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Dye Removal From Water by Zinc Ferrite-graphene oxide Nanocomposite

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ABSTRACT

n this work, zinc ferrite magnetic and zinc ferrite-graphene oxide nanocomposites were synthesized through a facile hydrothermal method and their absorbing capability for dye removal was studied. Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used to characterize the synthesized nanocomposite. The UV-Vis results showed that the addition of as-prepared magnetic nanoparticles on the graphene oxide sheets significantly improved the adsorption of organic dye pollutants from aqueous solution. Magnetic hysteresis measurements were done on a vibrant sample magnetometer (VSM) viewing the soft paramagnetic property of the resulting products at room temperature. Structural and morphological analyses were also performed in detail. The adsorption kinetics was described by pseudo-second-order model. Zinc ferritegraphene oxide nanocomposite could be recycled suitably and possessed of adsorptive property, so it can be developed as an inexpensive and alternative adsorbent for dye wastewater treatment. Prog. Color Colorants Coat. 11 (2018), 85-92[©] Institute for Color Science and Technology.

1. Introduction

The depletion of toxic dye wastewaters to the environment from industrial processes is a major environmental obstacle for water bodies. Organic dyes are one of the largest groups of contaminants discharged into wastewater from textile, dyeing and other industrial activities. Dyes are classified into anionic, cationic and non-ionic dyes. The deletion of anionic dyes is considered as the most challenging task as they are water soluble and generate very bright colors in water with acidic properties [1]. Different chemical, physical and biological separation technologies are used in the removal of these wastewaters [2]. The chemical pollutant removal using magnetic nanoparticle as adsorbent is an attractive field in water and wastewater treatment [3]. $ZnFe_2O_4$ with cubic spinel structure has been broadly utilized for this purpose. It also has other favorable properties such as little toxicity, low cost, and good chemical stability [4]. A number of methods have been used to synthesize magnetic $ZnFe_2O_4$ nanoparticles, including template methods, chemical coprecipitation methods, sol-gel, solvothermal, and microwave assisted combustion. Moreover, the vigorous magnetic property [5] of this substance can provide excellent magnetic separation efficiency from the aqueous solution as a dye adsorbent.

Magnetic nanoparticles and their composites with sheet materials such as graphene oxide (GO) have received enhancing consideration as adsorbents for removal of dye from water sources due to the high surface area and large adsorption capacity [6]. GO has high particular surface territory extending from 600 to 3500 m^2g^{-1} . The dispensability property of GO is ascribed to the much hydrophilic functional groups on the GO sheets [7]. Graphene oxide is a carbon-based nonmaterial that has uncovered the promising adsorptive properties [8]. GO is frequently used for dye adsorption [9]. For example, Shi et al. fabricated carbon $dots/ZnFe_2O_4$ nanocomposite and studied their applications for removal of methyl orange (MO) [10]. Fu et al. synthesized ZnFe₂O₄-graphene by hydrothermal method and studied the Methylene blue photocatalytic degradation, and recycling and photocatalytic mechanism [11].

In this research, zinc ferrite nanoparticles are synthesized with suitable surface area by an easy and accessible method without any additional treatment. Subsequently, $GO-ZnFe_2O_4$ nanocomposite is successfully prepared and its adsorption behavior is studied for water treatment.

2. Experimental

2.1. Materials and Methods

Iron (III) nitrate (FeNO₃·9H₂O), zinc nitrate $(Zn(NO_3)_2.6H_2O)$, graphite, sulfuric acid, hydrochloric acid, potassium permanganate, sodium hydroxide, hydrogen peroxide and methyl orange (MO) were supplied from Merck.

2.2. Preparation of GO

GO was produced by natural graphite powder through modified Hummers method [12]. In a typical synthesis, 0.5 g of graphite was added to 24 mL of 98% H₂SO₄, followed by stirring at room temperature for 2 h. After that, the mixture was kept below 5 °C by an ice bath, and 1.2 g of KMnO₄ was slowly added into the mixture. After being heated to 30–35 °C, the mixture was stirred for another 24 h. Then, 30 mL water was added to the mixture during a period of 5 min. Finally, 10 mL water and 5 mL of 30% H₂O₂ were added to the mixture to stop the reaction. A bright yellow solution was obtained. Then, the resulting mixture was washed by 5% HCl and H₂O until the pH was 5–6 and then dried to obtain the GO.

2.3. Synthesis of ZnFe₂O₄

 $ZnFe_2O_4$ nanoparticles were synthesized by hydrothermal method. Fe(NO₃)₃.9H₂O (2.02 g) and $Zn(NO_3)_2.6H_2O$ (0.725 g) were dissolved in deionized water (40 mL) to form a clear solution. NaOH was added dropwise to precipitate the solution. The mixture was continuously stirred for an hour and transferred to a 50 mL Teflon-lined autoclave. The sealed autoclave was maintained at 150 °C for 20 h, then cooled down to room temperature. The brown precipitate was collected by centrifugation, washed with distilled water and absolute ethanol for several times and dried in an oven at 60 °C for 12 h [13].

2.4. Synthesis of GO-ZnFe₂O₄

A typical procedure for the synthesis of $ZnFe_2O_4$ graphene nanocomposite was as follows: 50 mg of GO was added to 20 mL of water under ultrasonication for 2 h to form a steady GO colloid. Afterwards, 25 mg of synthesized $ZnFe_2O_4$ mixed with 10 mL water was added slowly to the colloid under ultrasonication for 30 min. Then the mixture was stirred for 24 h. The resulting product was separated by filtration and washed with absolute ethanol and deionized water, then dried at 50 °C for 12 h.

2.5. Adsorption experiments

The adsorption of dye (Methyl orange) from aqueous solutions by nanocomposite was studied as follows. The adsorption of dye was assessed by adding different concentrations of adsorbent/dye solution. After the agitation at a rate of 100 rpm for 30 min at 25 ± 1 °C, the solution was centrifuged and small amounts of the liquid were taken for further analysis. Methyl orange concentration in supernatant after nanocomposite separation was monitored by UV–Vis spectrophotometer at $\lambda_{max} = 465 \ nm$. The amount of adsorbed dye, q_t , was calculated by Eqs. (1) and (2):

$$q_t = \frac{(C_0 - C) V}{W}$$
(1)

$$E = \frac{(C_0 - C)}{C_0} \times 100\%$$
 (2)

where C_0 (mg/L) and C (mg/L) are the initial and the equilibrium concentrations of MO in the solution, respectively, V (L) is the total volume of the solution, and W (g) is the weight of the adsorbent.

2.6. Reusability test

In addition to the dye removal activity, stability is another important factor for determining the applicability of the catalysts. Regeneration of the adsorbents was carried out via desorption of MO from nanocomposite. Desorption of MO dye molecules was carried out using 50 mg adsorbent in 500 mL of 0.1 M NaOH solution (elution medium) for 48 h. After stirring at 200 rpm in a shaker at 24 ± 1 °C, the nanocomposite was dried at 60 °C for 24h.

2.7. Characterization of synthesized nanocomposite

Crystal structures of the samples were determined by using a Bruker D8 Advance Diffractometer with Cu-K_a radiation ($\lambda = 1.54$ Å). Fourier-transform infrared (FT-IR) spectra were recorded on a Bruker Tensor 27 (Biotage, Germany) using pressed KBr pellets. Scanning electron microscope (SEM) images were taken using a Field-Emission SEM operated at an accelerating voltage of 30 kV with a MIRA3TESCAN-XMU.

3. Results and Discussion

3.1. Characterization of nanocomposite

3.1.1. XRD analysis

The XRD diffraction patterns of the $ZnFe_2O_4$ and GO-ZnFe₂O₄ are shown in Figure 1. All the diffraction peaks confirmed the formation of single spinel phase of ZnFe₂O₄. Diffraction peaks of nanoparticles at 20 of 18.2°, 29.9°, 35.2°, 36.8°, 42.8°, 53.1°, 56.6°, and 62.1° are in a close agreement with the crystalline planes of 111, 220, 311, 222, 400, 422, 511 and 440 from the cubic system of zinc ferrite (JCPDS- 89-7412).

3.1.2. Magnetic properties

The magnetic property of the products was specified by vibrating sample magnetometer (VSM) with the highest applied field of 8.5 kOe at room temperature. Figure 2 shows the magnetization curves of ZnFe₂O₄ nanoparticles and GO-ZnFe₂O₄ nanosheet. The results showed that two samples demonstrated properties. The superparamagnetic saturation magnetization values (Ms) of the ZnFe₂O₄ nanoparticles and GO-ZnFe₂O₄ were 58, and 44 emu/g at 9,500 Oe, respectively. It was found that the encapsulation of these magnetic nanoparticles by the GO sheets leads to about 14 emu/g reduction of magnetic properties. These values are although strong enough for a suitable magnetic separation [14].



Figure 1: XRD patterns of the ZnFe₂O₄ and GO-ZnFe₂O₄.



Figure 2: Magnetization curves obtained by VSM at room temperature.



Figure 3: FT–IR spectra of (a) ZnFe₂O₄, (b) GO and (c) GO-ZnFe₂O₄.

3.1.3. Fourier transform infrared spectroscopy analysis

FT-IR provides information about the presence of functional groups and nature of molecular bonds in the materials. Figure 3 shows the FT-IR spectrum of the three samples in the range of 400-4000 cm⁻¹. Ferrites have two major metal bands in FT-IR spectra; the first band observes at 547 cm⁻¹ which corresponds to the metal at tetrahedral site (M_{tetra} -O) having inherent stretching vibrations while the lowest band observed at 450 cm⁻¹ corresponds to the octahedral metal stretching vibration (M_{octa} -O) [15]. Other absorption peaks at 3470 cm⁻¹ and 1650 cm⁻¹ correspond to the stretching and bending vibrations of H-O-H bonds on the surface

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(3a). The spectrum of GO shows all characteristic peaks of GO as reported by other researchers. The broad intense band at 3434 cm⁻¹ is assigned to the stretching of O-H. The peak at 1735 cm⁻¹ corresponds to the stretching of the C=O and COOH groups on GO sheets. The peak at 1631 cm⁻¹ (aromatic C=C) can be ascribed to the skeletal vibrations of unoxidized graphene domains. The C-O bond is associated with the band at 1084 cm⁻¹ (3b) [16]. In the FT-IR spectrum of the GO–ZnFe₂O₄ nanocomposite, a different peak corresponding to the M–O bond was appeared in the range of 540 to 550 cm⁻¹. The magnetic GO was synthesized successfully (3c).

3.1.4. Morphological characterization

Figure 4 shows the GO-ZnFe₂O₄ sheet-like structure with quasi-spherical nanoparticles spread over the surface of the GO, which indicated that GO was successfully coated with $ZnFe_2O_4$ nanoparticles.

3.2. Effect of adsorption dosage

Dye removal using different dosages of $ZnFe_2O_4$ and $GO-ZnFe_2O_4$ nanocomposite is shown in Figure 5.

Adsorbent samples (5, 10, and 20 mg) were added to a beaker containing 10 mL of 5 mg/L MO solution. The adsorption rate considerably enhanced by increasing the amount of the adsorbent. When 20 mg adsorbent was used in the presence of $GO-ZnFe_2O_4$ nanocomposite, it took 20 min to reach adsorption equilibrium. Finally, equilibrium was reached and then MO removal gently increased with increasing the amount of the adsorbents.



Figure 4: SEM micrographs for GO-ZnFe₂O₄.



Figure 5: Effect of the amount of adsorbent on adsorption: (A) ZnFe₂O₄ and (B) GO-ZnFe₂O₄.

3.3. Kinetics study of dye removal

The kinetic parameters are helpful to forecast the adsorption rate and give important data for designing and modeling the adsorption processes. To well understand the adsorption mechanism and kinetics, pseudo-first-order [16] and pseudo-second-order model were utilized to explore the kinetics of MO adsorption on the synthesized nanoparticles.

Pseudo-first order model:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t$$
 (3)

Pseudo-second order model:

$$\frac{t}{q_t} = \frac{1}{k_2 (q_e)^2} + \frac{t}{q_e}$$
(4)

where, q_e and q_t are the amount of adsorbed MO (mg g⁻¹) at equilibrium and at time t (min), respectively. In addition, k_1 represents the rate constant of pseudo-first-order reaction (min⁻¹), h is the initial rate constant and k_2 represents the rate constant of the pseudo-second-order reaction (g mg⁻¹ min⁻¹).

Figure 6(A) and (B) demonstrates the straight line plots of t/q_t vs. t and $log(q_e - q_t)$ vs. t for various initial dye concentrations for pseudo-second-order kinetic model and first-order kinetic model. The corresponding adsorption rate constants are also listed in Table 1. The credibility of each model studied by the correlation coefficient (R²) also the experimental and calculated data. For MO adsorption on GO-ZnFe₂O₄ nanocomposite, the correlation coefficient (R² = 0.978) of second-order kinetic model was higher than that of the first-order kinetic model (R² = 0.965).

Table 1: Kinetics constants for dye adsorption.

Adsorbent	Pseudo-first-order			Pseudo-second-order		
	K ₁ , min ⁻¹	q _e , mg/g	R ²	K ₂ , g/(mg.min)	q _e , mg/g	R^2
ZnFe ₂ O ₄	0.4855	13.61	0.969	0.1933	20.32	0.982
GO-ZnFe ₂ O ₄	0.4756	13.54	0.965	0.1612	20.25	0.978



Figure 6: Plots of t/q_t vs. t(A) and $log(q_e - q_t)$ vs. t(B) for MO adsorption for two magnetic nanoparticles.



Table 2: Linearized isotherm coefficients for dye adsorption.

Figure 7: Regeneration and reusability of (A) ZnFe₂O₄, (B) GO-ZnFe₂O₄.

3.4. Isotherm study of dye removal

Adsorption isotherms are elementary necessities for the design of adsorption systems intended for the removal of pollutants. Different isotherms such as Langmuir and Freundlich models were tried [17]. The adsorption isotherms of Langmuir (Eq. (5)) and Freundlich (Eq. (6)) are usually used to study the adsorption activity.

Langmuir equation can be written as follows:

$$\frac{C_e}{q_e} = \frac{1}{K_L Q_0} + \frac{C_e}{Q_0} \tag{5}$$

where C_e , K_L and Q_0 are the equilibrium concentration of dye solution (mg/L), Langmuir constant (L/mg) and the maximum adsorption ability (mg/g), respectively.

Freundlich isotherm can be expressed by:

$$\log q_e = \log K_F + \frac{\log c_e}{n} \tag{6}$$

where K_F is the adsorption ability at unit concentration (L/g) and 1/n is the adsorption intensity.

Based on the Langmuir and the Freundlich isotherms for dye adsorption, linear plots of C_e/q_e against C_e and $log q_e$ vs. $log C_e$ are designed. The values of Q_0 , K_L , K_F , 1/n, and R2 are shown in

Table 2.

3.5. Regeneration/desorption of adsorbent

As shown in Figure 7, the reusability of the nanocomposite for the adsorption of MO was also studied by performing a series of tests. $ZnFe_2O_4$ and $GO-ZnFe_2O_4$ were recycled three times under similar conditions. Before each stage, the adsorbent was collected with an external magnet, washed with ethanol, and deionized water several times to remove the adsorbed species, dried, and used again. The results presented not much more decrease in the decolorizing efficiency, which reveals the constant behavior of these products for added adsorption cycles for the water treatment.

4. Conclusions

In brief, we successfully produced magnetic $ZnFe_2O_4$ nanoparticles and GO-ZnFe₂O₄ nanocomposite with remarkable surface areas by a simple method; both magnetic nanocomposites were easily obtained via hydrothermal method. The study of adsorption efficiency of the resulting products showed a good adsorption capability of nanocomposite in comparison with zinc ferrite nanoparticles for water treatment by both magnetic characteristics for recovery and proper surface area can nominate the produced nanocomposite as a great adsorbent for water purification.

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