4/GOnanocomposites

The preparation of XFe_2O_4/GO composites was performed by two-step procedure as an early report [8]. In the typical experiment, a beaker containing 1.0 g XFe_2O_4 in 50 mL ethanol and another beaker containing 5 mL of GO colloidal suspension in 45 mL of water were put in an ultrasonic bath for 1h. After heating to 60 ^oC, the mixtures were transferred into a 500 mL beaker and then stirred to vapourize. The solid was dried at 90 ^oC and used for the next studies.

Adsorption experiments with cationic, anionic and neutral dyes.The nanocomposites were used as the adsorbents to remove methyl blue (cationic dye), congo red (anionic dye) and methyl red (neutral dye). The runs were employed in an Erlenmeyer flask containing 50 mL of dyes 15 mg/L at room temperature during 2 h. The solids were removed from the mixture using magnetic and centrifugal methods if any. The residual concentrations were confirmed by UV-Vis spectroscopy and dye removal was calculated by the following equation:

$$\text{Dye removal } (\%) = \frac{C_o - C_e}{C_o} x100 \quad (1)$$

where, C_o and C_e are initial and equilibrium concentrations (mg/L), respectively.

Results and Discussion

Textural characterization of XFe_2O_4/GO

The crystalline profile of XFe_2O_4/GO was firstly examined using the curves from XRD spectra in Fig. 1A. The GO provides no contribution of any typical peak stretching from 2θ = 9.2^o to 9.4^o. The main explanation might attribute to the unremarkable presence with roughly 5% of GO as synthesized. Yao and co-workers demonstrated that the GO was highly reduced as forming boding with XFe_2O_4 [9]. In addition, it is evident that the $CoFe_2O_4$/GO (30.3^o, 34.2^o, 44.3^o, 57.1^o), $MnFe_2O_4$/GO (26.2^o, 42.9^o, 54.4^o, 64.4^o) and $NiFe_2O_4$/GO (26.4^o, 30.4^o, 35.8^o, 43.4^o, 63.0^o) spectra show the crystalline data fitted well with structure of graphene oxide-based nanocomposites reported by the previous study [10].

To compare the magnetic capacity of XFe_2O_4/GO, the magnetic hysteresis loops were investigated using the VSM technique at 303 K (Fig. 1B). The $CoFe_2O_4$/GO saturation magnetization was measured as 4.49 emu/g, which is higher than the other counterparts. Moreover, the saturation magnetization for $CoFe_2O_4$/GO is found to be lower compared with the respective pure ferrite nanoparticles [8]. This phenomenon can be explained due to the contribution of non-magnetic graphene covered on the surface of ferrite [10]. However, the magnetization strength measured provides a great evidence in term of separation of XFe_2O_4/GO by a simple magnet.

Otherwise, FT-IR spectra of XFe_2O_4/GO with a various kind of typical functional groups are shown in Fig. 1C. The intensive stretching broad at about 3420 cm-1 originated from O-H stretching vibration. The sharp peaks at 1620 cm-1 are ascribed to C=O stretching of COO^- groups at edges of GO sheets. The bonds of metal-oxygen X-O can be verified by the presence of a peak at 518 cm^{-1} ($CoFe_2O_4$/GO), 502 cm^{-1} ($MnFe_2O_4$/GO) and 580 cm^{-1} ($NiFe_2O_4$/GO) [11].

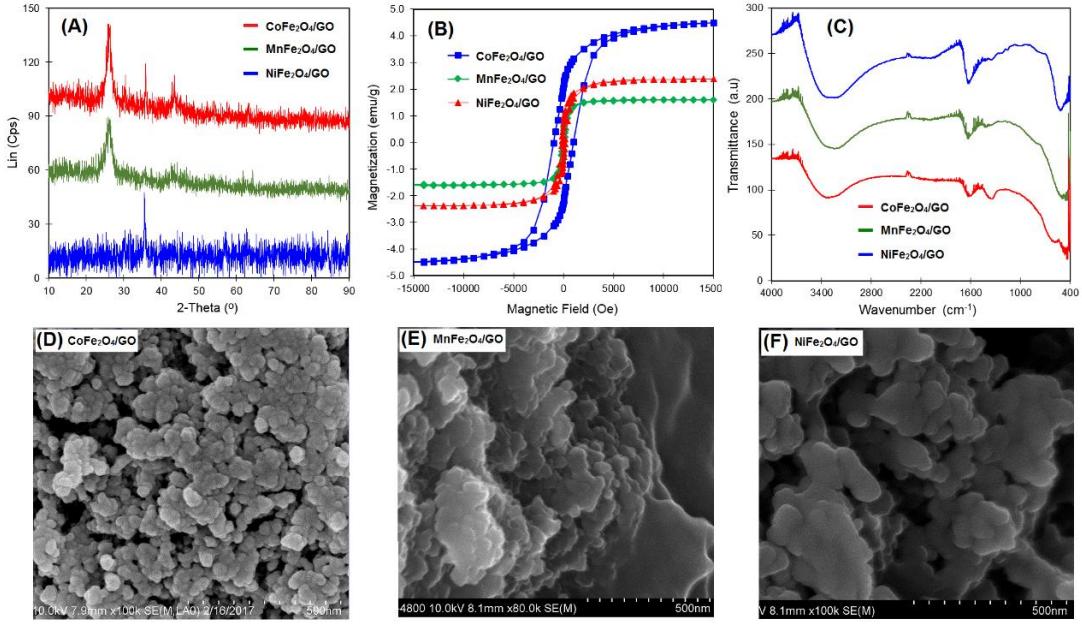

Figure 1: XRD spectra (A) VSM (B) FT-IR (C) and SEM images (D-F) of XFe2O4/GO (X = Co, Mn, Ni)

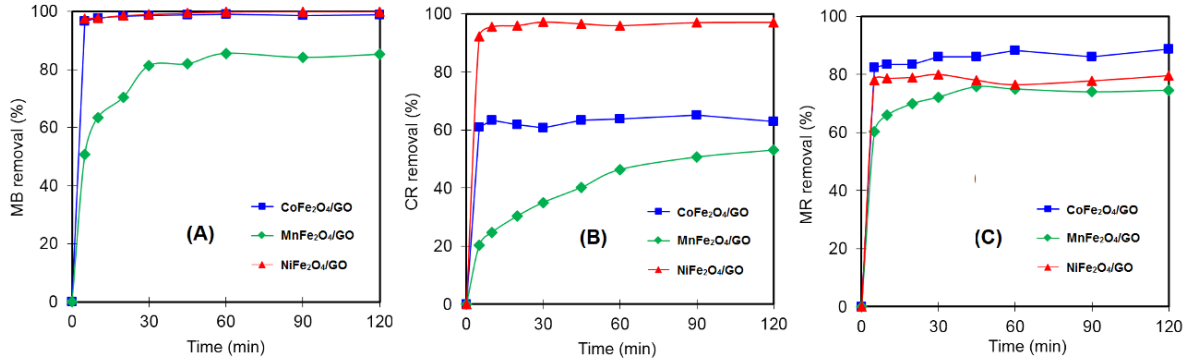

Figure 2: Effect of time on the adsorption of MB (A), CR (B) and MR (C) onto XFe2O4/GO

The SEM spectra in Fig. 1D-F show the morphological surface and particle size of XFe_2O_4/GO. The observation at 500 nm scale revealed there is a strong agglomeration and ordered distribution to form the particles like spheres. Wang et al reported that the effect of magnetic properties generated from the initial ferrite nanoparticles and the assembly among the primary particles by the Vander Waals forces are the main reason explained why the particles overlap closely [12]. Herein, we found that average diameter of particles 42 nm to 54 nm.

Removal of cationic, anionic and neutral dyes by XFe_2O_4/GO nanocomposites

In the present study the actual experiments were conducted to investigate the removal of MB, CR, and MR by XFe_2O_4/GO as shown in Fig. 2. For the cationic dye MB, XFe_2O_4/GO (X = Co, Ni) exhibited a rapid adsorption rate after only 5 minutes with approximately 100% removal for both. Meanwhile, $MnFe_2O_4$/GO obtained an equilibrium nature after 60 minutes with an average percentage of 85%. For the anionic dye CR, there was a considerable difference of removal yield between two materials XFe_2O_4/GO (X = Co and Ni) with more than 90% and 60%, respectively obtained for 5 minutes. By contrast, only 53% of CR was removed from water during 120 minutes by $MnFe_2O_4$/GO. For the neutral dye MR, there was an unremarkable difference in term of the removal efficiency of MR for all adsorbents, however, cobalt-based material gave a higher percentage 88% for 60 minutes. Generally, the nanocomposites with cobalt and nickel metal sites revealed the greatly higher removal efficiencies than the other.

Conclusions

The nanocomposites with cobalt, manganese, and nickel sites were successfully synthesized via the polymerized complex method. The properties of prepared materials were also structurally characterized with the various physical chemistry analysis techniques. Moreover, the XFe_2O_4/GO was proved as efficient materials, which could treat the various kinds of dyes including cationic, anionic and neutral with high removal efficiencies (53%-100%) after only 5-120 minutes of adsorption. Therefore, the present study showed that graphene oxide doped nanocomposites revealed a potential material for dye treatment.

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